38 Articles

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Ph.D

1975

Tetrahedron, 1962, Vol. 17, pp. 215 to 228. Pergamon Press, Ltd. Printed in Northern Ireland

BOND LENGTHS IN CYCLIC POLYENES $C_{2n}H_{2n}$ A RE-EXAMINATION FROM THE VALENCE-BOND POINT OF VIEW

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(*Received* 16 *February* 1961)

Abstract—The valence-bond resonance method for predicting bond lengths in conjugated hydrocarbon molecules has been reconsidered. New values are obtained for the variation of the fundamental exchange and Coulomb integrals with bond length. Application to the cyclic polyenes $C_{2n}H_{2n}$ shows that for large n there will be substantial bond alternation. Inclusion of Dewar structures diminishes this alternation, but does not destroy it.

1. INTRODUCTION

TWENTY-TWO years ago Lloyd and Penney[1] made calculations of the bond lengths in certain small conjugated molecules (e.g. butadiene and benzene) using the valence-bond (v.b.) method of resonance. But since that time practically no further calculations have been made with this approximation, and the molecular-orbital (m.o.) method has been almost exclusively adopted. During the last few years, however, several new considerations have been proposed, leading to substantial changes in our opinion with regard to several matters previously regarded as settled. Thus (1) the influence of the compressional energy[2–5] is now recognised to be of supreme importance in determining equilibrium bond lengths; (2) in any use of an order–length relationship to link bond order with bond length, it is admitted that the covalent radius of a trigonal carbon atom is less than that of a tetrahedral carbon atom, thus leading to a displaced order–length curve, in which the C—C single bond length[6,7] is about 1·50–1·51 Å; (3) in long chain polyenes $C_{2n}H_{2n+2}$ and in large cyclic polyenes $C_{2n}H_{2n}$ the bonds do not tend to equality[8] as n increases, but rather there is an alternating character represented, in an exaggerated form, by the familiar bond diagram = — = — = . . . = — =. The situation of equal lengths, as originally predicted[9] by naive use of simple bond order calculations, turns out to be a saddle point and not a true minimum of the energy. For large molecules the alternation of bond length is of

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[1] E. H. Lloyd and W. G. Penney, *Trans. Faraday Soc.* 35, 835 (1939).

[2] J. E. Lennard-Jones, *Proc. Roy. Soc.* A **158**, 280 (1937).

[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).

[4] C. A. Coulson, *Victor Henri Memorial Volume* p. 15. Desoer, Liège (1948).

[5] C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.* **48**, 293 (1952).

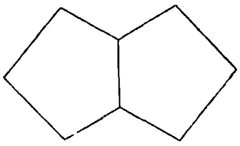
[6] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959).

[7] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959) who suggest an even shorter value 1·48 Å.

[8] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A **251**, 172 (1959) and later papers by the same authors.

[9] C. A. Coulson, *Proc. Roy. Soc.* A **169**, 413 (1939).

the order of 0·04 Å. A similar alternation is also predicted[10]—though with rather larger disparity between the shorter and longer bonds, of the order of magnitude 0·09 Å—in the hypothetic bridged ring molecule pentalene C_8H_6 (see I).



I

The results in references 8 and 10 were all obtained using the m.o. method, though without configuration interaction. It would seem desirable, therefore, to see to what extent the predictions depend on using this method. We have therefore thought it worthwhile to re-examine the same problems within the v.b. approximation. For this purpose it would have been pleasant to be able to use the numerical values of exchange and Coulomb integrals obtained by Lloyd and Penney[1], but we have not done so, and have preferred to work independently, though in a very similar spirit. In the first place the calculations of Lloyd and Penney require to be corrected so as to take account of the revised C—C trigonal single-bond radius, referred to in (2) above; and in the second place Lloyd and Penney, in their anxiety to take full account of all exchange terms, appear to us (see also reference 5 where further comments are made on this work) to have taken a σ-π exchange integral equal in magnitude to π-π exchange integrals. A rough estimation of these integrals suggests that this is not very probable, and so also does an elementary consideration of the likely contributions to the exchange integral from different regions of space. When we allow for these two changes, somewhat different curves are obtained for the Coulomb integral $Q(r)$ and the exchange integral $J(r)$ as functions of the bond length r.

The first part of this paper is therefore concerned with using certain experimental molecular magnitudes to deduce empirical $Q(r)$ and $J(r)$ curves. In the second part we show that when proper allowance is made for the σ-bond compressional energy, cyclic polyenes $C_{2n}H_{2n}$ are not expected to be regular polygons except for small n (in complete agreement with the m.o. results) though the critical value of n at which alternation sets in cannot yet be predicted accurately, since the Dewar-structures and more highly-excited structures also serve partly to weaken the strong tendency of the Kekulé structures to induce bond alternation. This surprising result differs from the usual belief that resonance among Kekulé structures tends to cause equality of bonds: but a very simple calculation does in fact show that this is not necessarily the case. Finally we present some detailed calculations for the cyclic polyenes $C_{2n}H_{2n}$ in which $2n = 6, 8$ and 10. Except in the case of benzene ($2n = 6$) these calculations are only illustrative, since neither C_8H_8 nor $C_{10}H_{10}$ are planar molecules. But we believe that these calculations, all made on the assumption of planarity, are sufficient to illustrate the general conclusions obtained earlier. We have also tacitly assumed all the valence angles to be 120°. Apart from benzene, this is manifestly impossible geometrically for small values of n. But it is possible, and probably occurs, for the larger molecules which have been isolated experimentally, and which we shall discuss in Sections 3 and 4.

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[10] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Molec. Phys.* **4**, 33 (1961).

2. THE FUNCTIONS $Q(r)$ AND $J(r)$

Let us represent the total energy of a π-electron molecule in the form

$$E_{\text{total}}(r_1, \ldots) = E_\sigma(r_1, \ldots) + E_\pi(r_1, \ldots) + E_{\pi\sigma}(r_1, \ldots) \tag{1}$$

where

$r_1, \ldots$ are the various bond lengths
E_σ is the total σ-bond energy
E_π is the total π-electron energy
$E_{\pi\sigma}$ is the total π-σ exchange energy.

We shall now make the assumption that either $E_{\pi\sigma}$ is so small in relation to the other terms of (1) that it may be neglected, or else it varies with bond lengths in so similar a way to E_σ that it may be incorporated in this latter function. This seems very reasonable, at least for molecules such as those being considered in this paper, for the distributions of π and of σ electrons are effectively uniform. It might, however, be less valid if heteroatoms were present, such as in pyridine. Thus (1) is replaced by

$$E_{\text{total}}(r_1, \ldots) = E_\sigma(r_1, \ldots) + E_\pi(r_1, \ldots) \tag{2}$$

In order to use this formula to determine the Coulomb and exchange integrals $Q(r)$ and $J(r)$ we must choose two molecules for which E_{total} is known experimentally; and we must also know the corresponding expressions for E_π and E_σ. If we adopt the usual approximations of orthogonality of all atomic orbitals, then the method of Pauling[11] enables us to write for ethylene

$$E_\pi^{\text{ethylene}}(r) = Q(r) + J(r), \tag{3}$$

and for benzene, when all bonds are equal

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}434\,J(r)\} \tag{4}$$

In writing (3) and (4) we have made the usual assumption that $Q(r)$ and $J(r)$ are the same functions of r for benzene and for ethylene. This implies—at very least—that we neglect direct *meta*- and *para*-interactions in the benzene ring. If we consider the two molecules at the same bond distance r, then $E_\sigma^{\text{benzene}}(r) = 6E_\sigma^{\text{ethylene}}(r)$, and so, using (3) and (4)

$$E_{\text{total}}^{\text{ethylene}}(r) - \tfrac{1}{6}E_{\text{total}}^{\text{benzene}}(r) = 0{\cdot}566\,J(r) \tag{5}$$

Empirical curves of $E_{\text{total}}(r)$ for ethylene and $\frac{1}{6}E_{\text{total}}(r)$ for benzene are drawn in Fig. 1. According to (5) their difference enables us to draw the curve of the exchange integral $J(r)$. This is also shown in the figure.

In drawing the curves for $E_{\text{total}}(r)$ we have used Morse functions of the usual form

$$W(r) = W_0\{e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\} \tag{6}$$

where the values adopted (which, apart from r_0, are identical with those adopted by Lloyd and Penney) are as shown in Table 1. Any alteration in the latent heat of sublimation of carbon would affect the values of W. For purposes of comparison we have accepted for our own calculations precisely the same values as Lloyd and Penney. These differ very little from the best modern values, and in such a way as to make only very minute changes in the calculated bond lengths. The values of r_0 in this table are

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[11] L. Pauling, *J. Chem. Phys.* 1, 280 (1933). For a simple account see C. A. Coulson, *Valence* pp. 228–236. Oxford University Press (1952).

now firmly established, and the parameter (a) is dependent upon the fundamental breathing frequency of each molecule. It is worth reporting that in some preliminary calculations we had tried to avoid the complication of a Morse function, with its exponential terms, by using a harmonic oscillator expression $\frac{1}{2}k(r - r_0)^2$ for the energy of a σ-bond. This expression is the one most widely used in m.o. calculations. But we found that the resulting $J(r)$ curve was seriously affected by this, and its use gave absurd numerical results for the equilibrium bond lengths of cyclic molecules. We therefore abandoned it, with regret. As an indication of the serious dependence of $J(r)$ on the choice of a Morse function of $E_{\text{total}}(r)$ instead of a parabolic law, we show in Fig. 2 rough diagrams of $J(r)$ and $Q(r)$ obtained by both techniques. It will be noticed at once that the curvature of $J(r)$ is changed in sign. This implies that d^2J/dr^2 also changes sign. Now questions of stability of a given set of bond lengths depend on the sign of d^2E_{total}/dr^2. Thus, if $J(r)$ plays any significant part in fixing the equilibrium

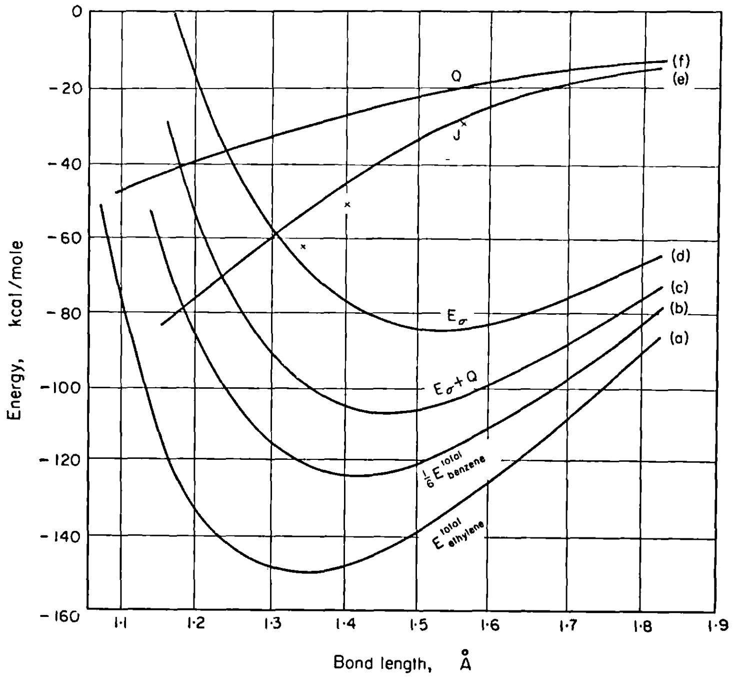

FIG. 1. (a) total energy E_{total} for ethylene (experimental); (b) one-sixth of total energy E_{total} for benzene (experimental); (c) $E_\sigma(r) + Q(r)$ deduced from (a) and (b); (d) assumed form of $E_\sigma(r)$; (e) $J(r)$ deduced from (a) and (b); (f) $Q(r)$ deduced from (c) and (d); crosses denote values of $J(r)$ calculated by Altmann[12].

TABLE 1

	W_0 (kcal/mole)	a (Å^{-1})	r_0 (Å)
Ethylene	151	2·189	1·34
Benzene	124	2·093	1·40
Ethane	84	2·028	1·54

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[12] S. L. Altmann, *Proc. Roy. Soc.* A **210**, 327, 343 (1951).

bond length—as it most clearly does—we can see why we may be led to unacceptable positions of stability or instability, if we abandon Morse functions in favour of the simpler parabolic ones. All our later work, therefore, will use only the Morse functions (6) and the parameters of Table 1.

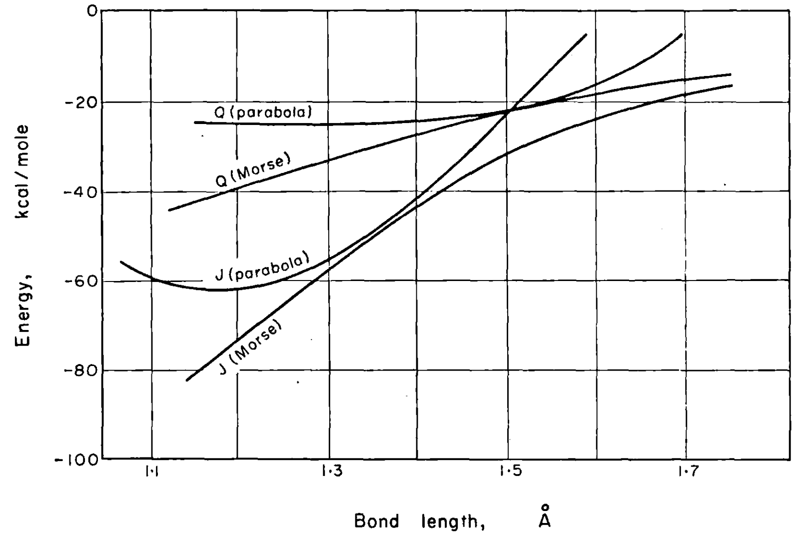

FIG. 2. Curves showing difference between exchange integral $J(r)$ and Coulomb integral $Q(r)$ with use of parabolic or Morse potential functions for ethylene and benzene.

We have still to determine $Q(r)$ and $E_\sigma(r)$ where this latter quantity is the σ-bond energy for a bond of length r, so that

$$E_\sigma(r_1, r_2 \ldots) = E_\sigma(r_1) + E_\sigma(r_2) + \ldots \tag{7}$$

Equations (2), (3), (4) and (7) allow us to write

$$E_\sigma(r) + Q(r) = 1{\cdot}767\,\frac{E_{\text{total}}^{\text{benzene}}(r)}{6} - 0{\cdot}767E_{\text{total}}^{\text{ethylene}}(r) \tag{8}$$

We have shown this quantity in Fig. 1. Since it depends only upon equations (2), (3), (4) and (6) it is independent of any assumptions that we may make about the nature of $E_\sigma(r)$, other than that the π-σ interactions are included in it.

Table 2, columns 2 and 3, shows the values of $J(r)$ and $E_\sigma(r) + Q(r)$, both in kcal/mole for various values of r, in Å. This is the table of values which we shall use in our later numerical work. At this stage it is not necessary to separate $E_\sigma(r)$ and $Q(r)$, since in all our applications we shall find that it is their sum which appears. This would not be the case if we were considering heteronuclear molecules, and then we should find that each was required separately. Simple analytical approximations to the functions in Table 2—valid to within 0·020 kcal. in the range $1{\cdot}34 < r < 1{\cdot}51$—are

$$J(r) = -41{\cdot}199 + 121{\cdot}2(r - 1{\cdot}42) - 114{\cdot}2(r - 1{\cdot}14)^2 \tag{9}$$

$$\begin{aligned} E_\sigma(r) + Q(r) = {} & -105{\cdot}905 - 39{\cdot}6(r - 1{\cdot}42) + 526(r - 1{\cdot}42)^2 \\ & -1000(r - 1{\cdot}34)(r - 1{\cdot}42)(r - 1{\cdot}51) \end{aligned} \tag{10}$$

The last figure in these numerical values is entirely without significance in any absolute sense: but for locating stationary values of the total energy it may have some significance.

There is not very much with which we may compare the numerical entries in Table 2. But Altmann[12], in some studies of the ethylene molecule, calculated $J(r)$, using a full twelve-electron Hamiltonian. For the distances 1·34, 1·39 and 1·54 Å he found values $-62{\cdot}9$, $-52{\cdot}4$ and $-28{\cdot}6$ kcal respectively. These vary in the right way as our values, and are of the right order of magnitude, though they differ by about 10 kcal for short bonds. In view of the different types of approximation involved in the two estimates of $J(r)$, this is probably as good agreement as may be expected.

TABLE 2

	Kekulé and Dewar structures		Kekulé structures only	
r	$-J(r)$	$-\{E_\sigma(r) + Q(r)\}$	$-J(r)$	$-\{E_\sigma(r) + Q(r)\}$
1·34	51·625	99·375	48·70	102·30
1·36	48·892	101·834	—	—
1·37	47·557	102·839	44·86	105·54
1·38	46·236	103·707	—	—
1·39	44·927	104·449	—	—
1·40	43·650	105·056	41·18	107·53
1·41	42·411	105·539	40·01	107·94
1·42	41·199	105·905	38·83	108·27
1·43	39·992	106·183	—	—
1·44	38·790	106·371	36·59	108·57
1·45	37·653	106·432	—	—
1·48	34·336	106·148	32·39	108·09
1·51	31·206	105·211	29·44	106·98

If we wish to go further than this, and obtain expressions for $E_\sigma(r)$ and $Q(r)$ separately, we must use some additional data. The most natural is $E_\sigma(r)$, which we could approximate as if it were the energy of a single bond between two trigonal carbon atoms. For this purpose we use a Morse curve in which the equilibrium length is not 1·54 Å, as in ethane, but is taken to be 1·51 Å, to allow for point (2) in the Introduction. It is not quite obvious which values we should choose for W_0 and a in equation (6); but we have, somewhat arbitrarily, chosen -84 kcal/mole and 2·028 Å^{-1} respectively. With this choice we can draw the $E_\sigma(r)$ curve of Fig. 1, and so determine $Q(r)$. For obvious reasons this curve is much less reliable than $E_\sigma(r) + Q(r)$, but in the region $1{\cdot}34 < r < 1{\cdot}54$ Å, it may be represented approximately by

$$Q(r) = -25{\cdot}275 + 49{\cdot}9(r - 1{\cdot}42) - 53{\cdot}5(r - 1{\cdot}42)^2 \qquad (11)$$

The difference between (10) and (11) is, of course, a representation of $E_\sigma(r)$.

We have now obtained approximate values of $J(r)$, $Q(r)$ and $E_\sigma(r)$. These are ready for application to our cyclic molecules. But before proceeding there is a point to consider. In (4) we have used the energy expression for the π-electrons of benzene, taking into account Kekulé and Dewar structures. It is not immediately obvious that we have any right to use this formula—and the implied $J(r)$—in larger molecules, where there will also be doubly-excited and more highly excited structures. But we shall assume that this is so, and shall try, when dealing with other molecules, to write down the expression for E_π analogous to (4), neglecting all structures other than the Kekulé and first-excited ones. It is doubtful that inclusion of the more highly-excited structures would seriously affect the predicted bond lengths and stabilities, though it is known[13] that for sufficiently large conjugated molecules the more highly-excited structures dominate over the less-excited. However, we can make an alternative calculation, in which we consider only Kekulé structures. If we do this, equation (3) is unchanged, and equation (4) is replaced by

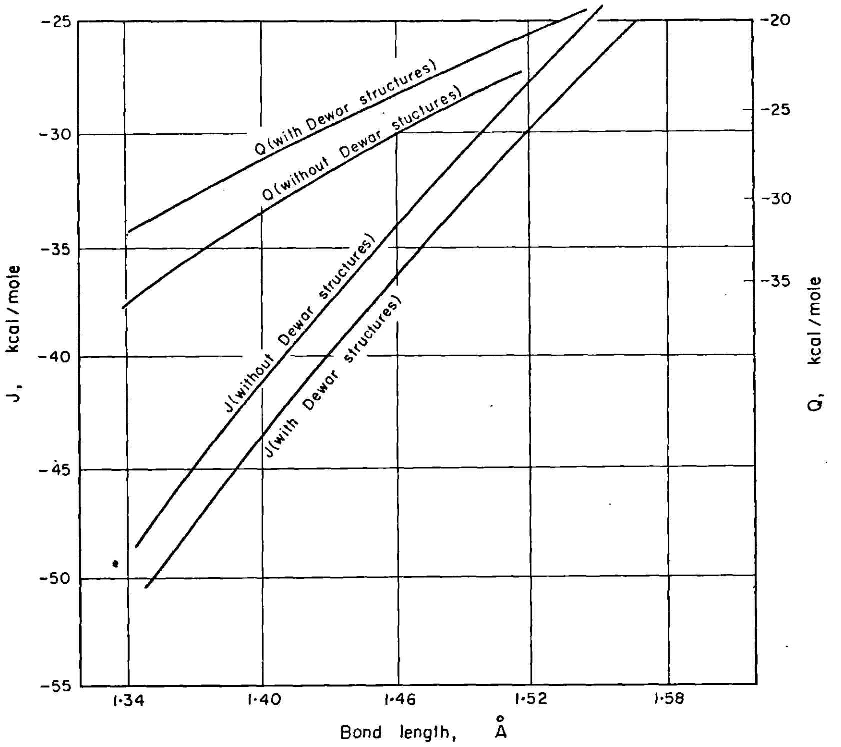

FIG. 3. Curves showing variation of exchange integral $J(r)$ and Coulomb integral $Q(r)$ when Dewar structures are included and when they are not included.

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}400\, J(r)\} \tag{12}$$

By an entirely similar process, this leads to values of $J(r)$ and $Q(r)$ which differ slightly from those previously determined (Table 2, columns 4 and 5). Fig. 3 shows, on a larger scale than Fig. 1, the variation of $J(r)$ and $Q(r)$ both with and also without inclusion of Dewar structures in benzene. The general variations are remarkably similar, leading to the view that predictions based on them would also be similar. Table 2 also allows a direct comparison of the values of $J(r)$ and $E_\sigma(r) + Q(r)$ in these two approximations.

3. THE CYCLIC POLYENES $C_{2n}H_{2n}$, n LARGE

Consider the cyclic polyene $C_{2n}H_{2n}$, represented for the case of n = 4, by II. We are supposing that the molecule is planar. This is known not to be true for cyclooctatetraene (II), but it must be more nearly true for the larger systems 2n = 18, 24

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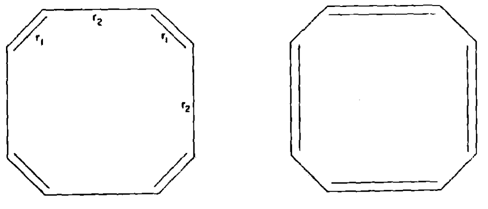
[13] See C. A. Coulson, *Proc. Roy. Soc.* A **207**, 91 (1951).

and 30 synthesized by Sondheimer, Wolovsky and Gaoni[14,15,16]. Let us suppose also, for the moment, that we use only the Kekulé structures. There are just two of these, for all n, and they are represented by (a) and (b). We have allowed for possible bond alternation by letting the bond lengths be alternately r_1 and r_2. If $r_1 < r_2$, as in the diagram, the structure (a) will be more energetically bonding than (b), and, as Coulson and Altmann[5] showed for the case of benzene (2n = 6), the resonance energy is drastically reduced as $r_2 - r_1$ increases. Thus when $r_1 = r_2 = 1{\cdot}39$ Å they found that the delocalization energy, defined as the difference in E_π between the localized bonding of a Kekulé structure and the delocalized energy of the corresponding resonance hybrid, was about 63 kcal/mole. But when $r_1 = 1{\cdot}39$ Å, $r_2 = 1{\cdot}54$ Å (they used the old value for the length of a pure trigonal carbon–carbon bond), the delocalization energy was only 9·6 kcal/mole. We shall now show that even when 2n is large, resonance of this kind contributes relatively little to the delocalization energy, and is certainly insufficient to favour a regular shape with equal bond lengths.



(a) (b)

II

If we write ψ_a and ψ_b for the Kekulé structures, and if the ground state wave function is

$$\Psi = c_1\psi_a + c_2\psi_b,$$

then the secular equations to determine the π-electrons energy E_π and the coefficients c_1, c_2 take the form

$$(\mathrm{n}Q_1 + \mathrm{n}Q_2 + \mathrm{n}J_1 - \frac{\mathrm{n}}{2}J_2 - E_\pi)c_1 + \frac{1}{2^{\mathrm{n}-1}}(\mathrm{n}Q_1 + \mathrm{n}Q_2 + \mathrm{n}J_1 + \mathrm{n}J_2 - E_\pi)c_2 = 0$$

$$\frac{1}{2^{\mathrm{n}-1}}(\mathrm{n}Q_1 + \mathrm{n}Q_2 + \mathrm{n}J_1 + \mathrm{n}J_2 - E_\pi)c_1 + (\mathrm{n}Q_1 + \mathrm{n}Q_2 + \mathrm{n}J_2 - \frac{\mathrm{n}}{2}J_1 - E_\pi)c_2 = 0 \tag{13}$$

In these equations Q_1 and Q_2 are the two Coulomb integrals, appropriate to bond lengths r_1 and r_2, and J_1, J_2 are the corresponding exchange integrals. The interesting feature of these equations lies in the coefficient $1/2^{\mathrm{n}-1}$ multiplying the off-diagonal elements in the resulting secular determinant. In the case of benzene this factor is 1/4, but for larger molecules it rapidly decreases, so that the roots of the secular determinant are given essentially by the diagonal elements. In fact, if $r_1 < r_2$ the lowest root is approximately

$$E_\pi = \mathrm{n}\left[Q_1 + Q_2 + J_1 - \tfrac{1}{2}J_2 + \frac{3J_2^2}{2^{2\mathrm{n}-1}(J_1 - J_2)}\right] \tag{14}$$

Thus the delocalization energy, which is given by the last term in (14) actually tends

[14] F. Sondheimer and R. Wolovsky, *Tetrahedron Letters* No. 3, 3 (1959).
[15] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.* **81**, 4755 (1959).
[16] F. Sondheimer, R. Wolovsky and Y. Gaoni, *J. Amer. Chem. Soc.* **82**, 755 (1960).

to zero as $n \rightarrow \infty$. In the case where $J_1 = J_2$ the approximation (14) must be replaced by:

$$E_\pi = n\left[2Q + \frac{J}{2}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)\right] \tag{15}$$

Here again it follows that for sufficiently large n, the delocalization energy tends to zero.

Thus on the basis of Kekulé structures alone, the larger cyclic polyenes would not be expected to be as stable as the smaller ones.

But we can also show that for sufficiently large n, the regular polygon with $r_1 = r_2$ is less stable than the alternating one with (say) $r_1 < r_2$. To do this we consider $E_{\text{total}}(r_1,r_2)$, which is the sum of E_π and E_σ where $E_\pi(r_1r_2)$ can be found from the equations (13), and where $E_\sigma(r_1r_2) = nE_\sigma(r_1) + nE_\sigma(r_2)$. It is obvious from symmetry considerations alone that there is a stationary value of the total energy when $r_1 = r_2$ and their common value is such that

$$\frac{d}{dr}\left[E_\sigma(r) + Q(r) + \frac{1}{4}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)J(r)\right] = 0 \tag{16}$$

This common value differs very little from that appropriate to benzene, though it actually increases slowly with n. With $r = 1{\cdot}400$ for $n = 3$, it becomes $1{\cdot}403$ for $n = 4$ and $1{\cdot}413$ for $n = 5$.

A tedious calculation, which we shall not reproduce, but which uses the appropriate $J(r)$ and $Q(r)$ from Fig. 3, shows that, at these stationary values, E_{total} is an absolute minimum in the case of benzene, but a saddle point for $n = 4$ and $n = 5$ and all higher values of n. Thus, using Kekulé structures only, benzene is predicted to be a regular polygon, but all larger even cyclic molecules should show bond alternation.

It is not possible to give a similar general demonstration when Dewar structures are included in addition to the Kekulé structures. But (see later) detailed calculation of the energy contours for a variety of values of r_1 and r_2 shows that almost certainly precisely the same situation obtains. We conclude, therefore, that in the larger cyclic polyenes the configuration of greatest stability is one with alternating bond lengths, in agreement with the results of m.o. theory.[8] But in our v.b. theory the alternation appears to set in earlier than in the m.o. theory. In view of the approximations in both, such divergencies are not altogether surprising.

It is worth writing down the expression for the total energy, which results from solving equations (13) for E_π and then adding E_σ. It will be convenient to write $\mathscr{E}_1$ for $E_\sigma(r_1) + Q(r_1)$, and $\mathscr{E}_2$ for $E_\sigma(r_2) + Q(r_2)$. Then for benzene, where $2n = 6$, and taking the negative value of the square root;

$$E_{\text{total}}(r_1,r_2) = 3\mathscr{E}_1 + 3\mathscr{E}_2 + \tfrac{3}{5}(J_1 + J_2) + \tfrac{6}{5}\{4(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}$$

for the case where $2n = 8$,

$$E_{\text{total}}(r_1,r_2) = 4\mathscr{E}_1 + 4\mathscr{E}_2 + \tfrac{20}{21}(J_1 + J_2) + \tfrac{16}{21}\{16(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

For the case where $2n = 10$,

$$E_{\text{total}}(r_1,r_2) = 5\mathscr{E}_1 + 5\mathscr{E}_2 + \tfrac{21}{17}(J_1 + J_2) + \tfrac{8}{17}\{64(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

Once again we see the growing importance of $J_1 - J_2$ as the size of the polyene increases.

4. DETAILED CALCULATIONS FOR 2n = 6, 8, 10

In more detailed calculations for the smaller molecules of this type, we have included both Dewar and Kekulé structures. In the case of benzene, with $r_1 \neq r_2$ there are five structures. The two Kekulé structures III(a)(b) will have different weights but the three Dewar structures, of which III(c) is one example, will all have the same weight. The secular determinant is a 3 × 3 determinant. This has already been given by Coulson and Altmann[5] in equation (3) of their paper. We have verified that this is correct. In our symbols it is

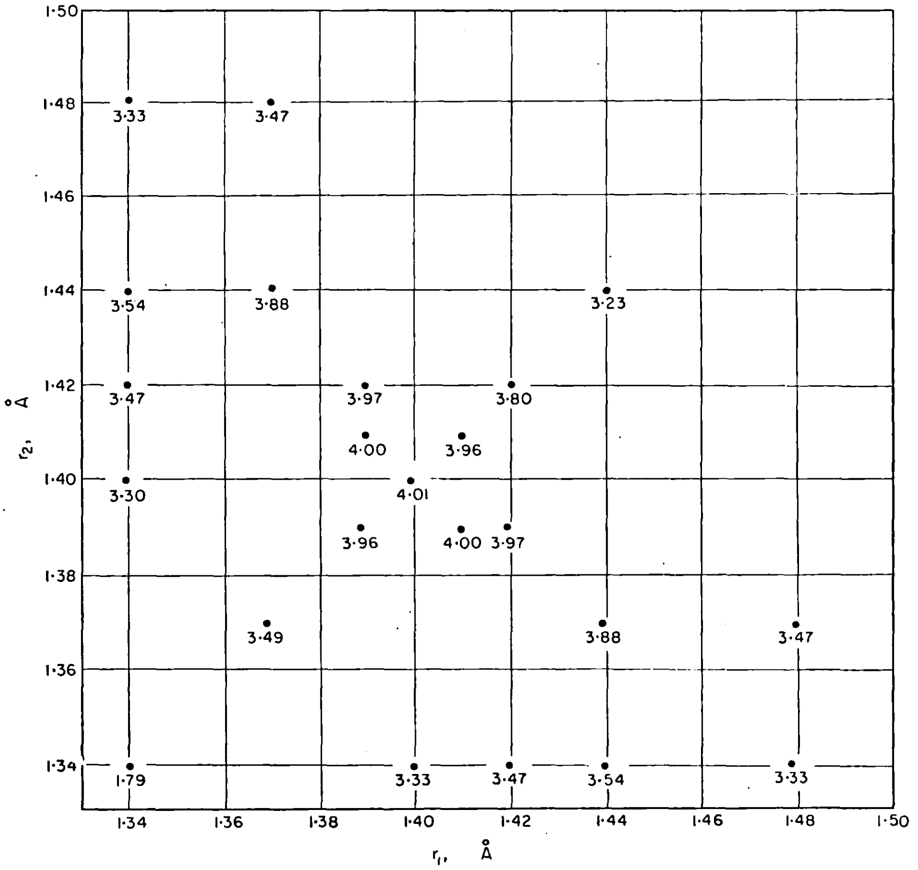
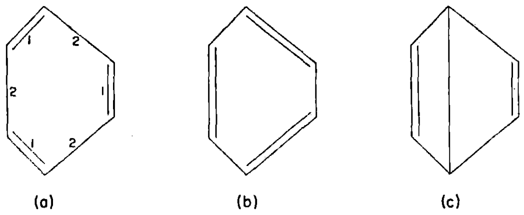


FIG. 4. Calculated values of the total energy $-E(r_1,r_2)$ for benzene, using Kekulé + Dewar structures. The zero of energy is taken at $E = -120$ kcal/mole.

$$24x^3 - 4(J_1 + J_2)x^2 - 2\{3(J_1 - J_2)^2 + 4J_1J_2\}x + (J_1 - J_2)^2(J_1 + J_2) = 0 \qquad (17)$$

where $6x = 3Q_1 + 3Q_2 - E_\pi$.

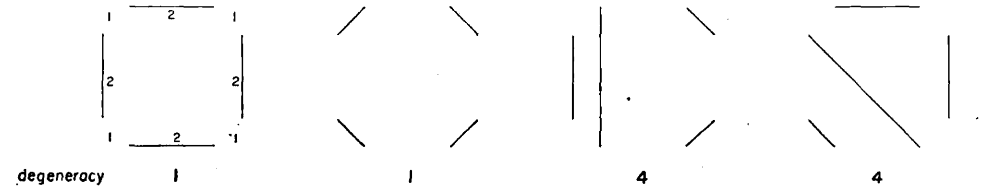
By choosing various combinations of r_1 and r_2 this equation can be solved numerically, and $E_\pi(r_1,r_2)$ obtained. By addition of $E_\sigma(r_1r_2)$ we obtain the total energy $E_{\text{total}}(r_1r_2)$. A typical set of such values is shown in Fig. 4. It is at once clear that the equilibrium value $r_1 = r_2 = 1{\cdot}40$ Å is the position of stable equilibrium, though the curve is much flatter along the line $r_1 + r_2 = 2{\cdot}80$ than along the line $r_1 = r_2$. This is just what we should expect from the known force constants of benzene in the two corresponding normal modes B_{2u} and A_{1g} respectively.



(a) (b) (c)

III

In the case of C_8H_8, there are 2 Kekulé structures and 8 Dewar structures, which divide up as in IV, where we have simplified the diagrams by only representing the π-electrons.



IV

The secular determinant is of order 4 × 4 and the equation for the energy is

$$2048x^4 - 160(J_1 + J_2)x^3 - 20\{24(J_1 - J_2)^2 + 23J_1J_2\}x^2$$
$$+ 28(J_1 + J_2)\{2(J_1 - J_2)^2 + J_1J_2\}x - J_1J_2\{7(J_1 - J_2)^2 - 20J_1J_2\} = 0 \quad (18)$$

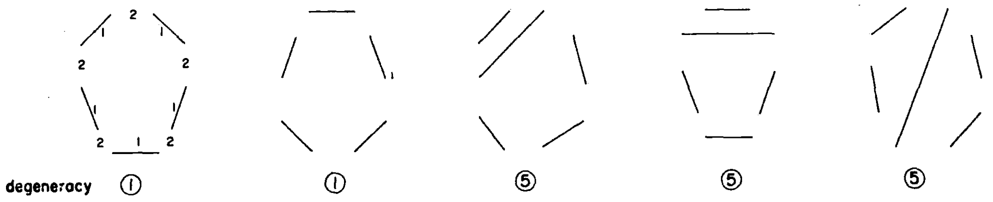
where, now

$$8x = 4Q_1 + 4Q_2 - E_\pi \quad (19)$$

A check on (18) may be found from the fact that it gives correct values when $J_1 = J_2$ and when $J_2 = 0$. The significance of $(J_1 - J_2)^2$, which depends on the degree of bond alternation, is very clear.

Fig. 5(a) shows a set of values of $E_{tot}(r_1,r_2)$ for various r_1 and r_2. Along the line $r_1 = r_2$ we have a minimum energy at $r_1 = r_2 = 1{\cdot}404$ Å. But Fig. 5(b), which shows the variation of energy along the line AB, where $r_1 + r_2 = 2{\cdot}81$ Å, suggests that the point (1·404, 1·404) is really a saddle point, and the stable configurations are at (1·375, 1·435) and (1·435, 1·375). Thus we predict a bond alternation with difference 0·06 Å. This is of the same order as that predicted by Longuet-Higgins and Salem[8], but rather larger.

In the case of n = 5, there are three types of Dewar structure:



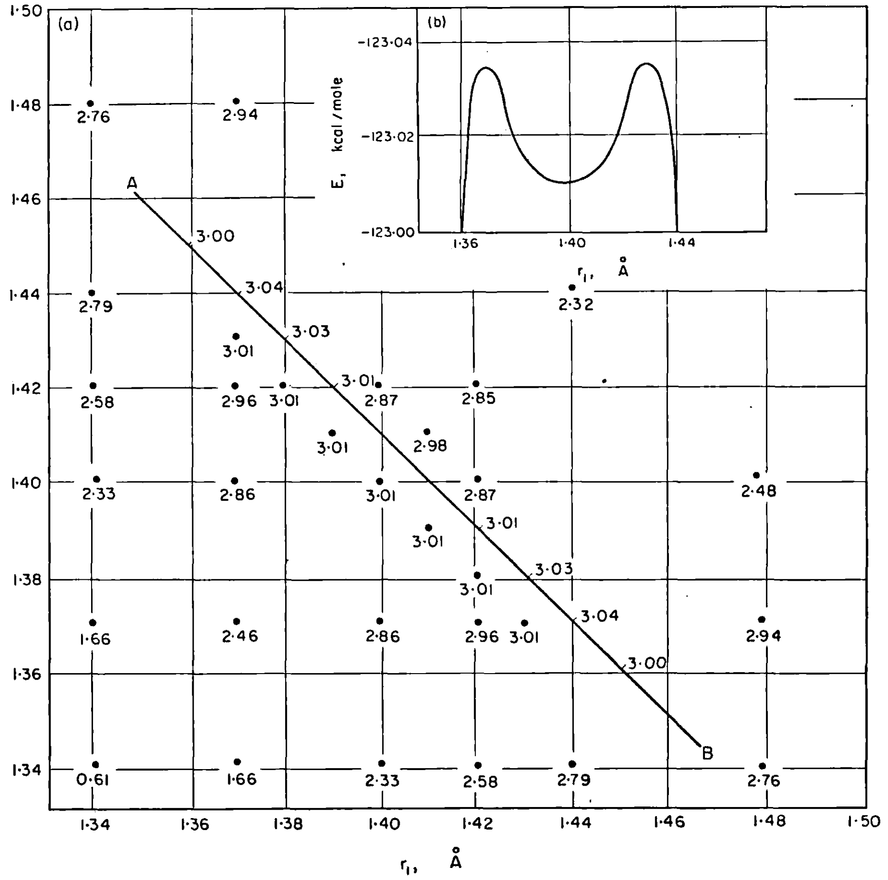


FIG. 5. Main diagram (a). Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar C_8H_8, using Kekulé + Dewar structures. The zero of energy is at $E = -120$ kcal/mole. Small inset diagram (b). Curve showing total energy along the line *AB* of (a), i.e. where $r_1 + r_2 = 2·81$ Å. The minimum energy occurs at $r_1 = 1·37$, $r_2 = 1·44$ Å, and the equivalent position $r_1 = 1·44$, $r_2 = 1·37$ Å.

The secular determinant is of order 5 × 5 and the equation for the energy eventually reduces to:

$$\begin{aligned} 31x^5 &- 11(J_1 + J_2)x^4 - x^3(738\{J_1^2 + J_2^2\} - 846J_1J_2) \\ &+ x^2(J_1 + J_2)(682\{J_1^2 + J_2^2\} - 1018J_1J_2) \\ &+ x[1043\{J_1^4 + J_2^4\} + J_1J_2\{7182J_1J_2 - 3302(J_1^2 + J_2^2)\}] \\ &+ (J_1 + J_2)[J_1J_2\{1730(J_1^2 + J_2^2) - 4470J_1J_2\} - 335(J_1^4 + J_2^4)] = 0 \end{aligned} \tag{20}$$

where

$$10x = 5Q_1 + 5Q_2 - E_\pi \tag{21}$$

This equation was checked by putting $J_1 = J_2$, when it is divisible by the equation derived *ab initio*
viz.

$$31x^3 - 22Jx - 444J^2x + 560J^3 = 0 \tag{20a}$$

The quintics obtained on inserting numerical values for J_1, J_2 were solved by means of the Oxford 'Mercury' electronic computer, and the energy surface (symmetrical about $r_1 = r_2$, of course) plotted. (Fig. 6).

It turns out that there is a much more definite minimum in this case (n = 5) than in the case n = 4. This occurs at $r_1 = 1{\cdot}365$ Å, $r_2 = 1{\cdot}455$ Å leading to a difference of 0·09 Å in the two bond lengths. From this result, it would appear that bond alternation tends to increase with the size of the rings (i.e. when including singly-excited structures in the calculation). It seems to us rather unlikely that subsequent addition of doubly-excited and higher structures would materially alter this. But it should be mentioned that the inclusion of the Dewar structures has led to a distinct change in the bond lengths: for a similar calculation using only the two Kekulé structures leads to bond lengths not greatly different from the values 1·51 and 1·34 Å appropriate to non-resonating single and double bonds.

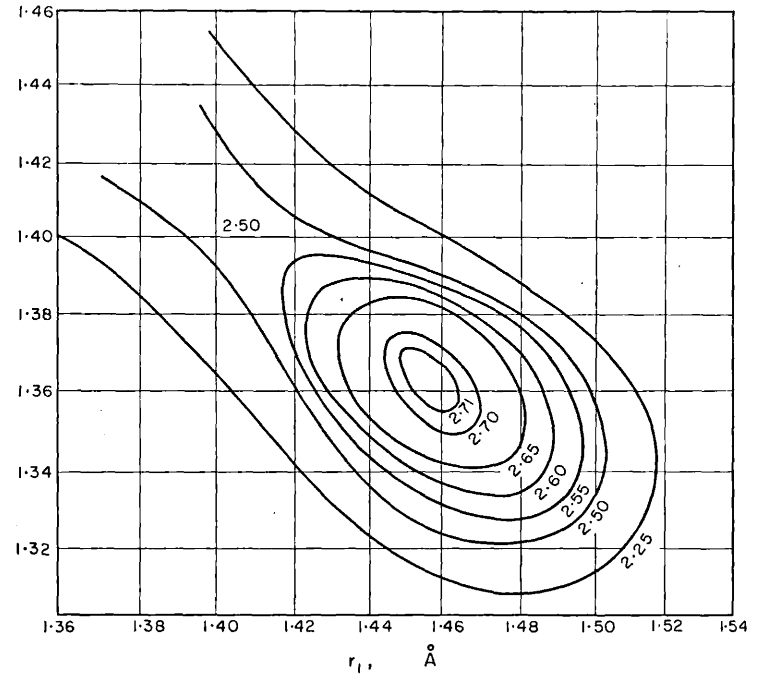


FIG. 6. Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar $C_{10}H_{10}$, using Kekulé and Dewar structures. The zero of energy is taken, as in Fig. 5, at $E = -120$ kcal/mole.

The difference in energy between the unsymmetrical and symmetrical structures can be seen, from Fig. 6, to be about 0·2 kcal. This, although quite definite, is not large, so that molecules of this kind would show rapid interconversion at room temperature. Further, since the interconversion motion would be slow at the saddle point, an X-ray diagram might easily show an apparently symmetrical appearance.

5. CONCLUSION

The discussion just given seems to us to show that in many respects the v.b. technique leads to very similar results to the m.o. technique, when applied to cyclic polyenes $C_{2n}H_{2n}$. Small members of this series will tend to have equal bond lengths, but larger ones will definitely show alternation. With Kekulé structures only it is found that beyond $2n = 8$ there is very little resonance, so that one of the two structures dominates the complete wave function. Even in the symmetrical configuration the resonance (more strictly, delocalization) energy is much smaller than in benzene. Inclusion of Dewar structures tends to favour more nearly equal bond lengths, but bond alternations of the order of 0·1 Å may occur.

Note added in proof: Since the manuscript was written, we have included doubly-excited structures in the description of the eight and ten membered rings. This makes almost no difference to the calculated bond lengths in the equilibrium configurations.

Tetrahedron, 1962, Vol. 18, pp. 875 to 878 Pergamon Press Ltd. Printed in Northern Ireland

BOND LENGTHS IN CONJUGATED POLYENES

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(*Received* 17 *February* 1962)

Abstract—Some conjugated polyenes have been examined using the valence-bond approximation including σ-bond compressional energy.

The appropriate exchange and coulomb integrals were obtained as functions of bond length, using spectroscopic and thermal data for benzene and ethylene.

These semi-empirical functions were then used in investigating linear and cyclic polyenes.

It was found that the bond lengths predicted for butadiene were in excellent agreement with experiment and that there should be appreciable bond alternation in longer chains. Similarly for $n > 3$, it was found that bonds should alternate in the cyclic polyenes $C_{2n}H_{2n}$ and that the degree of bond alternation tends to increase with n.

This agrees qualitatively with the recent application of simple molecular-orbital theory (including σ-bond compression) to long chain and large cyclic polyenes.

1. INTRODUCTION

In a previous paper,[1] bond lengths were examined in cyclic polyenes from a valence bond point of view.

Values for exchange, coulomb integrals and σ-bond energies were calculated from Morse functions obtained empirically for the C—C bond energies in ethylene and in benzene.

Thus if:

$$E_\sigma = E_\sigma(r) = \sigma\text{-bond energy}$$
$$J = J(r) = \text{exchange integral}$$
$$Q = Q(r) = \text{coulomb integral}$$

then the bond energies of ethylene and 'symmetrical' benzene are given by:—

$$E_{\text{ethylene}} = E_\sigma + Q + J$$
$$E_{\text{benzene}} = E_\sigma + Q + 0{\cdot}4J$$
$$E_{\text{benzene}} = E_\sigma + Q + 0{\cdot}434J \text{ (including Dewar structures)}$$

From these equations and the Morse functions describing E_{ethylene} and E_{benzene} in terms of r, the bond length, J(r) and $E_\sigma(r) + Q(r)$ were obtained.

This procedure was almost identical with that of Lloyd and Penney,[2] except that σ-π exchange interactions were assumed either to be negligible, or to vary in the same way as the term $(E_\sigma + Q)$, in which they could therefore be included.

To investigate cyclic polyenes then, assuming alternating bond lengths r_1, r_2, expressions for total energies were found in terms of $J(r_1)$, $J(r_2)$, $E_\sigma(r_1) + Q(r_1)$, $E_\sigma(r_2) + Q(r_2)$. The energies associated with various pairs r_1, r_2 could then be calculated and plotted on a contour diagram. The position of the absolute minimum of energy could thus be assessed.

It was found that for $n \geqslant 4$, the stable configuration of the cyclic polyenes $C_{2n}H_{2n}$ was the one with alternating bond lengths. Inclusion of Dewar structures smoothed out but did not destroy this effect.

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* Now at the Dyson-Perrins Laboratory, Oxford.

[1] C. A. Coulson and W. T. Dixon, Tetrahedron **17**, 215 (1962).

[2] E. H. Lloyd and W. G. Penney, *Trans Faraday Soc.* **35**, 835 (1939).

Recently, calculations have been carried out more accurately by means of the 'Mercury' computer. This has enabled us not only to tackle new problems, but also to recalculate the cyclic polyenes $C_{2n}H_{2n}$ for n = 3, 4, 5.

The functions J(r), $E_\sigma(r) + Q(r)$ had to be determined more accurately and the following table shows some of the numerical values* which were used:

r(Å)	J(r)	$E_\sigma(r) + Q(r)$ (kcal/mole)
1·34	51·6493	99·3507
1·36	48·9067	101·3163
1·38	46·2496	103·6891
1·40	43·6817	105·0308
1·42	41·2055	105·8977
1·44	38·8226	106·3412
1·46	36·5338	106·4079
1·48	34·3392	106·1405

Approximate analytical expressions for these functions are:

$$J(r) = -41{\cdot}23 + 121{\cdot}2(r - 1{\cdot}42) - 114{\cdot}2(r - 1{\cdot}42)^2$$

$$E_\sigma(r) + Q(r) = -105{\cdot}89 - 39{\cdot}6(r - 1{\cdot}42) + 52{\cdot}6(r - 1{\cdot}42)^2 - 1000(r - 1{\cdot}34)(r - 1{\cdot}42)(r - 1{\cdot}51)$$

(Correct to $\pm 0{\cdot}02$ kcal/mole)

2. LINEAR POLYENES $C_{2n}H_{2n+2}$

There has been much discussion about bond lengths in long chains[3–5] and it seems clear, from the absorption spectra, that bond lengths should alternate even when the chains are very long. Since this has been predicted by various MO treatments[6,7], it would be interesting to see whether the valence-bond method leads to similar conclusions.

In the calculations reported in this paper, Kekulé and Dewar structures are included in setting up secular determinants. Inclusion of more excited structures was not thought worth while, since their effect should be negligible according to the results obtained for cyclic polyenes (in which excited structures are more favourable). The following results were obtained:

BOND LENGTHS IN ORDER, STARTING FROM ONE END OF THE CHAIN (SYMMETRICAL ABOUT CENTRE BOND)

Ethylene	1·34 (Å)			
Butadiene	1·345	1·479		
Hexatriene	1·348	1·477	1·353	
Octatetraene	1·347	1·477	1·353	1·476

---

* It need hardly be said that these figures are not accurate to so many significant places on an absolute scale, but in order to find stationary values, a high degree of *relative* accuracy is required.

[3] H. Kuhn, *J. Chem. Phys.* **17**, 1198 (1949).

[4] M. J. S. Dewar, *J. Chem. Soc.* 3456 (1952).

[5] W. T. Simpson, *J. Amer. Chem. Soc.* **78**, 3585 (1956).

[6] S. Huzinaga and T. Hasino, *Prog. Theoret. Phys.* **18**, 649 (1957).

[7] Y. Ooshika, *J. Phys. Soc. Japan* **12**, 1238 and 1246 (1957).

The bond lengths in butadiene have been found by electron diffraction[8] to be 1·337 ± 0·005, 1·483 ± 0·01 (Å) so that there is excellent agreement here with experiment. There is very little smoothing out of the bonds even in octatetraene, compared with simple MO predictions;[9] i.e. for octatetraene: 1·361 1·424 1·379 1·419 (Å). It would appear then, that bond lengths should alternate in long chains also—and to a greater extent than expected from the simple MO method.

3. CYCLIC POLYENES $C_{2n}H_{2n}$

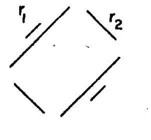
The problem of bond lengths in cyclic polyenes was attacked on three levels of complexity:

(i) Considering Kekulé structures only.
(ii) Including Dewar structures.
(iii) Including also doubly-excited structures. (i.e. two long bonds)

It is well known that the so-called 'excited structures' become more important as the number of atoms increases, because of the rapid increase in the number of canonical structures with n, i.e. in the case of cyclic polyenes $C_{2n}H_{2n}$:

n	Number of Kekulé structures	Number of Dewar structures	Number of doubly-excited structures
2	2	0	0
3	2	3	0
4	2	8	4
5	2	15	20
6	2	24	54

When bonds are assumed to alternate, care has to be taken to see which structures are degenerate and which are not. For example, adopting a set of Rumer diagrams which correspond to actual bond diagrams, there are ten types of doubly-excited structures when n = 6, including these, labelled 7, 8:



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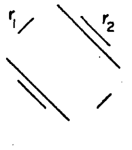
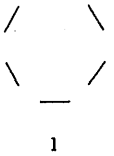
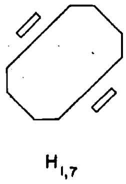


8

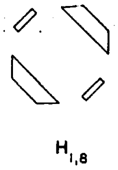
Now 7, 8 are not degenerate, in spite of having the same number of bonds, lengths r_1, r_2 (unless $r_1 = r_2$). This becomes clear if superposition diagrams are drawn, when some corresponding matrix elements are found to differ,—unexpectedly, from a naive point of view. e.g. with the Kekulé structure '1', $H_{17} \neq H_{18}$:



1



$H_{1,7}$



$H_{1,8}$

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[8] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[9] C. A. Coulson, *Proc. Roy. Soc.* **A169**, 413 (1939).

The following table summarizes the results obtained:

	Kekulé structures only			Including Dewar structures			Including doubly-excited structures		
n	r_1[a]	r_2[a]	ΔE[b]	r_1[a]	r_2[a]	ΔE[b]	r_1[a]	r_2[a]	ΔE[b]
2		1·393			1·393			1·393	
3		1·400			1·400			1·400	
4	1·346	1·493	0·89	1·375	1·435	0·023	1·378	1·432	0·013
5	1·343	1·506	1·06	1·360	1·460	0·25	1·365	1·455	0·16
6	1·340	1·510	2·8	1·355	1·471	0·40	1·358	1·465	0·294

[a] r_1, r_2 are adjacent bond lengths, in Angstroms.

[b] ΔE is the height of the saddle-point above the absolute minimum, in Kcal/mole.

There is apparently an increasing tendency towards bond alternation with increasing n. Inclusion of excited structures decreases, but does not destroy, the effect. Doubly-excited structures seem to have a relatively small effect on the energy surfaces.

These results are in qualitative agreement with the MO work by Longuet-Higgins and Salem,[10] who predicted that if rings are large enough, the stable configuration should be one with alternating bond lengths, the difference between adjacent bonds being about 0·04 Å. However, they found that for rings of the type $C_{4t+2}H_{4t+2}$, the less symmetrical form should be the more stable when $t \geqslant 8$; i.e. for rings larger than about $C_{34}H_{34}$. This contrasts with the results given in this paper, which indicate that bond alternation should occur in rings $C_{2n}H_{2n}$ when $n \geqslant 4$.

4. CONCLUSION

There is some experimental justification for this type of V.B. method because of:

(a) The excellent agreement between predicted and experimental bond lengths in butadiene.[8]

(b) Bond alternation is predicted for long chains (in agreement with the most recent interpretations of the UV spectra of long polyene chains).[6,7]

(c) Bond alternation is predicted for large cyclic polyenes, (the UV spectra of $C_{18}H_{18}$, $C_{24}H_{24}$ are difficult to explain if adjacent bonds are assumed to be equal in length).[11]

It appears, then, that this method predicts bond alternation in both long chain and large cyclic polyenes. Though the degree of bond alternation is rather larger than that predicted by the simple MO method, the two approaches do seem to lead to similar qualitative results, in these cases.

Acknowledgement—I would like to thank Professor Coulson for his encouragement and suggestions in preparing this paper.

[10] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A**251**, 172 (1959).

[11] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A**257**, 445 (1960).

(*Reprinted from Nature, Vol.* 196, *No.* 4857, *pp.* 891–892,
December 1, 1962)

Free Radicals formed during the Oxidation and Reduction of Peroxides

The reduction of hydrogen peroxide by transition metal ions is thought to involve hydroxyl radicals as intermediates[1]. We have found that dilute solutions of titanous ion and hydrogen peroxide (about 10^{-2} M) react together to form a free radical of short life. This has been observed by using a flow system in which the reactants are mixed just before entering the cavity of a Varian electron spin resonance spectrometer. The spectrum is a single line near $g = 2$, width about 3 gauss, the intensity of which at maximum flow-rate is proportional to $[Ti^{3+}]$ and $[H_2O_2]$ when these are low.

The radical may be $\cdot OH$ or $\cdot O_2H$, according to the reactions[1]:

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH^- + \cdot OH$$
$$\cdot OH + H_2O_2 \rightarrow H_2O + \cdot O_2H$$

There is evidence, however, that the perhydroxyl radical gives a much broader signal because, when hydrogen peroxide[2], *t*-butyl hydroperoxide, and cumyl hydroperoxide are oxidized by ceric ion, single lines of width 27, 14, and 6 gauss, respectively, are observed, presumably corresponding to peroxy radicals:

$$Ce^{4+} + RO_2H \rightarrow Ce^{3+} + H^+ + RO_2$$

An attempt to observe the *t*-butoxy radical in the reaction between *t*-butyl hydroperoxide and titanous ion resulted in the appearance of a quartet of intensities 1 : 3 : 3 : 1, the distance between adjacent peaks being about 24 gauss. This is apparently due to the methyl radical[3] arising from the reactions:

$$Ti^{3+} + Me_3COOH \rightarrow Ti^{4+} + OH^- + Me_3CO\cdot$$
$$Me_3CO\cdot \rightarrow Me_2CO + CH_3\cdot$$

These results suggest that the radical observed in the reaction between hydrogen peroxide and titanous ion is hydroxyl.

The signal corresponding to this radical disappears when the reactant solutions contain various aliphatic or aromatic compounds and is replaced by spectra of new radical intermediates. For example, 2-propanol gives a septet together with a weaker quartet, peak-to-peak distances being about 20 and 24 gauss, respectively. These are similar to spectra previously ascribed to $Me_2\dot{C}{-}OH$ and CH_3 which were observed in the solid state at low temperatures[3,4] except that the hyperfine line-widths which we observe are narrower (approximately 1·5 and 2·5 gauss, respectively).

These results confirm that the hydroxyl radical is very reactive, may be obtained in aqueous solution at room temperature, and can be used to generate other free radicals. A discussion of all the spectra and a description of the flow system will be published.

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[1] Url, N., *Chem. Rev.*, 50, 375 (1952). Higginson, W. C. E., Sutton, D., and Wright, P., *J. Chem. Soc.*, 1380 (1953). (See Cahill, A. E., and Taube, H., *J. Amer. Chem. Soc.*, 74, 2312 (1952)).

[2] Saito, E., and Bielski, B. H. J., *J. Amer. Chem. Soc.*, 83, 4467 (1961).

[3] Luck, C. F., and Gordy, W., *J. Amer. Chem. Soc.*, 78, 3240 (1956). Gordy, W., and McCormick, C. G., *ibid.*, 78, 3243 (1956).

[4] Fujimoto, M., and Ingram, D. J. E., *Trans. Farad. Soc.*, 54, 1304 (1958).

Printed in Great Britain by Fisher, Knight & Co., Ltd., St. Albans.

Reprinted from Proceedings of the Chemical Society, March, 1963, page 97

An Intermediate in Homolytic Aromatic Substitution

By W. T. DIXON and R. O. C. NORMAN
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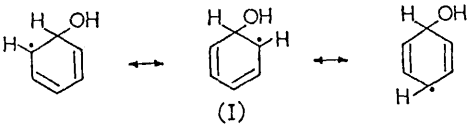
BENZENE reacts with titanous ion and hydrogen peroxide, to give phenol and biphenyl. We here report evidence that the resonance-stabilised radical (I) is an intermediate.

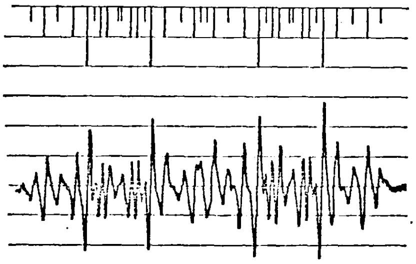


(I)

Warm, acidified aqueous solutions of titanous ion and hydrogen peroxide, each saturated with benzene, were allowed to react in a flow system less than 0·02 sec. before entering a cell in the cavity of a 100 kc./sec. Varian V4500 electron spin resonance spectrometer. The resulting spectrum (Figure) replaced the signal attributed to the hydroxyl radical which we have observed in the absence of benzene.[1] The reconstruction shown is based on coupling with two single protons (coupling constants, 36·0 and 13·4 gauss) (± 5%) and two pairs of protons (coupling constants, 9·3 and 2·9 gauss) (± 5%). This is consistent with the adduct (I) in which coupling would be expected with the six protons on carbon atoms but not with that on oxygen.[2]

When phenol was used in place of benzene, the formation of the phenoxy-radical was confirmed by its spectrum[3] (coupling constants: *o*-H, 6·4; *m*-H, 1·7; *p*-H, 9·7 gauss). This is almost identical in form with half the spectrum ascribed to radical (I), as expected from examination of the appropriate canonical structures, and leads to the assignment of three of the coupling constants for radical (I) (9·3, 2·9, and 13·4 gauss) to *o*-, *m*-, and *p*-protons, respectively. The smaller couplings for the phenoxy-radical arise from the additional possibility of delocalisation of the unpaired electron on to the oxygen atom. The largest splitting observed for radical (I) is evidently due to the proton on sp^3-carbon, which is favourably situated for interaction with the π-electron system in which the unpaired electron is found.

Our assignments for radical (I) receive further support from the similarity of the coupling constants to those of the related radical, cyclohexadienyl (CH_2, 50; *o*-H, 10·6; *m*-H, 2·6; *p*-H, 10·6 gauss).[4]



Spectrum of the intermediate, and reconstruction based on the coupling constants given in the text.

The formation of radical (I) is consistent with the absence of a hydrogen isotope effect in the formation of both phenol and biphenyl when benzene is oxidised with Fenton's reagent, which behaves similarly to the system of Ti^{3+} and H_2O_2.[5] Finally, the radical (I) is analogous to the intermediate postulated in the phenylation of benzenoid compounds on the basis of kinetic isotope effect measurements[6] and product analysis.[7]

One of us (W.T.D.) thanks the D.S.I.R. for a maintenance grant.

(*Received, December 20th*, 1962.)

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[1] Dixon and Norman, *Nature*, 1962, 196, 891.

[2] Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, p. 174.

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Preprinted from the Journal of the Chemical Society,
May, 1963, (572), pages 3119—3124.

572. *Electron Spin Resonance Studies of Oxidation. Part I. Alcohols.*

By W. T. DIXON and R. O. C. NORMAN.

When acidic solutions of titanous ion and hydrogen peroxide react immediately before passing through the cavity of an electron spin resonance spectrometer, a singlet is observed in the spectrum which is attributed to the hydroxyl radical. The addition of alcohols to the reactants results in the replacement of this signal by the spectra of organic radicals formed by abstraction of a hydrogen atom from a C–H bond or (in one case) by addition to C=C. Analysis of the spectra gives evidence about the structures of the radicals and hence about the course of the reaction.

Coupling constants for protons in different environments are reported and discussed.

FREE radicals produced by the abstraction of a hydrogen atom from alcohols have been extensively studied by electron spin resonance spectroscopy.[1,2] The technique which has been used consists of freezing a mixture of hydrogen peroxide and the alcohol, transferring the resulting glass to the cavity of an electron spin resonance spectrometer, and then observing the signals produced on ultraviolet irradiation. Hydroxyl radicals are produced initially and these diffuse and react with the alcohols.

From the point of view of studying the hyperfine structure of the spectra this solid-state method suffers from the disadvantage that the individual lines are considerably broadened by anisotropic coupling and complete resolution is not always obtained. Irradiation of solutions does not provide a practicable method for studying the radicals because they are generated comparatively slowly and are usually too short-lived to reach a steady concentration large enough for observation. We therefore investigated the possibility of generating radicals by a fast reaction, using a flow system in which the radicals could be observed less than 0·02 second after the reactants had been mixed.

We first studied in this way the reduction of hydrogen peroxide by transition-metal ions, which is reported to give hydroxyl radicals.[3] When ferrous ion reacted with hydrogen peroxide only a spectrum of six peaks, ~100 gauss apart, due to manganous ion impurity, was observed, and this signal could have masked one due to the hydroxyl radical. When, however, titanous ion, which did not give a detectable signal itself, reacted with hydrogen peroxide in acidic solution a sharp line of width 1 gauss was observed.*

The radicals likely to be present in this system are hydroxyl and perhydroxyl, produced by the reactions:

$$\mathrm{Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + \cdot OH + OH^-}$$

$$\mathrm{\cdot OH + H_2O_2 \longrightarrow H_2O + \cdot O_2H}$$

The spectrum of the perhydroxyl radical had been observed previously when hydrogen peroxide was oxidised by ceric ion, and consisted of a very broad singlet of width 27 gauss.[5] We repeated and confirmed this observation, and also examined the peroxyl radicals obtained by the oxidation by ceric ion of t-butyl and cumyl hydroperoxide, each of which gave a singlet.[4]

Spectra which have been ascribed to hydroxyl and perhydroxyl radicals have been observed in the solid state; both are doublets.[6] It is reasonable, however, that both spectra should be singlets in aqueous solution at room temperature because of the rapid exchange of the proton with the solvent. Coupling with a hydroxyl-proton in solution has been reported, but only in a very strongly acid medium.[7]

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* The stability and resolution of the spectrometer have been greatly improved since our preliminary result was reported.[4]

We therefore attribute the signal from titanous ion and hydrogen peroxide to the hydroxyl radical. In support of this assignment, titanous ion and t-butyl hydroperoxide gave a quartet (1 : 3 : 3 : 1; coupling constant 22 gauss) characteristic of the methyl radical.[8,9] This is consistent with the formation of the t-butoxyl radical which is known to break down to methyl: [10]

$$Ti^{3+} + Me_3C{\cdot}O_2H \longrightarrow Ti^{4+} + Me_3C{\cdot}O{\cdot} + OH^-$$

$$Me_3C{\cdot}O{\cdot} \longrightarrow {\cdot}CH_3 + Me_2CO$$

The amplitude of the signal from the reaction of hydrogen peroxide and titanous ion was examined as a function of the flow rate and the concentrations of the reactants. At constant concentrations the amplitude increased with increase in the flow rate, and the variations of log (amplitude) with log (concentration) at the maximum flow rate (about 5 ml. per second) are shown in Fig. 1. At low concentrations the slopes of both plots are unity, indicating that the radical concentration is proportional to $[Ti^{3+}]$ and to $[H_2O_2]$.

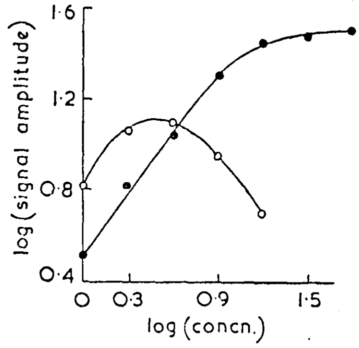

FIG. 1. Variation of signal with reactant concentrations. ● H_2O_2; ○ Ti^{3+}.

Two further observations were made. First, when sulphuric or perchloric acid was used to acidify the reactants the signal was much larger than when hydrochloric acid was used, possibly because of complex-formation by chloride ion. Secondly, when ferrous ion was added to the titanous solution the amplitude of the signal decreased, but the singlet was still observable despite the presence of the spectrum due to manganous ion. Evidently the one-electron reduction of hydrogen peroxide by titanous ion proceeds more readily than that by ferrous ion, as previously suggested.[11]

Aliphatic Radicals.—When aliphatic alcohols were added to the reactants the signal ascribed to ·OH was replaced by spectra due to organic radicals. In the simpler cases these were readily analysed.

(*a*) *Monohydric alcohols.* Methanol gave a triplet, each of whose lines is apparently an incompletely resolved doublet (Fig. 2). This corresponds to the expected radical $\cdot CH_2{\cdot}OH$ in which there is coupling with the two protons on carbon and possibly very weak coupling with the proton on oxygen.

t-Butyl alcohol gave a triplet of septets (Fig. 3) which is ascribed to $\cdot CH_2{\cdot}C(CH_3)_2{\cdot}OH$ formed by abstraction of a β-hydrogen atom. It should be noted that, although the stronger coupling is due to the protons on C_1, the six C_3-protons also give rise to significant splitting.*

Ethanol gave two quartets (Fig. 4), corresponding to $CH_3{\cdot}CH(OH){\cdot}$ in which the stronger coupling occurs with the three C_2-protons, and which is formed by abstraction of α-hydrogen.

Isopropanol (Fig. 5) gave a septet, expected for $(CH_3)_2C(OH){\cdot}$ formed by abstraction of α-hydrogen, on which was superimposed a weak quartet. The latter is ascribed to

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* The designations α, β, etc., refer to the position of the group concerned relative to that of the hydroxyl group, and C_1, C_2, etc., refer to the position relative to the carbon which bears the unpaired electron.

$\cdot CH_2\cdot CH(OH)\cdot CH_3$, formed by abstraction of β-hydrogen, which is to be expected by analogy with the result for t-butyl alcohol. Two of the three hydrogen atoms which couple with the unpaired electron are in a different environment from the third, but it is shown later that the coupling constants of C_1- and C_2-protons are very similar when there is no hydroxyl group on C_1.


FIG. 2. Spectrum from methanol.

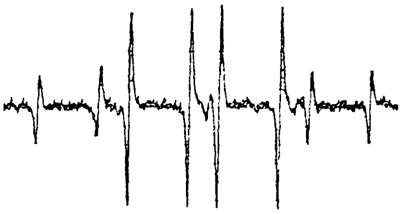


FIG. 4. Spectrum from ethanol.

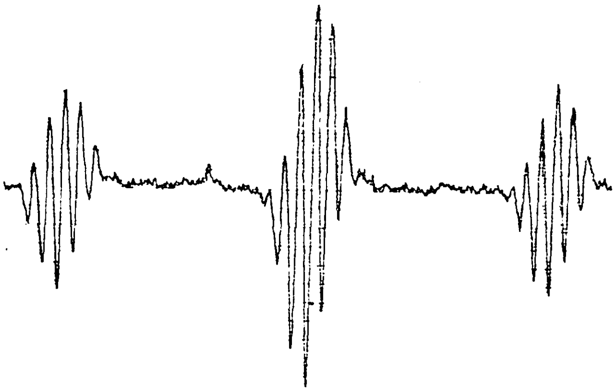


FIG. 3. Spectrum from t-butyl alcohol.


FIG. 5. Spectrum from propan-2-ol.

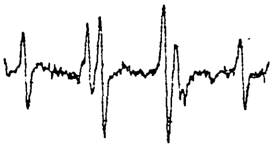


FIG. 6. Spectrum from propane-1,3-diol.

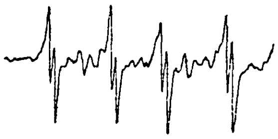


FIG. 7. Spectrum from propargyl alcohol.


FIG. 8. Spectrum from allyl alcohol.

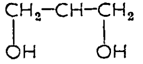
Aliphatic alcohols of more complex structure, such as propan-1-ol, butan-1-ol, and butan-2-ol, gave spectra of great complexity which corresponded to the presence of at least two radicals in each case. Isobutyl alcohol also gave a complex spectrum, but it contained four lines of equal intensity, rather more intense than the remainder, consistent with the presence of $(CH_3)_2CH\cdot CH(OH)\cdot$ in which (unequal) coupling occurs with the C_1- and C_2-protons.

(*b*) *Dihydric and polyhydric alcohols.* Propane-1,3-diol gave two triplets (Fig. 6), compatible with a radical $\cdot CH(OH)\cdot CH_2\cdot CH_2OH$. Pinacol gave a triplet, and pentaerythritol a doublet, corresponding to $\cdot CH_2\cdot CMe(OH)\cdot CMe_2\cdot OH$ and $\cdot CH(OH)\cdot C(CH_2\cdot OH)_3$, respectively.

The two αβ-diols, glycol and propane-1,2-diol, behaved differently: each gave a triplet, similar to that from methanol, superimposed on rather ill-defined lines. It is possible that the initially formed radicals undergo further reaction, including C–C bond cleavage, and that the observed radical in each case is $\cdot CH_2\cdot OH$, for formaldehyde is one of the products of the oxidation of glycol by Fenton's reagent.[12]

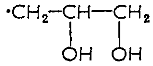
(*c*) *Unsaturated alcohols.* The two unsaturated alcohols examined behaved differently from each other. Propargyl alcohol gave four doublets (Fig. 7) (coupling constants: 18·5, 10·2, and 1·2 gauss), consistent with the resonance-stabilised radical $CH{\equiv}C\cdot CH(OH)\cdot \longleftrightarrow \cdot CH{=}C{=}CH\cdot OH$ in which the principal coupling occurs with the two protons on carbon and the smallest coupling arises from the proton on oxygen.

Allyl alcohol gave a spectrum consisting of a sextet on which was superimposed a weaker quartet (Fig. 8). Neither spectrum corresponds to the radical $\cdot CH(OH)\cdot CH{=}CH_2$ which would be formed by abstraction of hydrogen, but they are compatible with the products (I) and (II), respectively, of the addition of $\cdot OH$ to the double bond. The former contains five protons, and the latter three, which are expected (by analogy with the coupling constants for C_1- and C_2-protons in similar environments; see Table 1) to give the same coupling and hence a sextet and a quartet, respectively.



$HOCH_2-\dot{C}H-CH_2OH$

(I)



$\cdot CH_2-CH(OH)-CH_2OH$

(II)

The greater concentration of radical (I) than (II) is in accordance with the finding that, in an olefin $CH_2{=}CHX$, the methylene group is normally more reactive than the substituted carbon atom towards free-radical addition.

(*d*) *Phenol and quinol.* Phenol gave the phenoxyl radical[13] (coupling constants: *o*-H 6·4; *m*-H 1·7; *p*-H 9·7 gauss), and quinol gave the semiquinone radical[7] (coupling

TABLE 1.

Coupling constants of radicals.

Alcohol	Type of spectrum	Coupling constants (gauss) C_1–H	C_2–H	C_3–H
$CH_3\cdot OH$	Triplet (1 : 2 : 1)	17·2		
$CH_3\cdot CH_2\cdot OH$	Two (1 : 1) quartets (1 : 3 : 3 : 1)	15·0	22·0	
$(CH_3)_2CH\cdot OH$	Septet (1 : 6 : 15 : 20 : 15 : 6 : 1)		20·0	
	and weak quartet (1 : 3 : 3 : 1)	22·0	22·0	
$(CH_3)_3C\cdot OH$	Three (1 : 2 : 1) septets (1 : 6 : 15 : 20 : 15 : 6 : 1)	21·3		1·3
$(CH_3)_2CH\cdot CH_2\cdot OH$	Quartet (1 : 1 : 1 : 1)	12·7	20·0	
		20·0		
$(CH_2\cdot OH)_2$	Triplet (1 : 2 : 1)	18·4		
$HO\cdot CH(CH_3)\cdot CH_2\cdot OH$	Triplet (1 : 2 : 1)	(19·5) *		
$HO\cdot [CH_2]_3\cdot OH$	Two (1 : 1) triplets (1 : 2 : 1)	16·0	19·0	
$[C(CH_3)_2\cdot OH]_2$	Triplet (1 : 2 : 1)	22·4		
$C(CH_2\cdot OH)_4$	Doublet (1 : 1)	16·3		
$CH_2{:}CH\cdot CH_2\cdot OH$	Sextet (1 : 5 : 10 : 10 : 5 : 1)	20·5	20·5	
	and quartet (1 : 3 : 3 : 1)	21·0	21·0	

* This result is approximate because the complexity of the spectrum made it difficult to determine the centres of the peaks.

TABLE 2.

Effects of substituents on the coupling constants of C_1-protons.

Proton environment	Substituents		Source	Coupling constant (gauss)
	R	R′		
$\cdot CHRR'$	H	$-CH(CH_3)\cdot OH$	$(CH_3)_2CH\cdot OH$	22·0
	H	$-C(CH_3)_2\cdot OH$	$(CH_3)_3C\cdot OH$	21·3
	H	$-C(CH_3)(OH)\cdot C(CH_3)_2\cdot OH$	$[C(CH_3)_2\cdot OH]_2$	22·4
	H	$-CH(OH)-CH_2\cdot OH$	$CH_2{:}CH\cdot CH_2\cdot OH$	21·0
	$-CH_2\cdot OH$	$-CH_2\cdot OH$	,,	20·5
$\cdot CHR\cdot OH$	H		$CH_3\cdot OH$	17·2
	$-CH_3$		$CH_3\cdot CH_2\cdot OH$	15·0
	$-CH(CH_3)_2$		$(CH_3)_2CH\cdot CH_2\cdot OH$	12·7
	$-CH_2\cdot CH_2\cdot OH$		$HO\cdot[CH_2]_3\cdot OH$	16·0
	$-C(CH_2\cdot OH)_3$		$C(CH_2\cdot OH)_4$	16·3

constant 2·4 gauss). The effective abstraction of hydrogen from OH rather than from CH is here favoured by the resonance stabilisation in the radicals formed.

Coupling Constants.—The coupling constants obtained for the radicals formed by abstraction of hydrogen are set out in Table 1. The probable error in the data is 5%.

The coupling produced by a C_1-proton is influenced by the environment, as is apparent from examination of the data in Table 2.

Substitution of the hydroxyl group for hydrogen at the C_1-carbon appreciably reduces the coupling constant of the C_1-proton: the values of $\cdot CH_2\cdot OH$ and $\cdot CH_3$ are 17·2 and 22 gauss, respectively. This may arise from reduction in the spin density on carbon due to the mesomeric effect of oxygen (*e.g.*, $\cdot CH_2\cdot OH \longleftrightarrow {}^-CH_2\cdot{}^+\dot{O}H$).* The resulting stabilisation of the radical may underlie the greater ease of abstraction of hydrogen from α- than from β-carbon. Comparison of the coupling constants for the C_1-protons in methanol (17·2 gauss) and ethanol (15·0 gauss) shows that there is a small reduction when hydrogen is replaced by methyl.

The coupling constants of C_2-protons are hardly altered by the substitution of hydroxyl for hydrogen at the C_1-carbon; the small variations are probably within experimental error. Comparison of the coupling constants for the C_1-protons in pinacol and t-butyl alcohol with those of C_2-protons shows that the coupling of a C_2-proton is approximately equal to that of a C_1-proton when there is no hydroxyl group on the C_1-carbon. As discussed earlier, this supports the assignments made for the quartet from propan-2-ol and the sextet and quartet from allyl alcohol.

Conclusions.—The following conclusions are drawn:

(*a*) The hydroxyl radical abstracts a hydrogen atom from aliphatic alcohols, α-CH being rather more reactive than β-CH.

(*b*) Unsaturated alcohols may undergo either addition or abstraction, depending on their structure.

(*c*) The unpaired electron in the resulting radical is strongly coupled with both C_1- and C_2-protons, the extent of coupling being dependent on the nature of the adjacent groups.[2]

(*d*) Coupling with C_3-protons was observed in only one case, that of t-butyl alcohol. [This is unlikely to be exceptional, for we have also observed such coupling in the spectrum of $\cdot CH(CH_3)\cdot O\cdot CH_2\cdot CH_3$, derived from ether.]

(*e*) Coupling with a proton on oxygen is normally too weak to be observed. There are indications of its occurrence in the spectrum from methanol, and that from propargyl alcohol has been interpreted in these terms.

EXPERIMENTAL

A Varian (100 kc. $sec.^{-1}$) V4500 electron spin resonance spectrometer was used. The flow system (Fig. 9) consisted of two concentric tubes carrying the reactant solutions, the inner one

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* We are indebted to a referee for this suggestion.

having four small holes at its end through which the inner solution was forced into the outer one, perpendicularly to the direction of flow. The dead-space was about 0·1 ml. and the maximum flow-rate was 5 ml. sec.$^{-1}$. In this way the reacting mixture entered the flattened section of an aqueous solution cell in the spectrometer within 0·02 sec. of mixing.

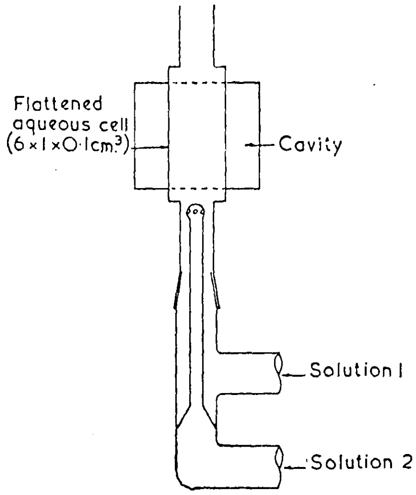

FIG. 9. Flow system.

The spectrum of the hydroxyl radical was observed as follows. One reactant solution contained 15% titanous chloride solution (B.D.H; iron-free) (20 ml.) and concentrated sulphuric acid (14 ml.) in water (2 l.), and the second contained 100-vol. hydrogen peroxide (6 ml.) and concentrated sulphuric acid (14 ml.) in water (2 l.). The spectrum was scanned at least twice during the passage of 4 l. of solution through the cavity.

Organic radicals were observed by adding the appropriate alcohol to each of the reactants to make the solutions ~M/10 with respect to the alcohol.

One experiment was carried out with a solution saturated with t-butyl hydroperoxide. In other experiments the concentration of either titanous chloride or hydrogen peroxide was varied while that of the other reactant was kept constant. The flow-rate could be reduced by means of an adjustable clip on the exit side of the cavity.

Experiments were also carried out with ceric sulphate (0·3 g./l.) in N-sulphuric acid as one reactant, and hydrogen peroxide (10 ml./l.; 100-vol.) and saturated solutions of t-butyl hydroperoxide and cumyl hydroperoxide, in N-sulphuric acid, successively, as the second reactant.

One of us (W. T. D.) thanks the D.S.I.R. for a maintenance grant.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, December 20th*, 1962.]

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society,
October 1964, (701), pages 3625—3634.

701. *Electron Spin Resonance Studies of Oxidation. Part II.*[1] *Aliphatic Acids and Substituted Acids.*

By W. T. DIXON, R. O. C. NORMAN, and (in part) A. L. BULEY.

The electron spin resonance spectra of the radicals formed by the reaction of the hydroxyl radical, generated from titanous ion and hydrogen peroxide in acid solution, with aliphatic acids, α-chloro-acids, α-hydroxy-acids, αβ-unsaturated acids, and a number of other aliphatic compounds are reported. Conclusions are drawn about the courses of the reactions; the activating or deactivating effects of substituents on the ease of abstraction, by ·OH, of hydrogen from C–H; stabilising influences in the radicals so formed; and the variation in the coupling constants of protons in different environments. Particular attention is given to the dependence of the coupling of C_2-protons on the conformation of the radicals.

WE have shown previously that the electron spin resonance (e.s.r.) spectra of short-lived organic radicals can be observed by mixing acidified solutions of titanous ion and hydrogen peroxide, in the presence of organic compounds, immediately before they flow into an aqueous cell in the cavity of the spectrometer.[1] Evidence was presented that the primary reaction is the one-electron reduction of the peroxide by titanous ion to give the hydroxyl radical, which then reacts with the organic compound. Attention was confined in Part I to the reactions of aliphatic alcohols, and it was shown that the technique both enables conclusions to be drawn about the mode of reaction of organic compounds with the hydroxyl radical and makes possible a systematic investigation of the variation in the magnitude of the coupling constants of protons in different environments with the unpaired electron in the radical. In the latter context the advantage of studying these radicals in solution instead of by solid-state techniques was stressed.

We now report results for a number of other aliphatic compounds, with particular reference to acids, α-chloro-acids, α-hydroxy-acids, and unsaturated acids. The data obtained for these compounds, together with the radicals to which the spectra are assigned, are set out in Table 1. Some of the more interesting spectra are reproduced in Figs. 1—6.

Abstraction from Saturated Compounds.—(a) *Acids.* Whereas the presence of an alcohol in approximately 0·1M-concentration caused the complete disappearance of the signal ascribed to ·OH, a similar concentration of acetic acid made little difference to this spectrum. When the concentration of acid was increased, however, the amplitude of the singlet decreased and there appeared with increasing intensity a spectrum consisting of a triplet together with a weaker quartet (Fig. 1). Finally, at a concentration of acetic acid ⩾2M, the singlet was entirely eliminated.

The triplet (coupling constant, 21·8 G) is ascribed to $\cdot CH_2\cdot CO_2H$, for which coupling constants of 21 [2] and 20·4 G [3] have been reported previously. The quartet is the spectrum characteristic of the methyl radical,[1] and it is concluded that methyl radicals are formed by the abstraction of a hydrogen atom from the carboxyl group of acetic acid, followed by decarboxylation [4] of the acetoxy-radical:

$$CH_3\cdot CO_2H + \cdot OH \longrightarrow CH_3\cdot C(=O)O\cdot + H_2O \qquad (1)$$

$$CH_3\cdot C(=O)O\cdot \longrightarrow \cdot CH_3 + CO_2 \qquad (2)$$

There was no indication of a spectrum which could be attributed to the acetoxy-radical (which should appear either as a singlet or as a quartet of much narrower splitting than the spectrum of $\cdot CH_3$), and this is consistent with the view that reactions (1) and (2) are essentially simultaneous.[5]

TABLE 1.

Spectra and coupling constants of radicals derived from acids, and the radicals to which the spectra are assigned.

		Coupling constants (G)				
Acid	Type of spectrum	C_1–H	C_2–H	C_3–H	OH	Radical
$CH_3\cdot CO_2H$	Triplet (1 : 2 : 1) and	21·8				$\cdot CH_2\cdot CO_2H$
	weak quartet (1 : 3 : 3 : 1)	23·1				$\cdot CH_3$
$CH_2(CO_2H)_2$	Triplet (1 : 2 : 1)	21·7				$\cdot CH_2\cdot CO_2H$
$(CH_3)_3C\cdot CO_2H$	Triplet (1 : 2 : 1) of septets (1 : 6 : 15 : 20 : 15 : 6 : 1)	21·8		0·7		$\cdot CH_2\cdot C(CH_3)_2\cdot CO_2H$
$CH_3\cdot CH_2\cdot CO_2H$	Triplet (1 : 2 : 1) of triplets (1 : 2 : 1) [a]	22·4	26·6			$\cdot CH_2\cdot CH_2\cdot CO_2H$
$CH_2Cl\cdot CO_2H$	Two (1 : 1) quartets (1 : 1 : 1 : 1) [b]	20·9				$\cdot CHCl\cdot CO_2H$
$CH_3\cdot CHCl\cdot CO_2H$	Quartet (1 : 3 : 3 : 1) of quartets (1 : 1 : 1 : 1) [c]	20·9				$\cdot CCl(CH_3)\cdot CO_2H$
$CHCl_2\cdot CO_2H$	Septet (1 : 2 : 3 : 4 : 3 : 2 : 1) [d]					$\cdot CCl_2\cdot CO_2H$
$H\cdot CO_2H$	Singlet					$\cdot CO_2H$ *or* $H\cdot CO_2\cdot$
$CH_2(OH)\cdot CO_2H$	Two (1 : 1) doublets (1 : 1)	17·8			2·6	$\cdot CH(OH)\cdot CO_2H$
$CH_3\cdot CH(OH)\cdot CO_2H$	Two (1 : 1) quartets (1 : 3 : 3 : 1)		17·1		2·0	$\cdot C(OH)CH_3\cdot CO_2H$
$CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H$	Two (1 : 1) triplets (1 : 2 : 1)		10·0		2·0	$\cdot C(OH)(CO_2H)\cdot CH_2\cdot CO_2H$
$CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CO_2H$	Two (1 : 1) doublets (1 : 1)		3·9		1·6	$\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot CO_2H$
$CO_2H\cdot CH{=}CH\cdot CO_2H$	Two (1 : 1) doublets [a]	21·1	12·7			$\cdot CH(CO_2H)\cdot CH(OH)\cdot CO_2H$
$CH_3\cdot CH{=}CH\cdot CO_2H$	Four quartets (1 : 3 : 3 : 1) [a]	22·0	25·8 [e]			$\cdot CH(CH_3)\cdot CH(OH)\cdot CO_2H$
			16·3 [f]			

[a] The assignments of these coupling constants are discussed in the text. [b,c,d] Coupling with chlorine nuclei: [b] 3·8, [c] 2·6, [d] 3·1 gauss. [e] Quartet. Doublet.

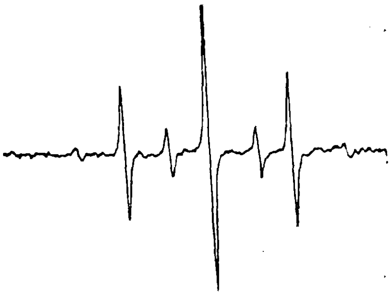

FIG. 1. Spectrum from acetic acid.

FIG. 2. Spectrum from chloroacetic acid.

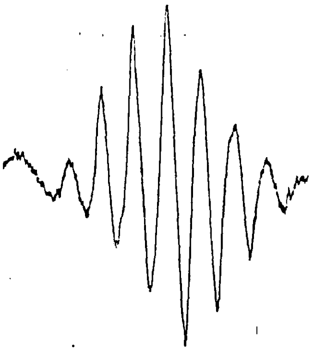

FIG. 3. Spectrum from chloral hydrate.

FIG. 4. Spectrum from lactic acid.

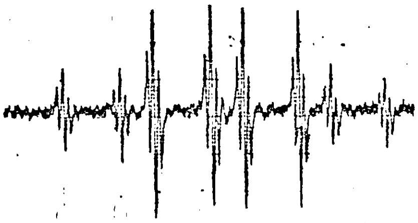

FIG. 5. Spectrum from diethyl ether.

FIG. 6. Spectrum from cyclobutane-1,1-dicarboxylic acid.

Malonic acid was less reactive than acetic acid, but at concentrations >2M the signal due to ·OH was eliminated and the spectrum consisted of a triplet (1 : 2 : 1) whose coupling constant was the same, within experimental error, as that of the triplet derived from acetic acid which was assigned to $\cdot CH_2\cdot CO_2H$. It is therefore probable that this same radical was present, formed analogously to the methyl radical from acetic acid:

$$CO_2H\cdot CH_2\cdot CO_2H \xrightarrow{\cdot OH} CO_2H\cdot CH_2\cdot CO_2\cdot \longrightarrow CO_2H\cdot CH_2\cdot + CO_2 \qquad (3)$$

The ·OH singlet was eliminated by a smaller concentration of propionic acid than was required by acetic acid. The spectrum obtained was too complex for complete analysis, but its strongest lines constituted a triplet of triplets, and this spectrum may be assigned with reasonable confidence to $\cdot CH_2\cdot CH_2\cdot CO_2H$, formed by abstraction of a β-hydrogen atom. As expected, this spectrum differs from that of the isomeric radical, $\cdot CH(CH_3)\cdot CO_2H$, obtained by γ-irradiation of a single crystal of L-alanine.[6]

Pivalic acid in 0·1M concentration caused the complete replacement of the ·OH signal and the appearance of an intense spectrum which consisted of a triplet of septets similar to that obtained from t-butyl alcohol.[1] This is ascribed to $\cdot CH_2\cdot C(CH_3)_2\cdot CO_2H$ and represents another example of the occurrence of weak splitting by C_3-protons.[1]

Formic acid gave a singlet of width about 2 G (cf. ref. 7) situated about 5 G upfield from the ·OH singlet. This may be the spectrum of either $H\cdot CO_2\cdot$ or $\cdot CO_2H$.

(*b*) *α-Chloro-acids.* Chloroacetic acid was more reactive than acetic acid and only a 0·2M solution was necessary for complete replacement of the ·OH signal. The resulting spectrum (Fig. 2), near $g = 2$, consisted of two quartets, each line being of the same intensity, indicative of coupling with ^{35}Cl and ^{37}Cl nuclei in the radical $\cdot CHCl\cdot CO_2H$.

Dichloroacetic acid was much less reactive and the ·OH signal was not eliminated even at molar concentration. The resulting spectrum, similar to that obtained from chloral hydrate (Fig. 3) but less intense and partly obscured by the residual ·OH singlet, was a septet of pattern approximately 1 : 2 : 3 : 4 : 3 : 2 : 1, as expected for $\cdot CCl_2\cdot CO_2H$.

α-Chloropropionic acid gave a comparatively simple spectrum consisting of a basic quartet each of whose lines was resolved into four. This is attributed to $\cdot CCl(CH_3)\cdot CO_2H$, and shows that α-abstraction is dominant over β-abstraction. The origin of some less intense lines was not clear, but by analogy with propionic acid some abstraction from the β-position would be expected.

(*c*) *α-Hydroxy-acids.* The α-hydroxy-acids examined were all more reactive than the corresponding unsubstituted acids and 0·1M solutions were sufficient to cause the complete disappearance of the ·OH signal. The spectra given by lactic acid (Fig. 4) and malic acid are assigned to the radicals $\cdot C(OH)(CH_3)\cdot CO_2H$ and $\cdot C(OH)(CH_2\cdot CO_2H)\cdot CO_2H$, respectively, which are produced on the abstraction of α-hydrogen atoms; these results indicate that the hydroxyl group activates the adjacent C–H bond towards reaction with ·OH, as suggested previously,[1] and as expected by analogy with the products formed by α-hydroxy-acids with Fenton's reagent which behaves similarly to the titanous–peroxide system.*

Two features of the spectra derived from α-hydroxy-acids are of particular interest. First, the narrow doublet splitting of each line (*e.g.*, Fig. 4) shows that there is weak coupling between the unpaired electron and the proton of the hydroxyl group, as has previously been observed in the spectrum of $\cdot CH(OH)\cdot CO_2H$, derived from the γ-irradiation of a single crystal of glycollic acid.[10] We did not observe such coupling in the spectra from alcohols with the exception of propargyl alcohol, although in the case of the triplet from methanol each line was apparently an incompletely resolved doublet,[1] and the present

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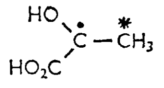
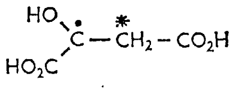
* It has been shown that the two systems behave similarly in the hydroxylation of benzenoid compounds.[8] Although free radicals are not detectable when titanous ion is replaced by ferrous ion in the strongly acidic conditions used in the present work and previously,[1] they are detectable with buffered solutions *ca.* pH 6 in the presence of EDTA.[9]

results prompted a re-examination of some of the alcohols. The lines in the spectrum from methanol were eventually resolved into narrowly spaced doublets (coupling constant, 1 G), but those from the other alcohols could not be resolved further.

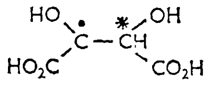
Secondly, the coupling constants of C_2-protons vary in a dramatic manner with the nature of the substituents on this carbon atom, as shown by the following series:



(I)



(II)



(III)

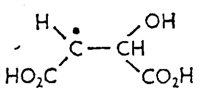
* Coupling constant (gauss) (I) 17·1; (II) 10·1; (III) 3·9.

The implications of these results are discussed below.

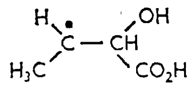
Finally, the spectrum from malic acid contained a weak signal whose lines were sufficiently displaced from those of the main spectrum for two doublets to be discerned. This pattern is the same as that obtained from maleic and fumaric acids and is probably therefore due to the same radical (IV), formed in this case by abstraction of a β-hydrogen atom.

(*d*) *Unsaturated acids*. Acrylic acid gave a complex spectrum with misshapen lines which appeared to result from the overlapping of several absorptions. It is probable that polymerisation occurred and that the observed spectrum was due to a mixture of a number of the resulting radicals.

Maleic acid and fumaric acid behaved similarly, giving the same spectrum of two doublets, assigned to the adduct (IV) of the hydroxyl radical and the double bond. Addition has been observed previously with allyl alcohol.[1]



(IV)



(V)

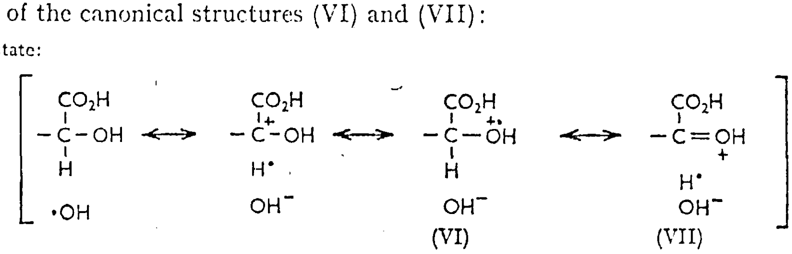
Crotonic acid behaved similarly in that the main spectrum consisted of four quartets, as expected for (V). Other, less intense lines were present, possibly due to radicals formed by the addition of ·OH to the other end of the double bond or by the abstraction of hydrogen from the methyl group.

(*e*) *Other acids*. The following acids gave spectra which could not be analysed because of their complexity: butyric, isobutyric, succinic and citric. Bromo-, dibromo-, trichloro-, iodo-, and cyano-acetic acids and glycine did not react perceptibly under the conditions employed.

The Reactivity of C–H *Bonds*.—The results above show that acids are considerably less reactive than alcohols towards ·OH; that two carboxyl groups have a greater deactivating influence than one; and that abstraction of hydrogen occurs preferentially at the carbon atom furthest from carboxyl (*e.g.*, in propionic acid). On the other hand, α-hydroxy-acids are more reactive than their unsubstituted analogues and abstraction occurs preferentially from the α-carbon atom.

These facts are consistent with the view which has been expressed previously that the hydroxyl radical has electrophilic character.[1,11] With acids, the $-I$ effect of the carboxyl group deactivates each C–H bond towards attack by the electrophilic radical, the extent of deactivation decreasing as the C–H bond is further removed from carboxyl. In this respect, the results parallel those observed in the free-radical chlorination of aliphatic acids by the electrophilic chlorine atom: for example, propionic acid is more readily substituted at the β- than at the α-carbon.[12] With α-hydroxy-acids, however, the more powerful deactivating effect of carboxyl at the α- than at the β-carbon is evidently more than offset by the mesomeric effect of the hydroxylic oxygen, which serves to lower the energy of the transition state for abstraction from the α-position, as expressed by the contribution of the canonical structures (VI) and (VII):

Transition state:



(VI) (VII)

Chloroacetic acid reacted more readily than acetic acid and this implies a stabilising effect by chlorine in the transition state analogous to that by oxygen. The lack of reactivity of bromoacetic acid and iodoacetic acid may derive from the smaller $+M$ effects of these substituents, while the lower reactivity of dichloroacetic acid than of chloroacetic acid may be the result either of steric hindrance or of the combined effect of two $-I$ substituents outweighing the $+M$ effect.

To examine further the electrophilic behaviour of ·OH, the reactions of a number of ethers, amines, aldehydes, and ketones were studied. The results for those compounds which gave spectra that could be analysed are recorded in Table 2.

First, to confirm that the activating power of the hydroxyl group in the abstraction of hydrogen by ·OH lies in the hydroxyl group itself and not in the oxyanion group (which should scarcely be present in significant concentration in the strongly acid condition), we examined three ethers. Diethyl ether gave a spectrum (Fig. 5) very similar to that from ethanol save that each line was split into a triplet. This spectrum is therefore unambiguously assigned to $\cdot CH(OEt)\cdot CH_3$ in which coupling occurs with one C_1-proton, the three C_2-protons, and the two protons on the methylene group. This last splitting (by C_3-protons) is similar to that observed in the spectrum from pivalic acid. Di-isopropyl ether behaved analogously to isopropyl alcohol in that the main spectrum was a septet ascribed to the radical formed by abstraction from the α-carbon, each line being an incompletely resolved doublet due to small coupling with the C_3-proton, while a weak quartet also present was ascribed to the radical formed by abstraction from the β-carbon. Ethylene glycol dimethyl ether gave a spectrum of which the most intense lines formed a triplet of triplets and can be assigned to $\cdot CH_2\cdot O\cdot[CH_2]_2\cdot O\cdot CH_3$, C_3-protons again being observed. The less intense lines could not be satisfactorily analysed, but may be the spectrum of $CH_3\cdot O\cdot\dot{C}H\cdot CH_2\cdot O\cdot CH_3$.

Thus, ethers behave similarly to alcohols both in their general reactivity towards the hydroxyl radical and in the fact that, as shown by diethyl ether, abstraction occurs preferentially from the carbon that bears the oxygen substituent.

Ammonia, methylamine, triethylamine, and pyridine had no effect on the ·OH signal, even when they were present in concentrations greater than molar. Since these compounds are essentially completely protonated in the acid conditions used, their lack of reactivity is evidently the result of the strong $-I$ effect of the positive pole. n-Propylamine was the simplest aliphatic amine from which abstraction of hydrogen occurred. It gave a spectrum which can reasonably be assigned to $\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_3^+$, resulting from abstraction from the carbon furthest from the protonated amino-group.

Ethanolamine was much more reactive than unsubstituted amines. Its spectrum, assigned to $\cdot CH(OH)\cdot CH_2\cdot NH_2$, gave clear evidence of the occurrence of coupling with nitrogen, and there was an indication of further splitting of magnitude about 1 G from the proton on the hydrogen group. Diethanolamine behaved analogously, except that there was no indication of coupling with the hydroxyl proton. Both these compounds evidently owe their reactivity towards ·OH to the presence of the hydroxyl substituent.

Hydrazine gave a spectrum of nine equally spaced lines (splitting, 11·5 G) whose

TABLE 2.

Spectra and coupling constants of radicals derived from various aliphatic compounds, and the radicals to which the spectra are assigned.

Compound	Type of spectrum	Coupling constants (G) C_1–H	C_2–H	C_3–H	O–H	N–H	N	Radical
n-Propylamine	Triplet (1 : 2 : 1) of triplets (1 : 2 : 1) [a]	22·5	26·9					$\cdot CH_2\cdot[CH_2]_2\cdot NH_2$
Ethanolamine...............	Three (1 : 1 : 1) triplets (1 : 2 : 1) of doublets (1 : 1)	18·1	11·8				10·3	$\cdot CH(OH)\cdot CH\cdot_2NH_2$
Diethanolamine	Three (1 : 1 : 1) triplets (1 : 2 : 1) of doublets (1 : 1)	18·4	10·8				11·1	$\cdot CH(OH)\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH$
Hydrazine	9 lines					11·5	11·5	$N_2H_4^{+\cdot}$
Acetone	Triplet (1 : 2 : 1), each line an incompletely resolved quartet	20·3		<1				$\cdot CH_2\cdot CO\cdot CH_3$
Diethyl ketone	Triplet (1 : 2 : 1) of triplets (1 : 2 : 1) [a]	22·1	24·7					$\cdot CH_2CH_2\cdot CO\cdot C_2H_5$
Formaldehyde...............	Two (1 : 1) triplets (1 : 2 : 1)	17·8			1·0			$\cdot CH_2\cdot OH$
Acetaldehyde	Two (1 : 1) quartets (1 : 3 : 3 : 1)	16·0	22·2					$\cdot CH(OH)\cdot CH_3$
Chloral hydrate	Septet (1 : 2 : 3 : 4 : 3 : 2 : 1) [b]							$\cdot CCl_2\cdot CO_2H$
Diethyl ether	Two (1 : 1) quartets (1 : 3 : 3 : 1) of triplets (1 : 2 : 1)	13·8	21·9	1·4				$\cdot CH(CH_3)\cdot O\cdot C_2H_5$
Di-isopropyl ether	Two (1 : 1) septets (1 : 6 : 15 : 20 : 15 : 6 : 1)		20·2	<1				$\cdot C(CH_3)_2O\cdot CH(CH_3)_2$
	and weak quartet (1 : 3 : 3 : 1)	21·7	21·7					$\cdot CH_2\cdot CH(CH_3)\cdot O\cdot CH(CH_3)_2$
Ethylene glycol dimethyl ether........................	Triplet (1 : 2 : 1) of triplets (1 : 2 : 1)	14·6		2·1				$\cdot CH_2\cdot O\cdot[CH_2]_2\cdot O\cdot CH_3$
Dimethyl sulphoxide......	Quartet (1 : 3 : 3 : 1)	23·1						$\cdot CH_3$

[a] The assignments of these coupling constants are discussed in the text. [b] Chlorine coupling, 3·1 G.

relative intensities were close to 1 : 6 : 17 : 30 : 36 : 30 : 17 : 6 : 1. This is similar to the spectrum of the radical-cation $N_2H_4^+$, obtained by the oxidation of hydrazine with ceric ion, except that the nine lines could not be resolved into the narrowly split groups previously observed.[13] This radical is isoelectronic with the radical–anion $C_2H_4^-$, having an unpaired electron in the antibonding π-orbital, and this may underlie the greater reactivity of hydrazine than of amines, but it is not clear whether the radical is formed by the abstraction of a hydrogen atom from the conjugate acid of hydrazine or by the removal of an electron, by $\cdot OH$, from hydrazine itself.

By analogy with acids, ketones would be expected to be less reactive than alcohols because of the $-I$ effect of carbonyl. This proved to be so, for acetone was required in 0·5 M concentration in order to eliminate the $\cdot OH$ signal completely: the resulting spectrum was a triplet, each of whose lines was an incompletely resolved quartet, and it is ascribed to $\cdot CH_2\cdot CO\cdot CH_3$. Diethyl ketone gave a complex spectrum from which nine lines forming three triplets could be picked out with reasonable certainty. This spectrum may be assigned tentatively to $\cdot CH_2\cdot CH_2\cdot CO\cdot Et$, corresponding to the result for propionic acid.

The three aldehydes investigated behaved in an unexpected manner. Formaldehyde and acetaldehyde, each carefully purified so as to be free of the corresponding alcohols, gave spectra which were identical to those derived from methanol and ethanol, respectively,[1] the spectrum from acetaldehyde containing in addition some weaker lines which could not be analysed. No signals were obtained when the reactions were carried out in the absence of hydrogen peroxide, so that one-electron reduction of the carbonyl groups by titanous ion cannot be responsible for the generation of the radicals. The mechanism of formation of these free-radical reduction products has been discussed separately.[14]

Chloral hydrate gave a spectrum (Fig. 3) with a pattern characteristic of coupling with two chlorine nuclei; there was no indication of coupling with protons. The pattern and coupling constant are identical to those obtained from dichloroacetic acid, and $\cdot CCl_2\cdot CO_2H$ is the simplest radical which could give rise to the observed spectrum. The formation of this radical requires that chlorine be lost from the organic compound, and, consistently with this, both chloride ion and chlorine were detected in the reaction products. We suggest that this radical results from reaction (4), in which the second step may be regarded as an intramolecular analogue of the intermolecular electron-transfers observed previously.[14]

$$CCl_3\cdot CH(OH)_2 \xrightarrow{\cdot OH} CCl_3\cdot\dot{C}(OH)_2 \longrightarrow \dot{C}Cl_2\cdot CO_2H + HCl \qquad (4)$$

Finally, two other compounds with strongly electron-attracting substituents attached to methyl were examined. Nitromethane had no discernible effect on the $\cdot OH$ signal, but dimethyl sulphoxide, although comparatively unreactive, gave a quartet identical with that of the methyl radical.[1] This radical may arise from addition of $\cdot OH$ to the sulphoxide group and subsequent cleavage of a C–S bond.

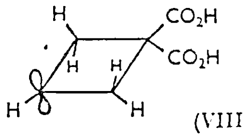
Coupling Constants.—(*a*) *C_1-Protons.* Inspection of the data in Tables 1 and 2 shows that the substitution of any one of the groups examined for a hydrogen atom in $\cdot CH_3$ or $\cdot CH_2X$ reduces the coupling constant of the C_1-proton(s). This is indicative of the reduction of the spin density at the carbon which bears the unpaired electron, and the effectiveness with which different substituents produce this result can be summarised as follows:

$$\mathrm{OAlk} > \mathrm{OH} > \,>\!\mathrm{CO} \sim \mathrm{Cl} > \mathrm{CO_2H} > \mathrm{Alk} > \mathrm{H}$$

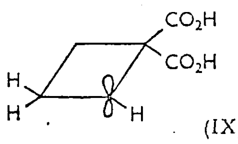
It is notable that both carbonyl and carboxyl groups diminish the ease of abstraction of hydrogen from the adjacent carbon relative to that from a distant C–H group, and yet both are able to delocalise the unpaired electron, as evidenced by the relative values of the coupling constants for $\cdot CH_3$, $\cdot CH_2\cdot CO\cdot Me$, and $\cdot CH_2\cdot CO_2H$. These two statements are not, however, inconsistent, and moreover they have a close parallel: chlorine and bromine atoms abstract hydrogen from the methyl group of *p*-nitrotoluene less rapidly than from toluene,[15] although the unpaired electron should be further delocalised in the *p*-nitrobenzyl radical than in the benzyl radical. The factors which influence the stabilisation of one radical relative to another do not necessarily have the same relative influence on the transition states which precede those radicals. In the case of abstraction from C–H both by chlorine and bromine atoms and by the hydroxyl radical, in each of which the unpaired electron is associated with a strongly electronegative atom, electron-attracting groups in the vicinity of the C–H bond can decrease the stability of the transition state, and hence the rate of abstraction,[15] while nevertheless stabilising by delocalisation the radical formed.

(b) C_2-*Protons.* Exceptionally large variations were noted in the magnitude of the coupling with C_2-protons in the radicals (I), (II), and (III), derived from lactic acid, malic acid, and tartaric acid. Coupling with C_2-protons has been attributed to a hyperconjugative mechanism, and its magnitude should be dependent on the dihedral angle, θ, between the C_2–H bond and the *p*-orbital which contains the unpaired electron, being minimal when the C_2–H bond lies in the nodal plane of this *p*-orbital ($\theta = 90°$), maximal when $\theta = 0°$, and in general proportional to $\cos^2 \theta$.[16] In (I) the average value of $\cos^2 \theta$ is 0·5, but in (II) and (III) the other substituents on the C_2-carbon should give rise to certain preferred conformations as a result of rotation about the C_1–C_2 bond. The lower values for the C_2-coupling constants in these instances are, then, consistent with the average values of $\cos^2 \theta$ being less than 0·5.

Detailed examination of the hypothesis that the magnitude of C_2-coupling follows a $\cos^2 \theta$ relationship requires the study of radicals in which the value of θ is known. As an initial approach to this problem we have investigated the reaction of cyclobutane-1,1-dicarboxylic acid with the titanous-peroxide system. This gave a spectrum (Fig. 6) which is apparently due to a mixture of the radicals (VIII) and (IX), the former giving two quintets, each of whose three centre lines overlaps with the lines of the two triplets given by the latter.



(VIII)



(IX)

The salient feature of this spectrum in the present context is that, while the extent of coupling with the C_1-proton is of the usual order of magnitude for such structural environments (21·5 G in each case), the coupling constants for the four C_2-protons in structure (VIII) and the two C_2-protons in structure (IX), 37·0 and 38·5 G, respectively, are considerably larger than those in radicals of similar structure but in which there is essentially free rotation about the C_1–C_2 bond (*e.g.*, $\cdot CH_2\cdot CH_2\cdot CO_2H$; see Tables 1 and 2). The cyclobutane ring is slightly buckled from the planar configuration,[17] but it is reasonable to assume for the present purposes that the radicals (VIII) and (IX) have planar carbon rings, particularly since some of the eclipsing interactions which lead to buckling in cyclobutane itself should be absent in the two radicals because the C_1-proton and the C_2-substituents are now in the staggered conformation. Thus, θ is approximately 30°, giving a ratio for $\cos^2 \theta$ for (VIII) or (IX) to $\cos^2 \theta$ (average) for a freely rotating system of 1·5. This is close to the ratios of the coupling constants for the C_2-protons in (VIII) and (IX) to that of the C_2-proton in $\cdot CH_2\cdot CH_2\cdot CO_2H$ (1·39 and 1·45, respectively).

Assignments of Coupling Constants.—Some of the coupling constants reported in Tables 1 and 2 which could not be unambiguously assigned earlier to specific protons may be assigned on the basis of the above discussion. The larger of the two doublet splittings in the spectra of the radicals formed by addition to maleic (or fumaric) acid and crotonic acid are of the order usually found for C_1-protons and are assigned as such, while the smaller value in each case is evidently due to the C_2-proton, and its magnitude is governed by the conformational situation. Similarly, the smaller of the two values for propionic acid, n-propylamine, and diethyl ketone is assigned to the C_1-protons and the larger to the C_2-protons.

EXPERIMENTAL

The spectrometer, the flow system, and the procedure for carrying out the reactions have been described.[1] The stability and reproducibility were checked periodically by examining the spectrum of an alkaline solution of potassium nitrosodisulphonate in a static system and, more frequently, by examining the spectrum from methanol in the flow system. In this way coupling constants could be measured to within ±0·3 G.

Two of us (W. T. D. and A. L. B.) thank the D.S.I.R. for maintenance grants.

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society,
December 1964, (934), pages 4850—4856.

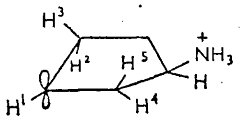
934. *Electron Spin Resonance Studies of Oxidation. Part III.*[1] *Some Alicyclic Compounds.*

By W. T. DIXON and R. O. C. NORMAN.

The electron spin resonance spectra of the radicals formed by the abstraction of a hydrogen atom from certain alicyclic compounds containing five- and six-membered rings are reported. Support is obtained for the view that the coupling between the unpaired electron and a C_2-proton * is dependent on the angle between the C_2–H bond and the singly occupied *p*-orbital. The results for the six-membered compounds which have been examined are satisfactorily interpreted on the basis that the radicals undergo chair–chair interconversion at a rate which is comparable with the difference in frequencies of the couplings of the axial and equatorial C_2-protons.

IN two previous Papers we described and discussed the electron spin resonance (e.s.r.) spectra of free radicals derived from the reaction of the hydroxyl radical with aliphatic compounds.[1,2] We now first report the spectra of the radicals obtained in a similar manner from a number of five- and six-membered alicyclic compounds and then show that the results can be interpreted in terms of two premises. The first is that the coupling between C_2-protons and the unpaired electron is angular-dependent, and the second is that the six-membered cyclic radicals which we have studied undergo very rapid chair–chair interconversion.

Description of the Spectra.—(*a*) *Five-membered rings.* Cyclopentylamine gave a spectrum consisting of four quartets, each having lines of relative intensities 1 : 3 : 3 : 1. This indicates coupling between the unpaired electron and three equivalent protons ($a_H = 36{\cdot}7$ gauss) and two non-equivalent protons ($a_H = 33{\cdot}4$ and $22{\cdot}0$ gauss). Our assignments of this spectrum to the radical (I) and of the coupling constants as shown are made on the following grounds.



(I)

Proton	Coupling constant (gauss)
H^1	22·0
H^2, H^3, H^4	36·7
H^5	33·4

First, since the amine is essentially completely protonated in the strongly acid conditions used and the hydroxyl radical is known to have electrophilic character,[1] abstraction of hydrogen should occur with least difficulty from the carbon atom furthest from the amine group, to give (I) (cf. the lack of reactivity of methylamine towards ·OH, and the formation of $\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_3^+$ from n-propylamine [1]). Secondly, the smaller of the doublet splittings is closely similar in magnitude to the values for C_1-protons in similar environments [1] and is therefore assigned to H^1. The triplet and the second doublet splitting remain to be assigned to the four C_2-protons. Of these four, H^5 is in a slightly different environment from the remainder in that it is approximately in an eclipsed conformation with respect to the ammonio-ion on the adjacent carbon atom † and may reasonably be expected to couple to a different extent from the remaining three, possibly as the result of an electronic interaction with the nitrogen pole. Moreover, an analogy to this argument exists in the results for the radicals derived from cyclobutane-1,1-dicarboxylic acid: the

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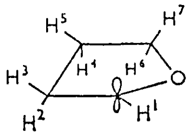
* *I.e.*, a proton on a carbon atom adjacent to the atom which bears the unpaired electron. For nomenclature, see Part I.[2]

† The various eclipsing interactions in (I) will presumably result in the ring's being slightly buckled from the coplanar situation, as it is in cyclopentane. Nevertheless, this must remain a close approximation.

C_2-proton coupling constants are 1·5 gauss less in the radical in which these protons are eclipsed by carboxyl groups on the adjacent carbon than in the radical in which they are eclipsed by hydrogen atoms.[1]

Tetrahydrofuran gave a spectrum consisting of two triplets, each of which was split further into seven lines (1 : 2 : 3 : 4 : 3 : 2 : 1), superimposed on some weak, ill-defined lines. This is attributed to the radical (II) on the following grounds.



(II)

Proton	Coupling constant (gauss)
H^1	12·4
H, H^3	28·2
H^4, H^5 *	0·9
H^6, H^7 *	1·8

* The assignments for these two pairs are tentative; see text.

Abstraction from the α-position is to be expected by analogy with the results for acyclic ethers.[1] Further, the doublet splitting is about the same as that of the C_1-proton in $\cdot CH(OEt)\cdot CH_3$, derived from diethyl ether, whereas the radical formed by abstraction from the β-position would be expected to give a C_1-proton splitting of about 20 gauss.[1] The triplet is therefore assigned to the two equivalent C_2-protons on the β-carbon atom. The narrowly spaced seven-line pattern is evidently the result of two further triplet splittings, one twice as great as the other. The coupling constants are of the usual order of magnitude for C_3-protons,[1,2] and the splittings are therefore ascribed to the two remaining pairs of protons, each of which is in a C_3-position. It is not possible unambiguously to assign each splitting to a particular pair, but since there is evidence that an ethereal oxygen atom which is bonded to a carbon possessing an unpaired electron acquires a considerable spin density,[1] it is probable that the larger of the two splittings is due to the C_3-protons next to oxygen, *i.e.*, to H^6 and H^7.

Three other five-membered cyclic compounds were examined. Cyclopentanol and cyclopentanone gave highly complex spectra, which could not be analysed, evidently because abstraction of hydrogen occurs from at least two carbon atoms in each molecule. Pyrrolidine caused only a small reduction in the amplitude of the singlet ascribed to the hydroxyl radical, evidently because of the deactivating effect of the protonated amino-group, and the resulting weak spectrum from the organic compound could not be analysed with certainty.

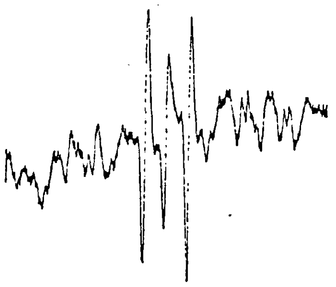


FIG. 1. Spectrum from cyclohexanol.

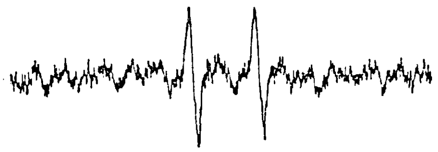
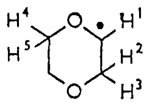


FIG. 2. Spectrum from cyclohexylamine.

(*b*) *Six-membered rings.* The spectrum from cyclohexanol (Fig. 1) contained three sharp central lines together with a number of other less intense lines. By analogy with the results for acyclic alcohols, the most reactive hydrogen in cyclohexanol (towards $\cdot OH$) should be that on the α-carbon, but there is also a number of hydrogens in only slightly less reactive positions (*e.g.*, four β-hydrogens) so that more than one radical would be expected (cf. the spectrum from isopropyl alcohol which consists of a strong spectrum of the radical formed by abstraction of the one α-hydrogen superimposed on a weak spectrum of the radical formed by abstraction of one of the six β-hydrogens.[2]) The nature of this complex spectrum is discussed further below.

The spectrum from cyclohexylamine (Fig. 2) was basically similar to that from cyclohexanol except that only two lines of much greater intensity than the remainder were present, equidistant from the centre. Again, abstraction from more than one C–H bond would be expected, for while the C–H furthest from the protonated amino-group should be the most reactive position for attack, the radical obtained by abstraction from one of the two γ-carbons should also be formed, by analogy with the result for cyclopentylamine.

Because of the difficulties in interpreting the spectra of mixtures of radicals, it was desirable to study the behaviour of a six-membered alicyclic compound which has only one type of C–H bond from which abstraction may occur and which is sufficiently water-soluble for application of the present experimental method. Dioxan was therefore chosen. It gave a spectrum (Fig. 3) consisting of four triplets together with two broad, unresolved lines each of which was at the centre of a pair of triplets. This is ascribed to the radical (III) in which coupling occurs with the C_1-proton (H^1), the two C_2-protons (H^2, H^3), and the two C_3-protons (H^4, H^5). The origin of the broad central lines and the magnitude of the coupling with the C_2-protons are discussed below.



(III)

Proton	Coupling constant (gauss)
H^1	17·2
$H^2 + H^3$	45·5 *
H^4, H^5	1·3

* The combined value of the coupling constants of H^2 and H^3; see Discussion.

Finally, piperidine gave a spectrum (Fig. 4) consisting of two triplets, each of approximate relative intensities 1 : 3·5 : 1. By analogy with the behaviour of other amines, the most probable radical to which this signal may be assigned is that which results from abstraction of hydrogen from the γ-position. The doublet splitting, 21·9 gauss, is of the usual order of magnitude for C_1-protons in similar environments and is assigned as such, but the two triplets (splitting: 48·9 gauss) are not due to coupling with two equivalent protons, for the relative intensities of the lines would then be 1 : 2 : 1. The nature of the spectral pattern is discussed below.

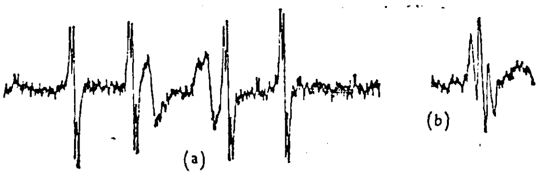


FIG. 3. Spectrum from dioxan: (*a*) complete spectrum; (*b*) triplet (1 : 2 : 1) structure of each of the sharp resonances revealed by slower scan.

FIG. 4. Spectrum from piperidine.

The Angular Dependence of C_2*-Proton Coupling Constants.*—It has been argued that, if the hyperfine coupling of C_2-protons occurs solely by a hyperconjugative mechanism, it should be zero when the C_2–H bond lies in the nodal plane of the unpaired electron and maximal when it is in a plane perpendicular to the nodal plane, and in general it should be proportional to $\cos^2\theta$, where θ is the angle between projections of the $2p_z$-orbital of C_1 and the C_2–H bond on a plane perpendicular to the C_1–C_2 bond.[3] Evidence for an angular dependence has recently accumulated from studies of acyclic systems at temperatures low enough effectively to prevent rotation about carbon–carbon single bonds.[3,4] For example, above 200°K the three C_2-protons in $Me\dot{C}H{\cdot}CO_2H$ couple equivalently, whereas below 100°K the complex spectra could be interpreted in terms of the non-equivalence of C_2-protons, this arising from differences in the value of θ for each proton.[5] It is found that, although the simple relationship between C_2-coupling and θ suggested above ($a_H \propto \cos^2\theta$) is fitted reasonably satisfactorily by the experimental data, closer agreement is obtained by elaboration of this relationship to the form of equation (1),

$$a_H = B_0 + B\cos^2\theta \tag{1}$$

where B_0 is between 3 and 4 gauss.[6,7]

The magnitude of the C_2-coupling in the radicals derived from five-membered rings can be understood in these terms. The value of θ for each C_2-proton is defined by the geometry of the ring, and although this is likely to be slightly distorted from coplanarity owing to eclipsing interactions, θ should be close to 30° and $\cos^2\theta$ close to $\frac{3}{4}$. This is larger than the *average* value of $\cos^2\theta$ ($\frac{1}{2}$) in acyclic systems, and it follows that the coupling constants should be correspondingly greater for the five-membered radicals, as observed. We have previously interpreted the values for the radicals obtained from cyclobutane-1,1-dicarboxylic acid in this way.[1]

Further, quantitative comparison of the data for five-membered cyclic radicals with those for acyclic radicals of otherwise similar structure enables equation (1) to be tested. The procedure may be illustrated for the radical (I) obtained from cyclopentylamine which may suitably be compared with $\cdot CH_2\cdot CH_2\cdot CH_2\cdot \overset{+}{N}H_3$ (IV), derived from n-propylamine.[1] First, account is taken of the fact that the spin densities at C_1 in (I) and (IV), as measured by the C_1-proton splittings (22·0 and 22·5 gauss, respectively) are slightly different, and the C_2-coupling in (IV) (26·9 gauss) is therefore multiplied by the factor (22·0/22·5). Application of equation (1), with insertion of a value for B_0 of 3·5 gauss, gives a value for B of $2(26{\cdot}9 \times 22{\cdot}0/22{\cdot}5 - 3{\cdot}5) = 45{\cdot}6$ gauss, from which the *predicted* value for the C_2-coupling in (I), assuming a value for θ of 30°, is given by:

$$a_H = 3{\cdot}5 + 45{\cdot}6\ (0{\cdot}75) = 37{\cdot}7 \text{ gauss} \tag{2}$$

This value is reasonably close to that (36·7 gauss) observed for the three C_2-protons in (I) which are thought not to be eclipsed by the protonated amino-group. Insertion of $B_0 = 0$ leads to $B = 52{\cdot}6$, and to a predicted value of 39·1 gauss, which is in less satisfactory agreement with experiment.

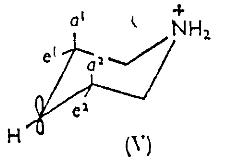
Application of the same procedure to the radicals formed from tetrahydrofuran, (II), and diethyl ether (for which the C_1- and C_2-couplings are 14·3 and 22·6 gauss, respectively [1]) leads to predicted values for the C_2-coupling in (II) of 27·7 and 29·4 gauss for $B_0 = 3{\cdot}5$ and 0, respectively. Agreement with the experimental value (28·2 gauss) is good, and again slightly better for $B_0 = 3{\cdot}5$.

The results for the five-membered cyclic radicals are therefore consistent with the thesis that the magnitude of the coupling of C_2-protons is angular-dependent, and moreover acceptable agreement is obtained with the results predicted by equation (1). It appears that the value for B_0 of 3·5 gauss is more satisfactory in this respect than $B_0 = 0$, but in view of the approximation that had necessarily to be made in the application of this equation to the five-membered radicals (that $\theta = 30°$), we do not suggest that the present results provide a wholly satisfactory test for finding the most appropriate value for B_0.

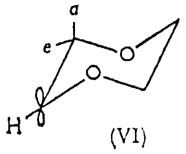
Chair–Chair Interconversions of Six-membered Cyclic Radicals.—Cyclohexane and many of its derivatives exist predominantly in two chair conformations which are interconvertible. The rate of interconversion is reduced by lowering the temperature, and this gives rise to changes in the nuclear magnetic resonance spectrum. At temperatures down to —50° a single peak is observed which represents the average effect of the axial and equatorial protons, and on further cooling this peak shows progressive broadening until, at —70°, two distinct peaks, incompletely resolved, are observed, corresponding to the individual effects of the axial and equatorial protons.[8] The broad absorption is a result of the lifetime uncertainty of a particular chair conformation and occurs when the rate of interconversion is comparable in magnitude with the difference in absorption frequencies due to the axial and equatorial protons.

The same principles apply to electron spin resonances. For example, the alternation in line-widths in the spectrum from a durenesemiquinone radical has been shown to be due to a rapid isomerisation between *cis*- and *trans*-forms of the radical, and the theory has been described.[9] The nature of the electron spin resonance spectra derived from piperidine and dioxan can be understood in similar terms. The values of θ for axial and equatorial C_2-protons differ, and from the discussion in the previous section these protons would be expected to couple to different extents with the unpaired electron. If, then, the six-membered cyclic radical interconverts from one chair into the other chair conformation at a rate comparable with the difference in couplings of the axial and equatorial protons, certain sharp and certain broad resonances should be observed in the spectrum.

Consider the radical (V) formed from piperidine. As a result of the interconversion of the chair conformation shown into the alternative chair conformation, the axial and equatorial protons change places. If, in a given case, an axial proton changes places with an equatorial proton of the same spin, there is no change in the total spin interaction so far as this pair of protons is concerned, but if the exchanging protons are of different spin a change in the total spin interaction results. In general, for one spin orientation of the C_1-proton, the situations shown in Table I can occur on interconversion.



(V)



(VI)

TABLE 1.

	Spin orientations in Chair I				Total spin interaction in		Difference in interaction on interconversion	Average
	a_1	e_1	a_2	e_2	Chair I	Chair II		
(1)	+	+	+	+	2a + 2e	2a + 2e	0	2a + 2e
(2)	+	+	+	−	2a	2e	2a − 2e	a + e
(3)	+	+	−	+	2e	2a	−2a + 2e	a + e
(4)	+	−	+	+	2a	2e	2a − 2e	a + e
(5)	−	+	+	+	2e	2a	−2a + 2e	a + e
(6)	+	+	−	−	0	0	0	0
(7)	+	−	+	−	2a − 2e	−2a + 2e	4a − 4e	0
(8)	+	−	−	+	0	0	0	0
(9)	−	+	+	−	0	0	0	0
(10)	−	+	−	+	−2a + 2e	2a − 2e	−4a + 4e	0
(11)	−	−	+	+	0	0	0	0
(12)	+	−	−	−	−2e	−2a	2a − 2e	−a − e
(13)	−	+	−	−	−2a	−2e	−2a + 2e	−a − e
(14)	−	−	+	−	−2e	−2a	2a − 2e	−a − e
(15)	−	−	−	+	−2a	−2e	−2a + 2e	−a − e
(16)	−	−	−	−	−2a − 2e	−2a − 2e	0	−4a − 4e

Of these, (1), (6), (8), (9), (11), and (16) result in no change in the total nuclear spin interaction on interconversion. Thus, in (1), the unpaired electron is always in the environment of two (+) axial and two (+) equatorial protons, and similarly in (16) it is always in the environment of two (—) axial and two (—) equatorial protons. Sharp resonances therefore occur at low and high field. The situations represented by (6), (8), (9), and (11), in which the effects of the nuclear spins nullify each other, lead to a sharp line at the centre of the field, and since there are four times as many ways in which this situation can occur as either (1) or (16), the centre line is four times as intense as the extreme lines. The remaining situations all lead to a change in nuclear spin interaction on interconversion, and this should result in there being broadened lines of intensity four at the two positions intermediate between the centre and extreme lines, and some broadening, of intensity two, about the central line. Since the intensity of an absorption in the derivative spectrum is proportional to the height of the peak and to the square of its width at half-height, the broad absorptions may be expected to be of very small amplitude with respect to the sharp ones and therefore difficult to discern.

When account is taken of the second possible orientation of the C_1-proton, this theory leads to the prediction that the radical (V) should consist of two groups of three sharp lines of intensities 1 : 4 : 1 together with weaker broad lines. Insofar as the sharp lines are concerned, the observed spectrum is close to this.

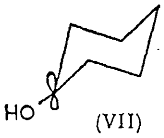
The radical (VI) derived from dioxan presents a simpler case since there is only one pair of C_2-protons. Interconversion of the two chair conformations gives rise to the possibilities in Table 2, for one orientation of the C_1-proton.

TABLE 2.

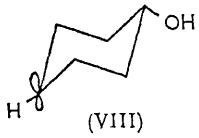
Spin orientations in Chair I		Total spin interaction in		Difference in interaction on interconversion	Average
a	e	Chair I	Chair II		
+	+	$a + e$	$a + e$	0	$a + e$
+	−	$a - e$	$-a + e$	$2a - 2e$	0
−	+	$-a + e$	$a - e$	$-2a + 2e$	0
−	−	$-a - e$	$-a - e$	0	$-a - e$

The spectrum should consist of two sharp lines of unit intensity at low and high field with a broad line of intensity two at their centre. When account is taken of the second possible orientation of the C_1-proton and of the triplet splitting from the C_3-protons, the observed spectrum is seen to have these characteristics.

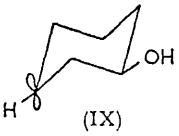
It is now possible to discuss the nature of the spectra derived from cyclohexylamine and cyclohexanol. That from cyclohexylamine resembles that from piperidine in having two lines of much greater intensity than the remainder near the centre, together with a number of lines of about one-quarter of this intensity towards the extremities of the spectrum. Although the exact spectral pattern cannot be discerned with certainty, it is probable that the main radical formed from cyclohexylamine has basically the same spectrum as that derived from piperidine. The spectrum from cyclohexanol also contains two intense lines around the centre, together with a third, slightly less intense line at the centre of the first two. On the basis of the above discussion it is likely that this spectrum is due to a mixture of the radicals (VII), (VIII), (IX), and (X), and that the central line and the two intense lines surrounding it are, respectively, the centres of a quintet due to (VII) and of two quintets due to (VIII) and (IX) (whose spectra should be the same within the limits of resolution of the spectrometer). The second and fourth lines of each quintet are, then, not discernible because they are subject to uncertainty broadening, while the extreme lines, which should be one-quarter of the intensity of the central ones, cannot be discerned with certainty from the background. It is noteworthy that (X) should give a spectrum in which *all* the lines are subject to uncertainty broadening and which would therefore be difficult to diagnose.



(VII)



(VIII)



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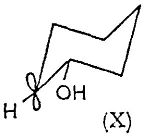

(X)

The individual coupling constants for the axial and equatorial protons in the radicals derived from piperidine and dioxan could in principle be measured by lowering the temperature at which their spectra are observed to the point at which the chair–chair interconversion rate is slow enough to give sharp resonances for each type of proton, but such experiments cannot be conducted with the aqueous solution technique which we have used. We know, however, the *combined* values of the coupling constants for these protons. If the value of θ for the axial C_2-proton is ω, that for the equatorial C_2-proton is (120 + ω). It follows that:

$$a_{ax} = B_0 + B\cos^2\omega$$
$$a_{eq} = B_0 + B\cos^2(120 + \omega)$$
$$a_{ax} + a_{eq} = 2B_0 + B[\cos^2\omega + \cos^2(120 + \omega)]$$

This leads to:

$$a_{eq} = \tfrac{1}{2}[a_{ax} + a_{eq} \pm \sqrt{3}\,(c - \tfrac{1}{2}B)(\tfrac{3}{2}B - c)],$$

where $$c = a_{ax} + a_{eq} - 2B_0.$$

For the radical from piperidine, $(a_{ax} + a_{eq}) = 48{\cdot}9$ gauss. A value for B can again be estimated from the data for $\cdot CH_2\cdot CH_2\cdot CH_2\cdot\overset{+}{N}H_3$, allowance being made for the difference in spin densities at C_1 in the two radicals. Solution of the above equations ($B_0 = 3{\cdot}5$) then gives values for a_{ax} and a_{eq} of 43·9 and 5·0 gauss, with corresponding values for θ of approximately 19 and 79°. A similar treatment for the radical from dioxan, calculations being based on the data for $\cdot CH(OEt)\cdot CH_3$, gives $a_{ax} = 41{\cdot}8$ gauss ($\theta = 26°$) and $a_{eq} = 3{\cdot}7$ gauss ($\theta = 86°$).

If each of the radicals obtained from piperidine and dioxan had a perfect chair conformation, the axial and equatorial C_2-protons would have values of θ of 30 and 90°, respectively, but slight distortion from this situation should occur in order that the CCC or CCO angle at the carbon from which hydrogen has been abstracted may enlarge from the tetrahedral value to one close to 120°. Although the precise geometry of the radicals is unknown, the values of θ derived above appear reasonable.

On the basis of our interpretation of the spectral patterns of the six-membered radicals, an approximate value for the rate of interconversion of the chair conformations can be deduced from the difference, Δν, in the couplings of the axial and equatorial protons.[10] In each case Δν ~38 gauss, so that the calculated rate of interconversion is of the *order* of 5×10^8 sec.$^{-1}$.

EXPERIMENTAL

The flow system and the procedure for the generation and observation of the radicals have been described.[2] The concentration of the organic compound necessary for the complete elimination of the signal ascribed to the hydroxyl radical and the consequent appearance of a spectrum from the organic radical was lower for the cyclic alcohols and ethers (<M/10) than for the amines (between M/5 and M) as expected from previous studies.[1]

The spectrometer was calibrated by examining the spectrum of $\cdot CH_2OH$ at frequent intervals,[2] and coupling constants were reproducible to within ±0·3 gauss.

We thank Dr. D. H. Whiffen of the National Physical Laboratory for most helpful discussions. One of us (W. T. D.) thanks the D.S.I.R. for a maintenance grant.

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[*Received, November 28th,* 1963.]

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Preprinted from the Journal of the Chemical Society,
December 1964, (935), pages 4857—4860.

935. *Electron Spin Resonance Studies of Oxidation. Part IV.*[1] *Some Benzenoid Compounds.*

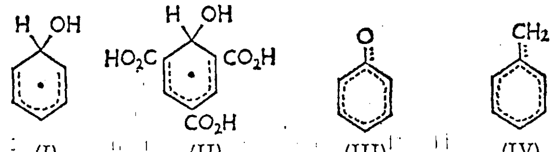
By W. T. Dixon and R. O. C. Norman.

The electron spin resonance spectra of the radicals formed by the interaction of acidified solutions of titanous ion and hydrogen peroxide in the presence of a number of benzenoid compounds are described. Interpretation of the spectra shows that benzene and trimesic acid give adducts (substituted cyclohexadienyl radicals) with the hydroxyl radical, while phenol, *p*-cresol, quinol, and toluene undergo abstraction of a hydrogen atom to give the corresponding phenoxy, semiquinone, and benzyl radicals. Conclusions are drawn from the values of the hyperfine splitting constants about the relative spin densities at the carbon atoms in these radicals, and the results are compared with calculated spin densities. An attempt to observe the phenyl radical by the one-electron reduction of the benzenediazonium cation gave a spectrum which is tentatively ascribed to the benzenediazonium radical.

We have previously described and discussed the electron spin resonance spectra of free radicals derived from the reactions of aliphatic compounds with the hydroxyl radical, generated by the interaction of titanous ion and hydrogen peroxide in acid solution.[1-3] In the present Paper we first describe the spectra obtained in this way from a number of benzenoid compounds and then discuss the hyperfine splitting constants of these radicals with reference both to those of other aromatic radicals and to theoretical calculations of unpaired spin densities in some of these systems.

Descriptions and Assignments of the Spectra.—The spectrum from benzene, its ascription to the radical (I), and the assignments of the coupling constants have been reported in a preliminary Note.[4] Improvement in the resolving power of the spectrometer and its calibration by reference to $\cdot CH_2OH$ in the flow system as secondary standard and to semiquinone in a static system as primary standard [2] have led to minor adjustments in the coupling constants, and the revised values are shown in (I). Assignments were based previously on comparisons of the spectrum from benzene with those of the phenoxy [5] and cyclohexadienyl [6] radicals, and further evidence for these has now been obtained by studying trimesic acid. This gave a spectrum consisting of a widely split doublet ($|a| =$ 24·4 gauss) each line of which was a triplet (1 : 2 : 1)($|a| = 2{\cdot}6$ gauss), and this can be unambiguously assigned to the radical (II). The similarity in the splitting due to the *meta*-protons in (II) and the smaller triplet in (I) reinforces the arguments on which our previous assignment was made.

Coupling constants (gauss)



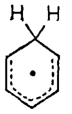
	(I)	(II)	(III)	(IV)
$a_{H\ (methylene)}$	36·0	24·4	—	16·4
$a_{o\text{-}H}$	9·2	—	6·9	5·1
$a_{m\text{-}H}$	2·8	2·7	1·9	1·6
$a_{p\text{-}H}$	13·4	—	10·1	6·3

Phenol and *p*-cresol gave spectra similar to those reported for the corresponding phenoxy radicals obtained by the oxidation of the phenols with ceric ion,[5] but with slightly different coupling constants [phenol: see (III) below; *p*-cresol: $|a_H|$ (methyl), 12·3; $|a_{o\text{-}H}|$, 6·1; $|a_{m\text{-}H}|$, 1·4 gauss]. Quinol gave the semiquinone radical ($|a_H|$, 2·4 gauss).

Toluene gave a complex spectrum which consisted of three sets of triplets (1 : 2 : 1) ($|a|$ = 16·4, 5·1, and 1·6 gauss) and one doublet ($|a|$ = 6·3 gauss). This is inconsistent with the radical's being an adduct of toluene and hydroxyl for there is no quartet splitting due to the methyl group, but the pattern of splittings is that expected for the benzyl radical, formed by abstraction of hydrogen from the side-chain. Further, the triplet splittings of 5·1 and 1·6 gauss and the doublet splitting of 6·3 gauss are related, respectively, to the corresponding splittings for the phenoxy radical (III) by factors which are the same within the experimental accuracy of the measurements (±0·3 gauss). This is not surprising since the benzyl and phenoxy radicals are isoelectronic, and helps to justify the assignments given in (IV).

Two reactions employing one-electron reducing agents were carried out in an attempt to observe the spectrum of the phenyl radical. The interaction between aqueous benzenediazonium sulphate and titanous ion in the flow system did not give rise to the spectrum of an organic radical, but when sodium dithionite was substituted for titanous ion there appeared five broad lines, of relative intensities approximately 1 : 2 : 3 : 2 : 1, together with a more intense line slightly displaced from the centre of the quintet. The pattern of the quintet corresponds to interaction of the unpaired electron with two nitrogen nuclei ($|a_{N1}| = |a_{N2}|$ = 9·3 gauss), and the spectrum is assigned to the benzenediazonium radical, $\mathrm{Ph{-}N{=}\dot{N}} \longleftrightarrow \mathrm{Ph{-}\overset{\cdot\cdot+}{N}{=}\overset{-}{N}}$. The broadening of the lines may have resulted from there being slight differences between the couplings of the two nitrogens and possibly also from the occurrence of weak, unresolved interactions with the aromatic protons.

Coupling Constants.—Certain inferences may be drawn from the values of the hyperfine splittings in the radicals (I)—(IV), together with corresponding data for the cyclohexadienyl radical (V). Of the two sets of splitting constants which have been published for (V), those of Fessenden and Schuler[7] were obtained from a more fully resolved spectrum.



(V)

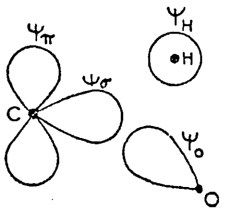
	Coupling constants (gauss)	
	Fischer[6]	Fessenden and Schuler[7]
$a_{\mathrm{H\ (methylene)}}$	50	47·71
$a_{o\text{-H}}$	10·6	8·99
$a_{m\text{-H}}$	2·6	2·65
$a_{p\text{-H}}$	10·6	13·04

(*a*) The ratios $a_{o\text{-H}} : a_{m\text{-H}} : a_{p\text{-H}}$ are constant within the limits of accuracy of the experimental method for the phenoxy, benzyl, cyclohexadienyl (values from ref. 7), and hydroxycyclohexadienyl radicals. If the reasonable assumption is made that the same *Q*-value[8] is appropriate to the *ortho*-, *meta*-, and *para*-protons in each (*cf.* ref. 6), the relative values of the unpaired spin densities at the *ortho*-, *meta*-, and *para*-carbon atoms are the same. The systems may be treated as odd-alternant hydrocarbon radicals, so that the spin densities at the *ortho*- and *para*-carbon atoms should be positive and that at the *meta*-carbon should be negative.

(*b*) The aromatic-proton splittings in (I) and (V) are considerably larger than those in (III) which in turn are larger than those in (IV), so that if the same *Q*-value applies, the unpaired spin densities at the aromatic carbons decrease in the order (I) ~ (V) > (III) > (IV). Looked at from a simple viewpoint, it would appear that an exocyclic methylene group takes a greater fraction of unpaired electron density from the nucleus than does exocyclic oxygen and that a saturated group in the ring takes only a small fraction of the total spin density.

(*c*) The hyperfine splittings of the aromatic protons in (I) and (II) are the same within experimental error as those reported for (V) by Fessenden and Schuler,[7] and it is therefore likely that the spin densities associated with the aliphatic groups in (I), (II), and (V) are also similar. In view of this it is interesting that there is so large a difference between the splittings due to each of the two methylene protons in (V) and the single aliphatic protons in (I) and (II).

A possible explanation for the difference between (V) and (I) can be suggested from a consideration of the mechanism of hyperconjugative coupling.[9, 10] A methylene group is usually treated in terms of bonding between sp^3-hybridised carbon orbitals and the hydrogen $1s$-orbital, but an alternative approach may be followed. This consists of setting up molecular orbitals using linear combinations of the hydrogen orbitals: one of these combinations, which has σ-symmetry, $\frac{1}{\sqrt{2}}[\mathrm{H}(1s)_1 + \mathrm{H}(1s)_2]$, forms a three-centre bond with an appropriately hybridised orbital of carbon (sp), and the other, which has π-symmetry, $\frac{1}{\sqrt{2}}[\mathrm{H}(1s)_1 - \mathrm{H}(1s)_2]$, may be combined with the $2p_z$-orbital of carbon. It is the latter orbital which can lead to an extension of the π-electron system when the methylene group is attached to an unsaturated centre, and this type of interaction is evidently important in cyclohexadienyl, as judged by the magnitude of the hyperfine splitting. When one hydrogen atom is replaced by hydroxyl in this radical, orbitals with approximately σ- and π-symmetry may be constructed from the hydrogen ($1s$) orbital and the appropriately hybridised orbital of the oxygen in the hydroxyl group (Figure): these are, respectively, $(1 + \lambda^2)^{-\frac{1}{2}}[\mathrm{H}(1s) + \lambda\psi_{\mathrm{OH}}]$ and $(1 + \lambda^{-2})^{-\frac{1}{2}}[\mathrm{H}(1s) - \lambda^{-1}\psi_{\mathrm{OH}}]$. For a particular value of λ, the first of these will result in zero overlap with the $2p_z$-orbital of the adjacent carbon, while the second can lead to overlap and hence delocalisation of the unpaired electron. For the same electron density in the group orbitals in (I) and (V), the spin density on the proton in (I) will differ from that on the methylene protons in (V) because λ will differ from unity, and this could account for the observed difference in the hyperfine splittings.



Orbital scheme for the >CH(OH) group of the radical (I). $\psi_{\mathrm{H}} = H(1s)$; ψ_{O} = approximate tetrahedral hybrid of the oxygen atomic orbitals; ψ_σ = appropriate hybrid orbital of carbon (sp); $\psi_\pi = \mathrm{C}(2p_z)$.

The difference between the splitting constants for the aliphatic protons in (I) and (II) may arise from steric interactions in (II) between the *ortho*-carboxyl groups and the substituents on the aliphatic carbon. If the hydroxyl group were thereby forced downwards from the plane of the aromatic system the methylene proton would adopt a position nearer to the molecular plane in which it is less favourably cited for hyperconjugative interaction.[3]

Comparison of Coupling Constants with Calculated Spin Densities.—The spin-density distribution of the benzyl radical has been evaluated by a number of methods,* as follows:

	Calculated spin densities				
Method	Methylene carbon	C_1	*o*-C	*m*-C	*p*-C
Simple Hückel M.O.	0·571	0	0·143	0	0·143
Self-consistent M.O.[11]	0·770	−0·102	0·161	−0·063	0·137
M.O. with five excited-orbital configurations [12]	0·634	−0·121	0·200	−0·072	0·231

The hyperfine splitting observed for the *meta*-protons in this radical points to the inadequacy of the simple Hückel theory. Insofar as experiment indicates that there is a higher spin density at the *para*- than at the *ortho*-carbon, the M.O. treatment which includes five excited-orbital configurations gives a more satisfactory fit then the self-consistent M.O. method, and indeed the ratios of the splitting constants of the *ortho*-, *meta*-, and *para*-protons, neglecting signs (1 : 0·3 : 1·2) are approximately equal to the ratios

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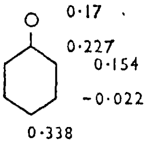
* A valence-bond treatment [13] used an incorrect wave function [14] and is therefore excluded.

of the spin densities at the corresponding carbon atoms calculated by the excited-orbital method (1 : 0·36 : 1·15).

The spin densities in the phenoxy-radical, calculated by a molecular-orbital treatment which included configurational interaction and with the parameters $\alpha_O = \alpha_C + 2\beta_{CC}$, $\beta_{CO} = \beta_{CC}$, are shown in (VI).[12] Agreement with experiment is much less satisfactory in this case.



(VI)

EXPERIMENTAL

The flow system and the procedure for the generation and observation of the radicals have been described.[2] Because of the low solubilities of benzene and toluene in water, the amplitudes of the spectra from these compounds were initially very small. This difficulty was satisfactorily overcome by using warm solutions and, in the case of toluene, by adding pyridine as co-solvent (1 : 1) to the reactant solution containing titanous ion. Very high microwave powers were necessary for these compounds, but despite this there was no indication of saturation, possibly because of the short life-times of the radicals.

In the attempt to observe the phenyl radical, the reactant solutions contained, respectively, sodium dithionite (5 g.) in water (2 l.) and diazotised aniline prepared from aniline (20 ml.), concentrated sulphuric acid (60 ml.), and sodium nitrite (17·5 g.) in water (2 l.).

One of us (W. T. D.) thanks the D.S.I.R. for a maintenance grant.

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PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.

Reprinted from
MOLECULAR PHYSICS, Vol. 9, No. 3, p. 201, 1965

The molecular orbital theory of some simple radicals

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(*Received* 6 *November* 1964)

In this paper the molecular orbital theory of hyperconjugation is extended in order to account for the hyperfine coupling constants observed in some simple but interesting free radicals, e.g. cyclopentyl, vinyl. Predictions are made for the phenyl radical.

1. INTRODUCTION

Much evidence for the theory of hyperconjugation has accumulated from electron spin studies and it is difficult to visualize how the relatively large coupling constants of methyl protons could arise except by actual delocalization of the odd electron. Indeed, recent calculations [1] have shown that the splitting observed from such protons is an order of magnitude larger than that predicted by a spin polarization mechanism similar to that which accounts for the coupling constants of protons situated in the nodal plane of the odd electron [2]. The assumption of hyperconjugation, on the other hand, does lead to estimates for the splitting due to methyl protons which are the right order of magnitude, for example in semiquinones [3] and alkyl radicals [4].

Coupling is observed not only from protons attached to a carbon atom of the conjugated system in which the odd electron is most likely to be found and those bonded to adjacent carbon atoms, but also from protons separated from the unsaturated system by two carbon atoms. To label these three types of proton, we shall call them α, β and γ protons respectively. β and γ protons are not in general held fixed in the nodal plane of the odd electron and our object in this paper will be to develop a molecular orbital theory which enables us to predict. within reasonable limits, the hyperfine coupling constants of such protons. Initially we shall consider symmetrical molecules to which we can apply the concepts of hyperconjugation theory [5, 6]. Having found it necessary to incorporate certain modifications into the model developed by Coulson and Crawford [6], in order to account for the experimental results, we shall derive a rather more general theory which can be applied, in principle, to any hydrocarbon. We shall then be able to account for the splittings of the protons in vinyl and to predict the proton coupling constants in the phenyl radical. Since we neglect configurational interaction throughout, we shall only be concerned with regions of positive spin density and make no attempt to calculate the coupling constants of protons held in the nodal plane of the odd electron.

2. THE HYPERCONJUGATION MODEL

One usually thinks of the methyl group being held together by two-centre bonds between tetrahedral hybrids of the carbon atom and the three hydrogen

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1s orbitals. An equivalent way of looking at it would be to consider multi-centre bonds formed between linear combinations of the hydrogen orbitals and appropriate orbitals of the carbon atom. These linear combinations can be chosen in such a way that only one of them has a non-zero overlap integral with the $2p_\pi$ orbital of the methyl carbon atom and it is this combination which leads to an extension of the π-electron system. When the methyl group is described in these terms the coulomb and more important resonance integrals associated with the hydrogen group orbitals are independent of the molecular conformation. Such a choice of basic wave-functions greatly simplifies calculations, for the π-electron system in the ethyl radical becomes similar to that in allyl and the molecular orbital of the odd electron can be written in the following manner:

$$\psi_{\text{M.O.}} = c_1\psi_1 + c_2\psi_2 + c_3\psi_3,$$

where ψ_1, ψ_2 are $2p_z$ orbitals of the α and β carbon atoms respectively and ψ_3 is the appropriate linear combination of the β hydrogen atomic orbitals. The coefficients c_1, c_2 and c_3 can, of course, be found by solving the secular equations.

In order to simplify the algebra, the matrix elements are defined in terms of α, β and S, which are the coulomb, resonance and overlap integrals occurring in the secular equations of benzene. If we assume that overlap integrals are proportional to the corresponding resonance integrals, we can define the following relationships for the normalized wave functions ψ_r [6]:

$$\int_\tau \psi_r\psi_s\,d\tau = p_{rs}S_1, \quad r \neq s,$$

$$\int_\tau \psi_r\mathscr{H}\psi_s\,d\tau = p_{rs}(\beta + \alpha S), \quad r \neq s,$$

$$\int_\tau \psi_r\mathscr{H}\psi_r\,d\tau = \alpha_r = \alpha + \delta_r\beta.$$

When we have either calculated or simply chosen values for the p_{rs} and δ_r it will be possible to solve the secular equations and find the molecular orbital of the odd electron. The splitting due to a proton will be proportional to the value of the probability functions of the odd electrons [7] at that proton, so we can write the following expression for the hyperfine coupling constant a, taking the ethyl radical as an example:

$$a = k|\psi_{\text{M.O.}}(p)|^2 = k|c_1\psi_1(p) + c_2\psi_2(p) + c_3\psi_3(p)|^2. \tag{1}$$

p defines the position in space of the proton in question and the constant k can be calculated directly in the case of the hydrogen atom. If ψ_0 is the value of the electronic ground-state wave function of the free hydrogen atom at its nucleus, then we can re-write equation (1) as follows:

$$a = 508\left|c_1\frac{\psi_1(p)}{\psi_0} + c_2\frac{\psi_2(p)}{\psi_0} + c_3\frac{\psi_3(p)}{\psi_0}\right|^2. \tag{1 a}$$

Now in every radical considered here, the odd electron goes into an orbital which is approximately non-bonding and this implies that by far the largest contribution to the coupling constant of a proton arises from spin density in the atomic orbital associated with it and that the small effects from more distant orbitals tend to cancel each other. We are therefore justified in simplifying equation (1 *a*) to the following form:

$$a \simeq 508\left(\frac{\chi_0}{\psi_0}\right)^2 c_h^2 = kc_h^2, \tag{2}$$

where c_h is the coefficient of the hydrogen atomic orbital, χ_0 is the value of this orbital at the proton, and k is the proportionality factor connecting spin density and the corresponding hyperfine coupling constant. If the atomic orbital, χ, to associate with hydrogen in a molecular orbital treatment of hydrocarbons is a hydrogen like 1s orbital with effective atomic number Z_h, then we can write from equation (2):

$$a = 508 Z_h^3 c_h^2. \tag{2 a}$$

In the first set of calculations the spin density in a methyl hydrogen orbital calculated for ethyl, using a given set of parameters, and by dividing into the observed coupling constant, 26·87 g. [11], a value for k is derived which can be used in similar calculations for other molecules. In effect this procedure eliminates the need to determine the best hydrogen wave-function to use in such a molecular orbital treatment, partly off-setting the weakness of introducing yet another empirical quantity into the theory.

The numbers ρ_{rs} and δ_r have in practice been used as parameters and we take the following values for them : $\rho_{12} = 0{\cdot}76$ or $1{\cdot}0$, $\rho_{13} = 0$, $\rho_{23} = 2{\cdot}5$, $\delta_1 = 0$, $\delta_2 = -0{\cdot}1$, $\delta_3 = -0{\cdot}5$. These two sets of parameters are close to those which have been used previously in calculations of dipole moments [6] and hyperfine coupling constants [3, 4]. In the radicals considered here, we assume that the carbon skeleton is planar and as symmetrical as possible, with carbon–carbon bond lengths 1·54 Å, carbon–hydrogen bond lengths 1·09 Å and angles between carbon–hydrogen bonds of $109\frac{1}{2}°$. In the case of cyclohexadienyl, the bond lengths in the conjugated system are taken to be 1·40 Å. The secular equations in the case of ethyl are as follows:

$$(\alpha - E)c_1 + \rho_{12}[\beta + S(\alpha - E)]b_2 = 0,$$
$$\rho_{12}[\beta + S(\alpha - E)] + (\alpha - E - 0{\cdot}1\beta)c_2 + 2{\cdot}5[\beta + S(\alpha - E)]c_3 = 0,$$
$$2{\cdot}5[\beta + S(\alpha - E)]c_2 + (\alpha - E - 0{\cdot}5\beta)c_3 = 0.$$

If we assume that the methyl group is rotating rapidly enough, then we can identify c_h^2 with $\frac{1}{3}c_3^2$ and thence calculate values for a_β. The results are shown in table 1.

	k	$(CH_3)_2\dot{C}H$	$(CH_3)_3\dot{C}$	Cyclo-C_3H_5	Cyclo-C_5H_9		Cyclo-C_6H_7	
		a_β	a_β	a_β	a_β	a_γ	a_{CH_2}	
$\rho_{12} = 0{\cdot}76$	948	24·6	22·7	38·8	36·2	0·08	52	gauss
$\rho_{12} = 1{\cdot}0$	585	23·4	20·8	35·8	35·4	0·10	51	,,
Experimental [11]	—	24·68	22·72	23·42	35·12	0·53	47·72	,,

Table 1. Methyl or methylene proton coupling constants.

The agreement between theory and experiment is generally quite good, except for the β-coupling in cyclopropyl and the γ-coupling constants in cyclopentyl. These points of disagreement together with the empirical method for determining constitute rather unsatisfactory features of the theory, and so we shall now examine the basis of hyperconjugation theory to see whether any simple modification will lead to improved agreement with observation.

3. Modified hyperconjugation model

In order to keep expressions relatively simple we shall consider a methylene group in a planar network of carbon atoms and omit overlap terms where they occur in the secular equations. In the actual computations we shall include overlap.

The hydrogen group orbital of π-symmetry is $(1/\sqrt{2})(\chi'-\chi'')$, where χ',χ'' are the two hydrogen wave functions.

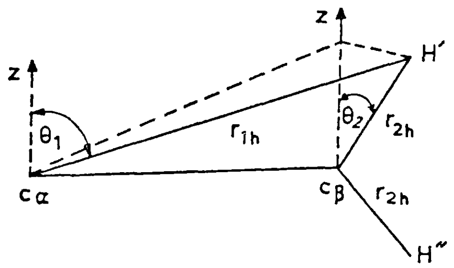


Figure 1. Diagram of C–CH$_2$ fragment.

If ψ_1, ψ_2 are the 2p$_\pi$ orbitals of the α, β carbon atoms, respectively, then the overlap integrals of the system are as follows:

$$S_{12}=\int_\tau \psi_1\psi_2\,d\tau,$$

$$S_{13}=\int_\tau \psi_1(1/\sqrt{2})(\chi'-\chi'')\,d\tau=\sqrt{2}\int_\tau \psi_1\chi'\,d\tau=\sqrt{2}\,S_{1h}\cos\theta_1$$

$$S_{23}=\sqrt{2}\,S_{2h}\cos\theta_2;$$

S_{1h} and S_{2h} are the overlap integrals between carbon 2p$_\sigma$ orbitals and hydrogen 1s orbitals at distances r_{1h}, r_{2h} respectively. θ_1 and θ_2 are the corresponding angles. These overlap integrals can be calculated exactly if we take the carbon and hydrogen atomic orbitals to be hydrogen-like. From the molecular orbital treatment of H_2 and H_2^+, we would expect the effective atomic number of hydrogen in a molecule to be about 1·2 [8, 9] and using Slater's rules [10] this parameter for carbon 2p orbitals is 3·25. Using these assumptions, the overlap integrals are as follows:

$$S_{12}=0{\cdot}189,\ S_{13}=0{\cdot}083,\ S_{23}=0{\cdot}563,\ S_{h'h''}=0{\cdot}192.$$

Assuming the overlap and resonance integrals are proportional to each other and that each carbon 2p orbital has a coulomb integral α, we can solve the secular equations, once we have decided on the relative value of the coulomb integral of the hydrogen group orbital. In order to be able to reproduce approximately the results of Coulson and Crawford [6], we give δ_3 the value $-0{\cdot}5$. From equation (2), k has a value of 878. The results of calculations using this modified hyperconjugation model, are shown in table 2.

	C_2H_5	$(CH_3)_2CH$	$(CH_3)_3C$	Cyclo-C_3H_5	Cyclo-C_4H_7		
	a_β	a_β	a_β	a_β	a_β	a_γ	
Calculated	27·1	22·8	20·3	24·1	38·2	2·9	gauss
Observed [11]	26·87	24·68	22·72	23·4	36·66	1·12	,,

	Cyclo-C_5H_9		Cyclo-C_6H_7	
	a_β	a_γ	a_{CH_2}	
Calculated	37·2	0·57	54	gauss
Observed [11]	35·12	0·53	47·72	,,

Table 2. Coupling constants using modified hyperconjugation model.

The agreement between theory and experiment is very good considering the rather crude assumptions concerning the geometry of the molecules, and we see that there is great improvement in the estimates of the coupling constants in cyclopentyl and cyclopropyl. The comparatively poor results for cyclobutyl can be attributed, at least partly, to the poor geometrical model and the calculations for isopropyl and tertiary butyl were not exact since the interactions between the methyl groups are dependent on the molecular conformations. In the latter case, an average was taken between extreme conformations. Long-range interactions were important especially in determining the order of magnitude of the γ-coupling constants and therefore it was necessary to include all possible resonance integrals when setting up the secular equations.

Similar calculations were carried out using 1·0 and $\sqrt[3]{2}$ for the effective number of hydrogen. The corresponding values for k should be 508 and 1016 if we were to be consistent, but it was necessary to adjust k using the ethyl radical standard in order to get realistic values for the coupling constants. The results shown in table 3 imply that 1·2 was indeed the best choice to make for the effective number of hydrogen.

	k	Cyclo-C_3H_5	Cyclo-C_5H_9		
		a_β	a_β	a_γ	
$Z_h = 1{\cdot}0$	838	22·8	36·9	0·91	gauss
$Z_h = \sqrt[3]{2}$	862	26·1	36·9	0·19	,,

Table 3. Variation of effective atomic number of hydrogen.

Now we shall generalize the theory developed in this section so that we can treat less symmetrical molecules to which hyperconjugation theory cannot be applied.

4. MORE GENERAL THEORY APPLIED TO VINYL AND PHENYL

All we need, to generalize the modified hyperconjugation model, is the relationship between the coulomb integrals for carbon 2s and carbon 6p orbitals, and this can be roughly estimated as follows:

By taking the coulomb integral α_3 in the previous section to be $\alpha = 0{\cdot}5\beta$, we fixed the coulomb integral of hydrogen α_h, for we have:

$$\begin{aligned}\alpha_3 &= \int_\tau (1/\sqrt{2})(\chi' = \chi'')\mathscr{H}(1/\sqrt{2})(\chi' = \chi'')\,d\tau \\ &= \alpha_h - \beta_{h'h''} \\ &= \alpha_h - \frac{S_{h'h''}}{S}\beta \\ &= \alpha_h - 0{\cdot}78\beta,\end{aligned}$$

i.e.

$$\alpha_h = \alpha + 0{\cdot}28\beta.$$

Now we assume, with Coulson and Crawford, that there is little or no contribution towards the dipole moment of the hydrocarbon in question from the σ-electron system [6]. If there is no net dipole moment between the hydrogen group orbital of σ-symmetry and the corresponding sp hybrid orbital of the methyl carbon atom, then their coulomb integrals must be identical. If α_s is the coulomb integral of a carbon 2s orbital, we can then deduce the required relationship:

$$\alpha + \tfrac{1}{2}(\alpha_s - \alpha) \simeq \alpha_h + 0{\cdot}78\beta,$$

i.e.

$$\alpha_s \simeq \alpha + 2{\cdot}12\beta.$$

We are now in a position to calculate, for any hydrocarbon, properties which are not too sensitive to the choice of the coulomb integrals α_h and α_s.

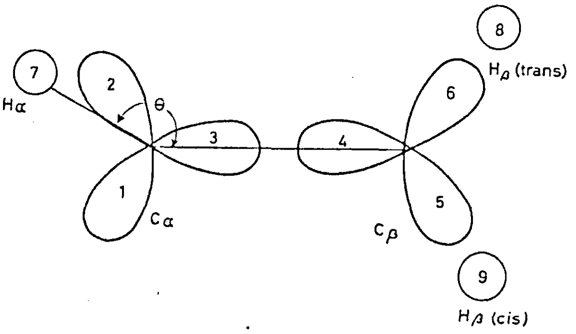


Figure 2. Atomic orbitals of the σ–electron system in vinyl.

The radical was assumed to be planar with carbon–carbon bond length 1·34 Å and carbon–hydrogen bond lengths 1·09 Å. The bond angles at the β carbon atom were taken to be 120°. As with ethylene and benzene, the secular determinant can be factorized to give σ and π molecular orbitals which, in the simple L.C.A.O. approximation, are independent of each other. The odd electron goes into the first antibonding orbital and is therefore associated with the σ-electron system which is symmetrical with respect to reflection through the plane of the page (figure 2). Solutions of the secular equations were obtained by means of a standard programme on the EDSAC computor and the results are shown in table 4:

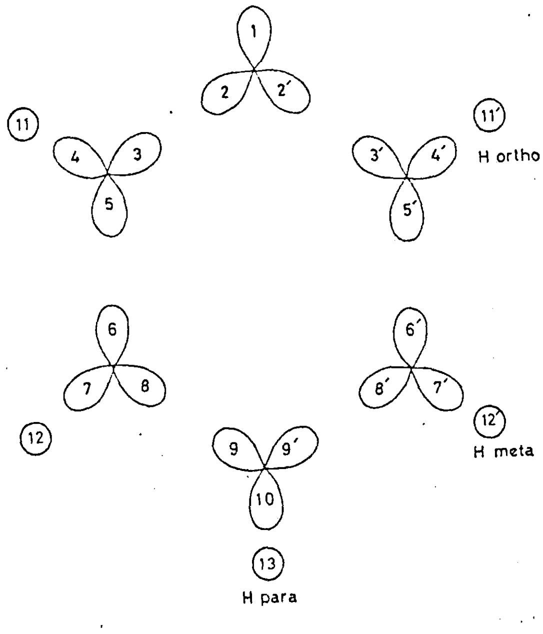
	$\theta=120$	$\theta=150$	$\theta=180$	Expt. [12]
c_1	0·91	0·86	0·94†	—
a_α	+35·8	+14·5	—	15·6 gauss
a_β (cis)	+32·7	+52·3	+72·2	34 ,,
a_β (trans)	+79·3	+82·0	+72·2	68 ,,

† In this case orbital 1 and $2p_\pi$ orbital of the α carbon atom.

Table 4. Coupling constants for the vinyl radical.

It is clear from these results, that we have accounted for most of the features of the observed spectrum and that θ probably lies between 120° and 150°. The large odd electron density in orbital 1, leads us to expect strong spin polarization of the orbitals around the α carbon atom, so the exact magnitude and sign of a_α is uncertain.

Further calculations show that the large trans-proton splitting arises almost entirely from the negative resonance integral of π-type between orbitals 1 and 2. Such a trans effect has been observed already in the M.O. theory of σ-electron systems [13]. Another interesting point is that the positive spin density associated



major coefficients:

$c_1 = \ 0{\cdot}87$

$c_3 = -0{\cdot}17$

$c_{11} = -0{\cdot}163$

$c_6 = \ 0{\cdot}253$

$c_{13} = \ 0{\cdot}143$

Figure 3. Atomic orbitals used in the phenyl calculation.

with the α hydrogen orbital is due almost completely to the inclusion of resonance integrals between sp_2 hybrid orbitals on the same carbon atoms.

When the coulomb integrals were estimated by the method of Pople and Santry [13], the results were almost exactly the same as those given in table 4. The geometry of the phenyl radical was assumed to be the same as that of benzene apart from the absence of one hydrogen atom. The odd electron goes into the first antibonding orbital which is the seventh of the thirteen molecular orbitals, symmetrical with respect to reflection through the two planes of symmetry. The coefficients of the orbitals are shown in figure 3, and the predicted coupling constants are $a_{\text{ortho}} = +23\cdot3$ g, $a_{\text{meta}} = +4\cdot2$ g and $a_{\text{para}} = +17\cdot9$ g. a_{ortho} is about the magnitude expected by comparison with a_β (cis) for vinyl and one would expect a_{meta} to be small, since the meta hydrogen atom is a long way from orbital 1. The large value of a_{para} is rather unexpected, but can be explained in the following manner: the comparatively large coefficient of orbitals 6 might be expected to arise from a similar trans effect to that which leads to the large a_β (trans) in vinyl. The para hydrogen is, however, in a trans position with respect to orbitals 6, so it would appear that the large a_{para} arises from a combination of two trans effects. Actually, we could estimate, roughly, all the coupling constants in phenyl from the known experimental coupling constants in vinyl and would get similar orders of magnitude to those calculated above. It would appear then, that the large a_{para} is a general consequence of molecular orbital theory and does not depend very much on the numerical approximations employed. Actually if negative overlap integrals are neglected the predicted coupling constants are: $a_{\text{ortho}} = 19\cdot2$ g, $a_{\text{meta}} = 3\cdot1$ g, $a_{\text{para}} = 0\cdot1$ g.

5. CONCLUSIONS

We may seem to have travelled a long way from the hyperconjugation theory of Coulson and Crawford, but our assumptions are identical with theirs, apart from a few numerical factors. It is probably worthwhile listing these assumptions: (*a*) Atomic wave functions are given by Slater's rules [10] except in the case of hydrogen, when the effective atomic number parameter is 1·2. (*b*) Resonance integrals are proportional to the corresponding overlap integrals. (*c*) The coulomb integrals are approximately as follows :

$$\text{carbon (2p)} - \alpha$$

$$\text{carbon (2s)} - \alpha + 2\cdot1\,\beta$$

$$\text{hydrogen (1s)} - \alpha + 0\cdot28\,\beta.$$

With this theory we have been able to predict, within reasonable limits, coupling constants in a variety of radicals and have confirmed the existence of a trans effect by means of which spin density may be transmitted through σ–electron systems.

The author would like to thank Professor H. C. Longuet-Higgins, F.R.S., for his help and encouragement and the Salters' Company for a maintenance grant.

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Theoret. chim. Acta (Berl.) 6, 359—361 (1966)

Some Consequences of the Magnetic Interaction of Protons and Electrons

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Received September 26, 1966

It is well known that, in a molecule, the magnetic moment of a nucleus interacts with nearby electrons in such a way that they are to a small extent 'unpaired'; that is, the two possible spin wavefunctions of an electron acquire different weights in different parts of the molecule [*1*—*3*]. We can see this most clearly in the simplest case, the hydrogen molecule $\mathrm{H}_a - \mathrm{H}_b$ (or rather, hydrogen deuteride). The magnetic effect of nucleus H_a leads to a mixing of singlet and triplet states and we may expect the lowest of these to be the most important in forming a ground-state wavefunction $|\,0\rangle_A$ which includes the perturbation [*1*]. If we form $|\,0\rangle_A$ from linear combinations of the two lowest states $|\,0\rangle$, $|\,1\rangle$ for which $s_z = 0$ we obtain the equation:

$$|\,0\rangle_A = |\,0\rangle + \lambda\,|\,1\rangle \qquad \text{(unnormalised)}\,. \tag{1}$$

In the valence-bond approximation [*4*] omitting overlap we can rewrite this equation:

$$|\,0\rangle_A = (1+\lambda)\,|\,0\rangle + 2\lambda[a\alpha(1)\,b\beta(2) - a\alpha(2)\,b\beta(1)] \tag{2}$$

where:

$$|\,0\rangle = \tfrac{1}{2}\,(ab + ba)\,(\alpha\beta - \beta\alpha)$$
$$|\,1\rangle = \tfrac{1}{2}\,(ab - ba)\,(\alpha\beta + \beta\alpha)$$

a, b, are the 'spatial' atomic orbitals of H_a, H_b respectively and α, β the electron spin eigenfunctions. Eq. (2) tells us that according to the sign of λ, either α or β spin will be preferred near to H_a, other things being equal. This equation also shows that the opposite spin would then be associated with the other atomic orbital which goes into the formation of the bond. When we add the interaction of the nucleus H_b with the electrons we again modify the distribution of electron spin and we get two terms for the interaction energy. One is of second order and is of the same type as we have implied for H_a and the other is the first order interaction with the excess spin density induced by H_a. The magnitude of this first order interaction will be determined largely by the values of the atomic orbitals a, b, at their respective nuclei and in the case when the molecule is rotating rapidly and at random, we can write:

$$J_{ab} \sim a_0^2\, b_0^2\,, \tag{3}$$

where J_{ab} = coupling constant

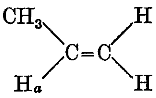
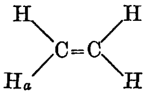
a_0, b_0 = values of a, b, at nuclei H_a, H_b respectively.

This result follows because the dominant term in the Hamiltonian will be the Fermi Contact term [5]. The relation (3) could have been deduced alternatively, but less instructively, by using the 'averaged energy' approximation.

Now suppose that we replace H_b by a hydrocarbon radical fragment R- so that the molecule becomes R–H_a. We might expect the C–H_a bond to be approximately 'isolated' from the rest of the molecule and neglecting differences in electronegativity, we might expect a relationship such as that shown in Eq. (3) still to be applicable. The atomic orbital b would now be the appropriately hybridised orbital on the carbon atom, or more exactly, if we speak in molecular orbital terms, the 'singly occupied MO of the fragment R-' and will be centred mainly on the carbon atom adjacent to H_a. This leads to two implications. The first is that the C^{13}–H coupling constants should be proportional to the 's-character' of the carbon hybrid orbital [6], i.e. we would expect J_{sp}, J_{sp^2}, J_{sp^3} to be in the ratios $\frac{1}{2} : \frac{1}{3} : \frac{1}{4}$ in that order. This agrees very well with the experimental values [6].

The second is that the coupling constants between H_a and the other nuclei should be approximately proportional to the spin densities at those nuclei in the radical R-. Now there are a few radicals which are of σ- rather than π-type and in which we would expect little change in geometry on addition of a hydrogen atom to complete the molecule. In this case the spin distribution around the radical can be measured by the hyperfine splitting of lines in its E.S.R. spectrum. We should therefore expect to find a simple proportionality between the coupling constants in the radical and corresponding proton-proton interactions in the molecule as measured by N.M.R. A glance at table shows that such a relationship does appear to exist, to a certain extent. The correlation for geminal protons is poor; but then the largest alteration in geometry on forming the radical would be expected to be on the α-carbon atom. The difference between the ratios for the different types of molecule may be attributed to structural changes (e.g. lengthening of C=C bond when acetylene loses a hydrogen atom) and/or to differing excitation energies. The experimental results for the olefinic compounds and radicals do however give us some confidence in a method for working out proton spin spin coupling constants in hydrocarbons, i.e. they will be proportional to the spin densities at the nuclei

Table. *Comparison of some hyperfine coupling constants in radicals (electron-proton) and in corresponding molecules (proton-proton)*

molecule	electron-proton coupling constants in radical R-(gauss)	proton-proton coupling constants in molecule RH (c/s)	ratio gauss/(c/s)
	a_{CH_3} = 19.5 [7]	J_{CH_3} = 6.4 [8]	3.0
	a_{trans} = 58.9	J_{trans} = 16.8	3.5
	a_{cis} = 32.9	J_{cis} = 10.0	3.3
	a_{gem} = 15.7 [9]	J_{gem} = 2.9 [6]	5.4
	a_{trans} = 68.5	J_{trans} = 19.0	3.6
	a_{cis} = 34.2	J_{cis} = 11.7	2.9
H_a—C≡C—H	a_H = 16.1 [9]	J_H = 9.1 [6]	1.6
H_a—D	a_D = 78.3	J_D = 43 [10]	1.9

in the appropriate hypothetical radical fragment. The determination of such spin densities is often comparatively easy and so we have another way of approaching the theory of hyperfine interactions in N.M.R. spectra.

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MOLECULAR PHYSICS, 1966, VOL. 11, NO. 6, 601–603

A simple formula for some nuclear spin–spin coupling constants

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(*Received* 12 *September* 1966; *modified* 27 *September* 1966)

Usually the computation of nuclear spin–spin coupling constants involves a great deal of labour since it is necessary to know the ground state [1–3] and often, excited state [4] wave functions. The simplified approach to this problem which is given below is valid only when the nuclei concerned are connected to the rest of the molecule by strongly localized bounds, and when we need only consider contributions to the coupling constants arising from Fermi contact terms in the Hamiltonian.

Let A and B be labels for the two magnetic nuclei and their atomic orbitals and let them be connected in the molecule by a chain of atoms —C . . . . . . D—, the nearest neighbour to A being C. Suppose the connection between A and the part of the molecule containing B is made by means of orbitals ψ_a and ψ_c which are linear combinations of the atomic orbitals chosen so that they each have the minimum interaction with the rest of the molecule and still give a good description of the A–C linkage. ψ_a contains ψ_A, a combination of the atomic orbitals A, but none of the atomic orbitals of C. Similarly ψ_c contains no atomic orbital of A. ψ_a and ψ_c interact together to form a bond which is approximately 'isolated' from the rest of the molecule.

We can describe this bond in terms of M.O. theory:

$$|\mathrm{AC}\rangle_{\mathrm{M.O.}} = (\psi_a+\lambda\psi_c)_i(\psi_a+\lambda\psi_c)_j(\alpha\beta-\beta\alpha)/\sqrt{2}(1+\lambda^2+2\lambda S) \qquad (1)$$

and in this case ψ_a, ψ_c will be the singly occupied orbitals of the fragments obtained by breaking the C–A bond homolytically.

In valence-bond terms the wavefunction associated with the bond would be:

$$|\mathrm{AC}\rangle_{\mathrm{V.B.}} = (\psi_a\psi_c+\psi_c\psi_a)(\alpha\beta-\beta\alpha)/2(1+S_{ac}^2) \qquad (2)$$

and ψ_a, ψ_c would be defined in terms of exchange integrals i.e.

$$\left\langle \psi_a\psi_{\mathrm{D}} \left| \frac{1}{r_{12}} \right| \psi_{\mathrm{D}}\psi_a \right\rangle \approx 0, \text{ etc.}$$

Using Ramsey's approximation [1], the interaction energy of A and B is:

$$E_{\mathrm{AB}} = \langle 0|\delta_{1\mathrm{A}}\delta_{2\mathrm{B}}|0\rangle/\Delta E, \qquad (3)$$

where

$|0\rangle$ = the ground-state of the molecule,

$\delta_{1\mathrm{A}}$, $\delta_{2\mathrm{B}}$ = Dirac δ-functions,

ΔE = an 'average' excitation energy.

If λ is not too different from unity in equation (1), then both M.O. and V.B. theories lead us to the following kind of expression for the coupling constant:

$$J_{\mathrm{AB}} \approx k_{\mathrm{AB}} \psi_a^2(\mathrm{A}) \psi_c^2(\mathrm{B}), \tag{4}$$

where k_{AB} is a constant for the two nuclei and contains the ' adjustable ' parameter ΔE.

$$\psi_a(\mathrm{A}) = \text{value of } \psi_a \text{ at nucleus A},$$

$$\psi_c(\mathrm{B}) = \text{value of } \psi_c \text{ at nucleus B}.$$

We have assumed that $\psi_a(\mathrm{B}) \approx \psi_c(\mathrm{A}) \approx$ zero. For proton-proton splittings we may re-write (4) as:

$$J_{\mathrm{AB}} \approx K_{\mathrm{AB}} C_{\mathrm{B}}^2, \tag{5}$$

where C_{B}^2 is the spin density at B in the ' C ' radical fragment and K_{AB} is a constant for the two types of nuclei and the molecule.

We would only expect this formula to be useful when there is very little interaction between the bonds A–C, D–B formed from the orbitals pairs (ψ_a, ψ_c), (ψ_b, ψ_d), respectively, and this generally limits its use to the cases when nuclei are separated by an odd number of bonds [5]. We can test this limited usefulness in simple M.O. terms and the table shows that the correlation between experiment and theory is quite good for protons, when we fix K_{AB} (i.e. ΔE) empirically.

	Calculated (c/s)			Observed (c/s)	
Molecule	*a*	*b*	*c* [4]		
Ethane	8†	8†	8†	8	[8, 9]
Propane(1 : 2)‡	6·7	7·0	—	7·3	
Isobutane(1 : 2)‡	6·0	6·3	—	6·8	
Cyclopropane‡	7·1	—	—	7–8	
Ethylene gem.	10·6	—	—	2·9	[8]
cis.	9·7	—	9·6	11·6	
trans.	23·4	—	14·8	19·1	
Benzene ortho	6·9	4·8	—	8–9	[10]
meta	1·2	2·0	—	2–3	
para	5·3	4·1	—	0·5	

a: derived from results in ref. [6].
b: derived from results in ref. [7].
†: used as standard.
‡: vicinal, average.

Table 1. Proton–proton coupling constants in some hydrocarbons.

The agreement between theory and experiment is poor in the case of geminal protons as we might expect, since there is then an appreciable direct interaction between them. The reason why the values calculated for para-coupling constants are so poor is not clear at the moment. The advantage of using simple M.O. theory in conjunction with (5) is that one only needs to evaluate the coefficients of a single (approximately non-bonding) molecular orbital.

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Reprinted from CHEMICAL COMMUNICATIONS, 1966, page 870.

A Relationship between Coupling Constants in E.s.r. and N.m.r. Spectra

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FROM a relatively simple viewpoint the C–H* bond in an organic molecule R–H* is approximately localised and may be described by means of a linear combination of the orbitals containing odd electrons in the H· and R· fragments.[1] The geometry of R· is as in the molecule and not, of course, the same as that of the free radical which has the same formula.

Using this way of describing the bond, it can be shown that the scalar coupling of the proton H* with other nuclei in the molecule RH* should be approximately proportional[2] to the spin densities at those nuclei in the fragment R·, provided certain conditions are fulfilled. For example, the hyperfine splittings observed in the e.s.r. spectrum of α-methylvinyl are in a constant ratio to the corresponding proton spin–spin coupling constants in propene (in this case the fragment and the free radical are almost identical).

Now both in the free radical and in the hypothetical fragment formed by abstraction of a hydrogen atom from a substituted ethane, the odd electron is largely confined to a single atomic orbital on the α-carbon atom, as long as the substituents are not unsaturated. If the attached groups do not interact appreciably with each other then their effects are approximately additive, *i.e.*, each substituent absorbs a certain proportion of the spin density on the α-carbon atom. Suppose that the ratio of the spin density on the methyl hydrogen atoms in $RR'\dot{C}Me$ to that on the α-carbon atom is λ_r for the free radical and λ_f for the fragment. The ratio of the hyperfine coupling of the methyl protons with the odd electron in these two odd-electron systems will be:

$$\frac{\lambda_r}{\lambda_f}\left(\frac{1+\lambda_f}{1+\lambda_r}\right) \text{ for ethyl, } \frac{\lambda_r}{\lambda_f}\left(\frac{1+2\lambda_f}{1+2\lambda_r}\right) \text{ for isopropyl,}$$

$$\text{and } \frac{\lambda_r}{\lambda_f}\left(\frac{1+\lambda_f+\lambda_f'}{1+\lambda_r+\lambda_r'}\right) \text{ for } R\dot{C}HMe$$

where λ_r', λ_f' pertain to the substituent R. Provided that the differences $\lambda_r - \lambda_f$, $\lambda_r' - \lambda_f'$ *etc.*, are small, then these ratios will have almost the same value for different molecules. We

TABLE

Coupling constants of methyl protons

R^1	R^2	(a) N.m.r. (c./sec.)[3]	(b) E.s.r. (gauss)[4]	Ratio [gauss/(c./sec.)]
H	H	8·0	26·87	3·4
Me	H	7·3	24·68	3·4
Me	Me	6·8	22·72	3·3
OH	H	6·97	22·0	3·2
OEt	H	6·96	21·9	3·1
OH	Me	6·05	20·0	3·3
OPr	Me	5·98	20·0	3·3
CO_2H	Me	7·41	26·6	3·6

(a) with the odd electron in the radicals $R^1R^2\dot{C}Me$ and
(b) with H^* in the molecules $R^1R^2CH^*Me$.

might therefore expect the methyl proton splittings, observed in the e.s.r. spectra of α-substituted ethyl radicals, to be proportional to the corresponding proton spin–spin coupling constants obtained from the proton magnetic resonance spectra of similarly substituted ethanes. From the Table it would appear that this expectation is realised.

(*Received, October* 21*st*, 1966; *Com.* 804.)

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Reprinted from

Talanta, 1966. Vol. 13, pp. 1199 to 1200. Pergamon Press Ltd. Printed in Northern Ireland

Analysis of peracetic acid solutions

PERGAMON PRESS
OXFORD NEW YORK LONDON PARIS

Talanta, 1966, Vol. 13, pp. 1199 to 1200. Pergamon Press Ltd. Printed in Northern Ireland

Analysis of peracetic acid solutions

(*Received* 7 *February* 1966. *Accepted* 18 *March* 1966)

ANY estimation of peracetic acid has to take into account the hydrogen peroxide which normally accompanies it in solution. The methods given in the literature[1-4] for such an estimation rely on differences in the reactivity of the two peroxides, but generally assume that any hydrolysis which may occur during the analysis may be neglected.[2,3] We have found that this assumption is not justified, especially at low pH, and have therefore developed some alternative procedures which are relatively easy to carry out.

EXPERIMENTAL

The first step was to determine total peroxide concentration, by standard iodometry.[5] An excess of potassium iodide solution was added to the sample of peracetic acid solution, and the liberated iodine titrated with standard thiosulphate. When the blue colour first disappeared, a few drops of ammonium molybdate solution were added, thus bringing back the colour. The titration was continued till the solution again became colourless. Exclusion of air from the solutions made no appreciable difference to the results if the titrations were carried out in less than 5 min.

The second step, the estimation of the individual peroxides, was complicated by the hydrolysis of peracetic acid:

$$CH_3CO_3H + H_2O \rightleftharpoons CH_3CO_2H + H_2O_2$$

Two methods of analysis were developed to allow for this.

(a) *Volumetric method using cerium(IV)*

Although cerium(IV) reacts rapidly with hydrogen peroxide but not with peracetic acid, it is not suitable for direct titration of mixtures of the two, because the end-point is difficult to see (the usual redox indicators apparently react with peracetic acid and so can not be used). Another point which had to be considered was that cerium(IV) solutions must contain a high concentration of acid, and so appreciable hydrolysis of the peracetic acid could occur during the actual titrations. This problem was solved by decreasing the time during which the peracetic acid was in a strongly acidic medium.

The following procedure was adopted: known volumes of peracetic acid and cerium(IV) ammonium sulphate solutions were mixed, the latter in excess, then rapidly diluted with a solution containing an excess of iodide. The liberated iodine was subsequently determined with standard thiosulphate. If the titres corresponding to given volumes of peracetic acid and cerium(IV) solutions were t_1 and t_2 respectively, and the titre for a mixture of these two volumes was t_3, then the titre corresponding to the hydrogen peroxide in the peracetic acid solution must be $\frac{1}{2}(t_1 + t_2 - t_3)$. As long as the operations were carried out within a few minutes, the results were self-consistent (*i.e.*, within 1 %).

Difficulties were experienced when permanganate was used to oxidise the hydrogen peroxide, because of interaction between the manganese(II) and the peracetic acid, which was made evident by the appearance of deep crimson or purple colours in the solutions.

(b) *Spectrophotometric method*

An unknown concentration of hydrogen peroxide may be determined by forming the peroxytitanium(IV) complex and measuring the absorbance of the resulting solution at 410 mμ. Known volumes of peracetic acid solution and an excess of titanium(IV) sulphate in dilute sulphuric acid were mixed, the time noted, and the solution transferred to a 1-cm cell. The absorbance was measured at known time intervals. The initial concentration of hydrogen peroxide could be found by extrapolation and comparison with the absorbance of standardised solutions of the complex. The results agreed with each other, and with those of the volumetric method using cerium(IV), to within about 1 %. Table I shows some typical values.

TABLE I.—SPECTROPHOTOMETRIC DETERMINATION OF PEROXIDE

Hydrogen peroxide added *ml*/100 *ml**	Absorbance	Peracetic acid added *ml*/100 *ml**	Absorbance
0·8	0·377	1·00	0·164
1·2	0·569	2·00	0·323
1·6	0·770	3·00	0·490
—	—	4·00	0·655

* Sample diluted to 100 ml with acidic titanium(IV) solution.

The ratio of the concentrations of hydrogen peroxide in the comparison solution and in the peracetic acid solution was 2·92 ± 0·02 from the photometric measurements compared with 2·94 ± 0·01 from the volumetric analyses. It was assumed that all the oxidising power of the peracetic acid solution was due to the two peroxides.

Analytical grade reagents were used, and the solutions were about 0·1*N* concentration. The sample of peracetic acid, which contained about 10% of hydrogen peroxide, 20% of peracetic acid and 70% of acetic acid, was diluted 100-fold.

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Summary—In the estimation of peracetic acid in aqueous solution, hydrolysis of the peroxy group must be taken into account. The best volumetric method is an indirect one using cerium(IV) as the oxidant, followed by iodometric titration of the excess of cerium(IV). A spectrophotometric estimation of the hydrogen peroxide present, based on the peroxytitanium(IV) complex is satisfactory if measurements are made at known time intervals and extrapolated to zero time.

Zusammenfassung—Bei der Bestimmung von Peressigsäure in wäßriger Lösung muß die Hydrolyse der Peroxygruppe in Rechnung gestellt werden. Die beste volumetrische Methode ist eine indirekte mit Cer(IV) als Oxydans, mit nachfolgender jodometrischer Titration des Überschusses an Cer(IV). Eine spektrophotometrische Bestimmung von vorhandenem Wasserstoffperoxyd, die sich auf den Peroxytitan(IV) komplex stützt, ist zufriedenstellend, wenn in bekannten Zeitabständen gemessen und auf die Zeit Null extrapoliert wird.

Résumé—Dans l'estimation de l'acide peracétique en solution aqueuse, on doit prendre en considération l'hydrolyse du groupe peroxy. La meilleure méthode volumétrique est une méthode indirecte, utilisant le cérium(IV) comme oxydant, l'excès de cérium(IV) étant ensuite dosé par iodométrie. Une estimation spectrophotométrique de l'eau oxygénée présente, basée sur le complexe peroxytitanique(IV), est satisfaisante si les mesures sont effectuées à des intervalles de temps connus et extrapolées au temps zéro.

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REPRINTED FROM CHEMISTRY AND INDUSTRY, 1967, pp. 789—790

Charge Delocalisation in some Elimination Reactions

By W. T. Dixon

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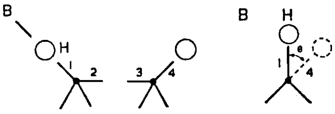
It is well-known that E2 reactions occur most rapidly when the departing groups are *trans* with respect to each other. Sometimes, however, facile elimination takes place when the groups are situated in *cis* positions, *e.g.* in some substituted cyclopentyl systems; but in these cases there is either some special activation to consider, or the groups nearly eclipse each other.[1,2] The stereochemistry of these E2 reactions can be explained in a relatively simple manner by means of the following molecular orbital model: suppose a base $\bar{B}$: approaches an α-hydrogen atom in the molecule $H\text{-}\overset{\alpha}{\underset{\wedge}{C}}\text{—}\overset{\beta}{\underset{\wedge}{C}}\text{-}X$ and that the dihedral angle between C_α–H and C_β–X is θ



The labels B, H, X refer to corresponding atomic orbitals and 1, 2, 3, 4 to carbon sp^3 (or sp^2) hybrid orbitals.

In order to simplify the equations we shall assign the same coulomb integral to all of the atomic orbitals, for this enables us to consider only a single molecular orbital in determining the charge distribution.

The resonance integrals which we shall consider and which are significant in this problem are:

for the interactions 1–H, 2–3 and 4–X, the resonance integral is $\beta=1$; for B–H, γ; for 1–4, $\gamma_\pi \cos\theta$ (this interaction is of π-type); and finally for the type 1–2 the resonance integral is γ'. The charge distribution is given by the coefficients of the non-bonding orbital and these are:

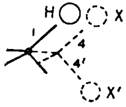
$c_H=c_2=c_4=\cancel{\theta}0$

$c_1/c_B=-\gamma$, $c_3/c_B=\gamma\gamma'$, $c_X/c_B=\gamma\{-\gamma_\pi \cos\ \theta+\gamma'^2\}$. From the results of various extended Hückel calculations[3] it would appear that $1/4 \sim \gamma_\pi \lesssim \gamma'$ and hence there are two positions of maximum transfer of negative charge on to X:

$$\text{(i) } \theta = 180°,\ c_X/c_B = +\gamma_\pi + \gamma'^2$$
$$\text{(ii) } \theta = 0°,\ c_X/c_B = -\gamma_\pi + \gamma'^2$$

Presumably the more easily the charge drifts on to X the more easily will it tend to leave as X^-. This drift is largest when X is *trans* relative to the α-hydrogen and will be further enhanced if X is a strongly electron-attracting group. In this way we explain the preference for *trans*-elimination.

Now let us consider the situation when the groups are held in eclipsing positions



$$\textit{cis},\quad \theta = 0°,\ c_X/c_B = -\gamma_\pi + \gamma'^2$$
$$\textit{gauche},\ \theta = 120°\ c_X/c_B = +\gamma_{\pi/2} + \gamma'^2$$

Since both γ_π and γ' are much less than 1/2 and $\gamma_\pi \lesssim \gamma'$ it is clear that the concentration of negative charge on X in the *gauche* case is comparatively small and therefore *cis*-elimination occurs in this type of molecule.

The reason why *cis* elimination is so rare in the absence of activating groups on the α-carbon, is that the substituents tend to arrange themselves to be as staggered as possible; this implies a dihedral angle of more than 30°, in general, and so the charge developed on a '*cis*' group as $\bar{B}$: approaches is small.

It is interesting to note that if the α-hydrogen atom is removed completely the charge distribution in the alkyl 'σ-anion' would still follow the same pattern, so that the steric course of the reaction should be the same, provided that X^- is lost before inversion can occur at the α-position, other things being equal.

Received March 11, 1967

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Reprinted from CHEMICAL COMMUNICATIONS, 1967, page 402.

Nuclear Magnetic Resonance and Bimolecular Eliminations

By W. T. DIXON

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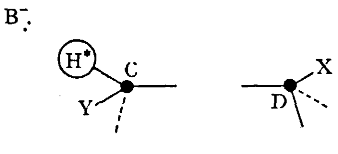
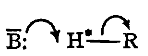
As two molecules approach one another, their electrons tend to be redistributed so that the potential energy is kept as small as possible at any given moment. Eventually the system reaches a point where the potential energy is at a maximum (*i.e.*, at the transition state) and thereafter it loses potential energy as it disintegrates into the products of the interaction. In this Communication we shall consider the period before the transition state is reached in nucleophilic *E*2 or *E*1*cB* reactions[1].



As the base B:⁻ approaches a hydrogen atom H* in the molecule H*–R, its negative charge becomes dissipated to a more or less extent over the fragment R at the same time as the bond (covalent) B–H is formed. It is reasonable to suppose that the more easily the negative charge drifts away from B:⁻ in this situation, the easier it will be for the hydrogen atom H* to be eliminated. There may or may not be synchronous loss of Y⁻ from C or X⁻ from D. Now bonds between hydrogen atoms and nonmetals are usually relatively independent of other bonds in a molecule, and it follows from this that the distribution of charge in the R fragment in the initial stages of the reaction



is the same as that in the negative ion R⁻. In simple MO theory, the delocalisation of the charge from B:⁻ occurs mainly *via* the highest occupied MO of R⁻, which is the same as that occupied by the odd electron in the radical R·. Furthermore, it has been shown that the spin density at a proton in R· is approximately proportional to the spin–spin coupling of that proton with the H* nucleus.[2] Now the greater the degree of delocalisation of the odd electron in R·, the lower is the coupling constant between H* and a given type of vicinal proton; also, from the above arguments, the more favourable is elimination of H* under nucleophilic attack. As a test for these ideas we examine first some effects of conformation in alkene derivatives:

TABLE. *Coupling constants*[3] J (*c./sec.*) *in some halogenoethylenes*

	$CH_2:CH_2$		$CH_2:CHBr$	
Molecule	*cis*	*trans*	*cis*	*trans*
J	11·6*	19·1†	0·1	15·2
J/J_{ref}	1	1	0·61	0·80

	$CH_2:CHCl$		(*cis*) $CHCl:CHCl$		(*trans*) $CHCl:CHCl$	
Molecule	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
J	7·3	14·6	5·3	—	—	12·1
J/J_{ref}	0·63	0·76	0·46	—	—	0·63

† Reference.

From the Table we can see that maximum delocalisation, and hence preferred elimination, occurs when a proton is *trans* with respect to a halogen atom. This is to be expected from the coupling constants in ethylene, which indicate that more of the excess of negative charge tends to collect on the atom *trans* rather than *cis* with respect to H*. In a similar way we would expect *trans*-elimination to be favoured in cyclohexyl halides ($J_{trans}\sim12$, $J_{gauche}\sim4$ c./sec.)[3] but *cis*-elimination when vicinal atoms are held in eclipsing positions (*e.g.*, in cyclopropanes $J_{cis}\sim9$, $J_{gauche}\sim5$ c./sec.).[3] A special case of *cis*-elimination occurs when aryl halides ($J_{ortho}\sim9$, $J_{meta}\sim2{\cdot}5$, $J_{para}\sim1$ c./sec.) react with certain nucleophiles to give benzyne intermediates. The so called Saytzeff rule can also be explained, in these terms, for from the vicinal coupling constants[3] *i.e.*, CH_3CH_3 (8), $(CH_3)_2CH_2$ (7·3), and $(CH_3)_3CH$ (6·8 c./sec.), we would expect preferred elimination from tertiary carbon [*e.g.*,: $(CH_3{}^1)_2{\cdot}CH^2{\cdot}CH^3{\cdot}Cl{\cdot}CH_2{}^4{\cdot}CH_3{}^5$ $J_{1,2}\sim6{\cdot}8$, $J_{4,5}\sim7{\cdot}3$ c./sec., therefore elimination of H^2 preferred.]

If we wished to compare rates of elimination from different molecules, the situation becomes more complex, since we then have to take into account the ease of loss of halogen ion *etc.*, and this is affected by solvent and the substituents on the D carbon atom.

(*Received, March 17th*, 1967; *Com.* 262.)

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COUPLING CONSTANTS AND REACTIVITIES IN ALIPHATIC SYSTEMS

by W.T.Dixon

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PERGAMON PRESS
OXFORD NEW YORK LONDON PARIS

Tetrahedron Letters No.27, pp. 2531-2534, 1967. Pergamon Press Ltd. Printed in Great Britain.

COUPLING CONSTANTS AND REACTIVITIES IN ALIPHATIC SYSTEMS

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(Received 29 April 1967)

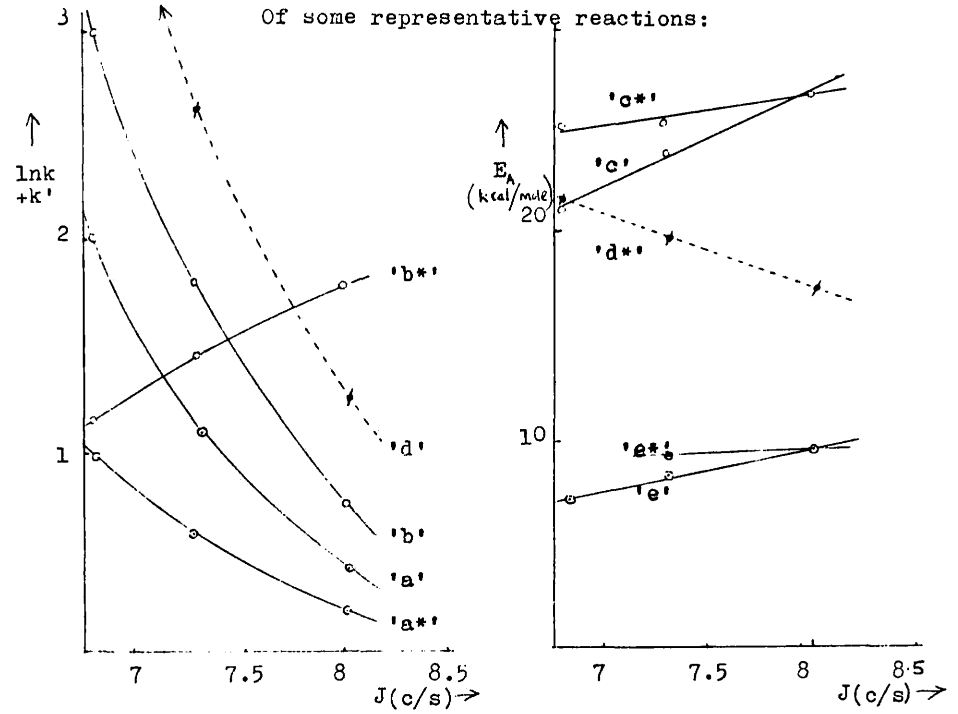
With the advent of extended-Huckel molecular orbital theories (1) and their application, via perturbation theory, to the rates of various reactions (2), it may become unnecessary to guess at transition states and factors affecting their energies, to the same extent as before (3). Unfortunately, molecular orbital theories tend to contain parameters which are adjusted to suit the situation, and this is why it is desirable to find theories which simply relate different properties of a molecule with each other. In this paper we hope to demonstrate a connection between reactivities and magnetic resonance spectra, at least in some particular cases.

Many reactions involve the loss of a group X from a molecule RX (e.g. loss of halide ion in the hydrolysis of alkyl halides) and this process may, or may not, be facilitated by the approach of a group Y_X to X and/or a group Y_R to some part of the fragment R-. As Y_X approaches X its charge/spin gets transferred to the fragment R- and in general, the greater the degree of transfer the weaker the R-X bond becomes. If this bond is stretched in the transition state then we expect that the more easily R- can accommodate the appropriate charge or spin, initially associated with Y_X, the lower will be the activation energy of a reaction in which X is lost. The chief factor assisting in this transference of charge/spin from Y_X, in the cases we shall consider, is the degree of delocalisation in the fragment R-(4).

FIG. I

Empirical relationship between coupling constants and rates

Of some representative reactions:



J = vicinal methyl proton coupling constant, either as measured or as estimated in compounds (i) $\overset{\curvearrowleft}{\mathrm{CH_3}\underset{\alpha}{\mathrm{C}}\mathrm{H}}\mathrm{RR'}$, for curves a,b,c,d,d*,e - which illustrate the effects of α-substituents on the rates of reactions of $\mathrm{CH_3CRR'X}$; (ii) $\overset{\curvearrowright}{\underset{\beta}{\mathrm{C}}\mathrm{HRR'}\underset{\alpha}{\mathrm{C}}\mathrm{H_3}}$, for curves a*,b*,c*,e*,- which show the effects of β-substituents in reactions of $\underset{\beta}{\mathrm{C}}\mathrm{HRR'}\underset{\alpha}{\mathrm{C}}\mathrm{H_2X}$.

k= rate constant, k'= constant for each curve, E_A = activation energy.

a, a* :- E2, $\bar{\mathrm{O}}\mathrm{Et}$ catalyst, RBr → olefin (3) _ Saytzeff-type

b, b* :- E2, $\bar{\mathrm{O}}\mathrm{Et}$ catalyst, $\mathrm{R\overset{+}{S}Me} \rightarrow$ olefin (3) - Hoffman-type

c, c* :- E1, gas phase, RBr → olefin (7) - Saytzeff-type

e, e* :- Radical abstraction, $\tfrac{1}{2}\mathrm{RH} + \tfrac{1}{2}\mathrm{CH_3} \rightarrow \tfrac{1}{2}\mathrm{R\cdot} + \tfrac{1}{2}\mathrm{CH_4}$ (4)

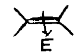
d :- S_N1, $\mathrm{RBr} + \bar{\mathrm{O}}\mathrm{H} \rightarrow \mathrm{ROH} + \mathrm{B\bar{r}}$ (3)

d* :- S_N2, $\mathrm{RBr} + {}^*\mathrm{B\bar{r}} \rightarrow \mathrm{R^*Br} + \mathrm{B\bar{r}}$ (3)

Y_X = solvent (?) for a,b,d; β-H for c.

Y_R = $\bar{\mathrm{O}}\mathrm{Et}$ for a,b; $\bar{\mathrm{O}}\mathrm{H}$ for d; $\mathrm{B\bar{r}}$ for d*; α-Br for c.

the incoming nucleophile are sufficient to offset their rather feeble delocalising (hyperconjugative) power, i.e. rate is determined by the ease of approach of Y_R.

Rates of addition reactions may similarly be connected with N.M.R./E.S.R. coupling constants by considering them as the reverse of eliminations; i.e. the initial step is addition of an electrophile or radical, E, to give a species somewhere between the π-complex  and the σ-fragment allowing maximum delocalisation  .
Hence we expect this initial addition to be such that the most favourable ion/radical is formed; usually this means that the electrophile/radical adds to the carbon attached to the largest number of hydrogens.

e.g. Addition to $(\overset{1}{C}H_3)_2\overset{a}{C}=\overset{b}{C}H\overset{2}{C}H_3$

In molecule: $(\overset{1}{C}H_3)_2\overset{a}{C}H.\overset{b}{C}H_2\overset{2}{C}H_3$, $J_{a1} \approx 6.8$ c/s, $J_{b2} \approx 7.3$ c/s, therefore initial addition is to carbon atom 'b'. This accounts for Markownikoff's rule and the direction of radical addition of HBr.

The stereochemistry of addition/elimination reactions may be correlated with splittings in magnetic resonance spectra in a similar manner.

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A Molecular Orbital Theory of Proton Spin–spin Coupling Constants

By **W. T. Dixon**, Bedford College, Regents Park, London N.W.1

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SECTION A
Inorganic, Physical and Theoretical Chemistry

1967

A Molecular Orbital Theory of Proton Spin–spin Coupling Constants

By W. T. Dixon, Bedford College, Regents Park, London N.W.1

If equivalent orbitals are used in the description of carbon–hydrogen bonds, a very simple formula for proton–proton coupling constants in hydrocarbons may be derived. Only two MO parameters, one for the π-interactions of carbon hybrid orbitals and one for the interaction of orbitals on the same atom, are needed to reproduce most of the observed trends in the hyperfine splitting of proton magnetic spectral lines. Addition of a further parameter makes it possible to estimate the actual magnitude of coupling constants. The scalar interaction of protons appears to take place largely by means of π-interactions, often within the so-called σ-skeleton of a molecule.

SINCE Schrödinger equations cannot generally be solved exactly, we usually express the eigenfunctions of a molecular Hamiltonian as a linear series, the terms of which are most sensibly chosen so that the series converges as rapidly as possible. For example, it is convenient if these functions form a linearly independent set and reflect the geometry of the molecule. Very often the eigenfunctions of a simplified Hamiltonian are chosen as bases; usually, however, we cannot solve even simplified problems exactly, so then the terms forming such a series are approximate eigenfunctions of a simpler Hamiltonian. Such a situation arises when we try to calculate spin–spin interaction energies, and in this case the eigenfunctions are expressed in terms of those associated with the spin-free Hamiltonian $\mathscr{H}_0$. Since magnetic effects are normally very small, it is legitimate to treat them as perturbations and the coupling between two nuclei in a molecule, with zero resultant electronic spin, is given to the second order by equation (1) [1]:

$$E_{AB} = \frac{\sum_{r=1}^{\infty} \langle 0|\mathscr{H}_A|r\rangle\langle r|\mathscr{H}_B|0\rangle + \langle 0|\mathscr{H}_B|r\rangle\langle r|\mathscr{H}_A|0\rangle}{E_0 - E_r} \quad (1)$$

where $E_0,|0\rangle$ = lowest eigenvalue and associated eigenfunction of H_0; $E_r,|r\rangle = r^{th}$ eigenvalue and eigenfunction of $\mathscr{H}_0$; $\mathscr{H}_A$ and $\mathscr{H}_B$ are the perturbations due to nuclei A,B, respectively. One way of simplifying this equation is to replace the excitation energies $(E_r - E_0)$ by a sort of average ΔE and then we obtain,[1]

$$E_{AB} = \frac{\langle 0|\mathscr{H}_A\mathscr{H}_B + \mathscr{H}_B\mathscr{H}_A|0\rangle}{\Delta E} \quad (2)$$

Equation (2) contains the apparent advantage that we need only know the ground-state of the molecule to calculate E_{AB}, but there is no reason to suppose that the same value of ΔE can be used for different pairs of nuclei. Some results using ΔE effectively as an empirical parameter are quite good,[2] on the other hand others are poor; [2,3] one of the main difficulties being that when (2) is used in conjunction with molecular orbital theory, predicted coupling-constants are bound to be positive.[3]

Perhaps a more satisfactory way of simplifying equation (1) is to limit the number of terms, and such a method has been applied to simple hydrocarbons with some success.[4] In this Paper a third approach will be used which is equivalent to a combination of the two mentioned above. In this method we consider only two excited states and these correspond to excitations of the two C–H bonds associated with the protons in question.[5]

Derivation of Formulae.—Suppose hydrogen atoms A,B are attached to atoms C,D, respectively, in the molecule which we are going to discuss in simple molecular orbital terms, neglecting overlap in setting up the secular equations. As basis functions we shall employ mainly the atomic orbitals but instead of ψ_1, the atomic orbital of A, we shall use the linear combination $a = \sum_{r\neq 2} c_r'\psi_r$, where ψ_r is the r^{th} atomic orbital. The coefficients c_r' will be chosen so that the integrals β'_{ar} $(= \int_\tau a(\mathscr{H} - \alpha_r)\psi_r d\tau,\ \alpha_r = \int_\tau \psi_r\mathscr{H}\psi_r d\tau)$ are zero when $r \neq 1,2$; $\mathscr{H}$ is the one electron Hamiltonian for the molecule. This choice is unique because we have the normalisation condition for a and n-2 equations of the type $\beta'_{ar} = 0$, for determining n-1 coefficients. ψ_2 is an appropriately hybridised orbital of atom C, *e.g.*, *sp* for acetylene, sp^2 for ethylene, and sp^3 for ethane, and is replaced as a basis function by the combination $c = \sum_{r\pm 1} c_r\psi_r$. The coefficients c_r are determined by the equations $\beta'_{cr} = 0, r \neq 1,2$. In a similar way we replace ψ_3 the atomic orbital of B by $b = \sum_{r\neq 4} c_r'''\psi_r$, and ψ_4 the corresponding hybrid orbital of D by $d = \sum_{r\neq 3} c_r''\psi_r$ and define $\beta'_{br} = \beta'_{dr} = 0,\ r \neq 3,4$. Defined in this way, function c is, for example, the highest occupied orbital in the fragment obtained by abstracting atom A leaving the geometry of the rest of the molecule unchanged.

Now we are ready to set up the secular equations for the molecule using a,b,c,d and the atomic orbitals ψ_5...... as basis functions. The resonance integrals β_{ab}, β_{ad}, β_{cb}, β_{cd} will be small and we can construct two molecular orbitals, *i.e.*, approximate equivalent orbitals [6] which involved only a and c which can be associated with the bond C–A. One of these is bonding, *i.e.*, $(a + \lambda c)(1 + \lambda^2)^{-\frac{1}{2}}$, and the other antibonding, *i.e.*, $(\lambda a - c)(1 + \lambda^2)^{-\frac{1}{2}}$. Similarly, two approximate equivalent orbitals can be constructed which involve only b and d and which can be associated with the bond B–D.

Of the excited states, those corresponding to the lowest single excitations of the A–C, B–D bonds are by far the most important in determining the magnitude of the Fermi Contact Interaction between the nuclei A and B and therefore we consider only the two corresponding terms in equation (1). If differences in electronegativity are not too large the coupling constant J_{AB} is given by

$$J_{AB} = -(K_{AB}/2)(a_B^2 + b_A^2 - c_B^2 - d_A^2) \quad (3)$$

where K_{AB} is a constant for a given type of molecule and involves a sort of average excitation energy $\Delta E'$ for the lower excited states of the molecule, and f_X is the value of function f at a nucleus X. If A and B are in similar situations the expression in (3) can be simplified to:

$$J_{AB} = K_{AB}\ (c_B^2 - a_B^2) \quad (4)$$

In hydrocarbons, when the protons are separated by an odd number of bonds $c_B^2 \gg a_B^2$, so we can often simplify (4) even further to:

$$J_{AB} = K_{AB}c_B^2 \quad (4a)$$

Equations (4) and (4a) have already been applied to a few hydrocarbons using extended Hückel theories,[5a] and also have been used to relate the e.s.r. spectra of certain radicals with the n.m.r. spectra of corresponding molecules.[5a,b] In this Paper we shall use a simple form of molecular orbital theory in order to correlate the n.m.r. spectra of a wider range of compounds.

Molecular Orbital Theory.—The following treatment is essentially a particular view of hyperconjugation.[6] The compounds which we are going to discuss are all hydrocarbons and we shall assume that we can use the

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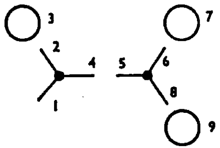
same coulomb integrals for all the basis functions, *i.e.*, the various carbon hybrid and hydrogen orbitals. When the theory is applied for geminal protons we have to use equation (4), otherwise equation (4a) suffices, since in general we need only know the odd electron distribution in the radical R- to find the coupling of " A " with other protons in the molecule R-A.[5] Translating this into MO terms, we only have to find the coefficients of the atomic orbitals in a single molecular orbital the energy of which will have very nearly the same value as one of the coulomb integrals. In these terms all the coefficients except one are small. Let us take the σ-fragment from ethylene as an example:



(I)

1,2,4,5,6,8 are carbon sp^2 hybrid orbitals
3,7,9 hydrogen 1s orbitals

Geometry : bond angles 120°; C–C, 1·34 Å; C–H, 1·08 Å. In some computations of coupling constants in alkyl, vinyl, and phenyl radicals, the author [5,7] found that the results were sensitive to only a few of the resonance integrals which were treated as semi-empirical parameters. The following parameterisation was found to give the simplest adequate treatment of coupling constants either in n.m.r. or in e.s.r. spectra.

$$\beta_{2,3} \approx \beta_{4,5} = \ldots\ldots = 1$$
$$\beta_{1,6} = \beta_{2,8} = -\gamma_\pi - \gamma_\sigma$$
$$\beta_{1,8} = \beta_{2,6} = +\gamma_\pi - \gamma_\sigma$$
$$\beta_{1,2} = \beta_{5,6} = \tfrac{1}{3}(\alpha_s - \alpha_p) = \gamma$$

Where α_s, α_p are carbon 2s, 2p coulomb integrals respectively; $\pm\gamma_\pi$ is the π-type of interaction between the p components of the hybrid orbitals, *e.g.*, in ethylene,

$$\gamma_\pi = \tfrac{1}{3}\beta_\pi \cos^2 30 = \tfrac{1}{2}\,\beta_\pi$$

β_π is the π-resonance integral, and γ_σ is the interaction of hybrid orbitals (non-bonded) along the line of the nuclei and is expected to be small.[4]

In solving the secular equations for the " vinyl " radical, above, we find from third, fifth, seventh, and ninth rows, for the non-bonding orbital,

$$c_2 = c_4 = c_6 = c_8 = 0$$

and from the other rows,

$$c_3 = c_5 = -\gamma c_1$$
$$c_7 = (\gamma_\pi + \gamma_\sigma + \gamma^2)c_1$$
$$c_9 = (-\gamma_\pi + \gamma_\sigma + \gamma^2)c_1$$

Using equation (4a) we obtain,

$$J_{cis} = K_{AB}\,(-\gamma_\pi + \gamma_\sigma + \gamma^2)^2 c_1^2$$
$$J_{trans} = K_{AB}\,(+\gamma_\pi + \gamma_\sigma + \gamma^2)^2 c_1^2$$

We can see that $J_{trans} > J_{cis}$ provided that $\gamma_\sigma + \gamma^2 > 0$. There is evidently a marked similarity between this type of system and so-called π-electron systems in which there are non-bonding molecular orbitals [8] (*i.e.*, alternate atomic orbitals have zero probability). However here we have to consider two paths by which odd electron density is transmitted through the molecule, *i.e.*, *via* α- and π-interactions of non-bonded, hybrid atomic orbitals. The rule for finding the coefficients is not as simple as in the pure π-electron case and there is rather a low degree of delocalisation due to heavy " damping " by the relatively strong C–H and C–C bonds.

Choice of values for parameters. We shall choose the parameters semi-empirically so that we get good predications for J_{cis} and J_{trans} in ethylene using equation (4a). The total spin density on the β-protons in the vinyl radical was found, by extended Hückel calculations,[7] to be approximately 1/8. This gives us a third relationship,

$$\left.\begin{array}{r} K_{AB}\{\gamma_\pi + \gamma_\sigma + \gamma^2\}^2 N^{-2} \approx 19{\cdot}1 \\ K_{AB}\,\{-\gamma_\pi + \gamma_\sigma + \gamma^2\}^2 N^{-2} \approx 11{\cdot}6 \\ 2\{\gamma_\pi{}^2 + (\gamma_\sigma + \gamma^2)^2\}N^{-2} \approx 1/8 \end{array}\right\} \qquad (5)$$

where N is a normalisation factor. Satisfactory values for the parameters, which approximately reproduce the equations in (5) are,

$$\gamma_\pi = \tfrac{1}{4},\ K_{AB} = 286 \text{ c./sec.},\ \sqrt{\gamma_\sigma} + \gamma^2 = 1/4\sqrt{2}$$

Little is to be gained by including γ_σ, so we shall equate it with zero and use the value $1/(4/\sqrt{2})$ for γ. The maximum value of the π-type overlap integral involving two carbon sp^3 hybrid orbitals situated on adjacent carbon atoms 1·54 Å apart (bond angles 109½°), is very nearly the same as in the ethylene case above; *i.e.*, $\tfrac{3}{4}\ S_\pi$ (1·54) $\cos^2 19\tfrac{1}{2}$, where S_π (1·54) is the π-overlap integral for two carbon 2p orbitals at that distance. As in the extended Hückel treatment,[7] we assume that resonance and overlap integrals are approximately proportional to each other, so to maintain simplicity we shall take the same value for γ_π in ethane as in ethylene. The only other important parameter we shall need to know in the calculations involving equation (4a) is the ratio of β in acetylene to that in ethylene. This ratio is 9/11 assuming a C–C bond length of 1·20 Å in acetylene and an exponent of 1·625 for carbon 2s and 2p orbitals. From the overlap integrals, the various types of C–C and C–H bond are not very different from each other, so we shall make them all equal to our unit of energy. A hydrogen exponent of 1·2 was used throughout [7] and a C–H bond distance of 1·08 Å.[9]

Calculation of geminal proton coupling constants. First

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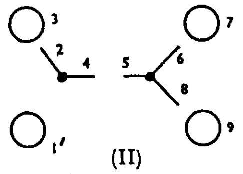
[7] W. T. Dixon, *Mol. Phys.*, 1965, **9**, 201.

[8] J. A. Pople, *Quart. Rev.*, 1957, **11**, 273; H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 283; M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357; K. Fukui, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Japan*, 1962, **35**, 1475; C. A. Coulson, " Valence," Oxford University Press, Oxford, 1961, ch. 7.

[9] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

we shall consider two cases when it is not legitimate to replace equation (4) by (4a). For ethylene we need to look at the following orbital systems,



(II)

We have discussed (I) already and in order to find the second term in equation (4) it is necessary to consider (II) and to include interactions which are unimportant in (I); these are as follows:

$$\gamma_{hh} = \beta_{1',3}/\beta_{2,3} = S_{1',3}/S_{2,3} = 2/7$$
$$\gamma_{h} = \beta_{1,3}/\beta_{2,3} = S_{1',2}/S_{2,3} = 1/4\sqrt{3}$$

The coupling of the geminal protons is given by,

$$J_{gem} = K_{\mathrm{AB}}(c_3^2 - c_3'^2) \qquad (6)$$

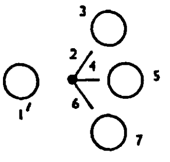
where

$$c_3 \approx -\gamma c_1$$
$$c_3' \approx -\gamma_h c_1'$$

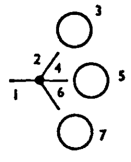
Insertion of numerical values leads to a result which compares favourably with the observed coupling constant (+2·5 c./sec.);[10] *i.e.*, J_{gem}(ethylene) = +2·6 c./sec.

A similar result has been obtained using the V.B. method.[11]

In an analogous way we can calculate the geminal coupling constant in methane, considering the following orbital systems:



(II)



(I)

Values of the integrals are: $\beta_{1,2} = (\frac{3}{4})\gamma$, $\beta_{1,3} = (\frac{5}{4})\gamma_h$ and $\beta_{3,5} = S_{3,5}$(methane)$/S_{3,5}$(ethylene) $= (5/4)\gamma_{hh}$. The coupling constant found for the protons in methane is found to be −3·5 c./sec., so that the sign is correct although the value is rather too small (empirical value −12·4 c./sec.).[12]

Coupling of Protons Separated by more than Two Bonds.—In this section we shall deal mainly with cases to which equation (4a) may be applied. We shall not consider the interaction of σ- and π-electronic configurations but shall, in the first place, examine the transmission of magnetic effects through what is generally called the σ-skeleton of a molecule. The agreement between theory and experiment is surprisingly good, considering the simplicity of the model. In these calculations the methyl groups were supposed to be rapidly rotating and an "ideal" geometry was chosen for the alicyclic compounds. Also, since we considered only type (I) (above) orbital systems, effectively only three parameters were used in calculating the results shown. Any movement away from the perfect chair conformation of cyclohexane leads to a reduction in axial–axial proton coupling and this could account for the high predicted value in the Table, since rings which are prevented from flapping by bulky groups are probably distorted.

TABLE 1

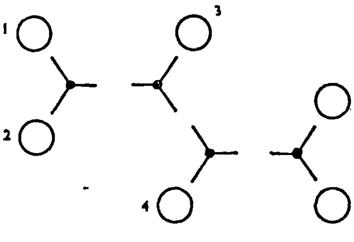
Vicinal coupling constants (c./sec.)

	C_2H_4		MeCH*:CH$_2$			EtH
	J_{trans}	J_{cis}	$J_{\mathrm{H^*-Me}}$	J_{cis}	J_{trans}	J_{vic}
Calc.	19·0	11·5	7·1	10·7	17·1	7·9
Obs.	19·1	11·6	6·4	10·0	16·8	8·0

	Me_2CH_2	Me_3CH	cycloC_6H_{12}		cycloC_3H_6	
	J_{vic}	J_{vic}	J_{ax-ax}	J_{ax-eq}	J_{cis}	J_{gauche}
Calc.	7·3	6·75	16·5	2·7	4·8	12·7
Obs.	7·3	6·8	12	4	5—6	8—9

Long-range coupling constants. In most cases where coupling takes place between protons separated by more than two carbon atoms, it is necessary to invoke the participation of π-electrons in explaining the transmission of spin density from one part of a molecule to another.

In the case of *trans*-butadiene, however, we do not have to postulate such a mechanism for we can explain the observed coupling constants by referring only to the orbitals which are symmetrical with respect to reflection through the plane of the molecule, *i.e.*, its σ-skeleton:



$$J_{1,3} = K(-\gamma_\pi + \gamma_\sigma + \gamma^2)^2$$
$$J_{2,3} = K(\gamma_\pi + \gamma_\sigma + \gamma^2)^2 \sim J_{3,4}$$
$$J_{1,4} \approx 0,\ J_{2,4} = 4K\gamma^2(-\gamma_\pi + \gamma_\sigma + \gamma^2)^2$$
$$J_{1,5} \approx K(\gamma_\pi + \gamma_\sigma)^2(-\gamma_\pi + \gamma_\sigma + \gamma^2)^2$$
$$J_{1,6} \approx K(\gamma_\pi + \gamma_\sigma)^2(\gamma_\pi + \gamma_\sigma + 3\gamma^2)^2$$
(K = Constant.)

For benzene, also, the results are good when we consider only the σ-orbitals, except that the predicted coupling between *para*-protons is much too large (see Table 2). The negative splittings which often arise when protons are separated by an even number of bonds are not included in our theory because we neglect (*a*) the polarisation of the C–H bond in the σ-fragment by the comparatively large induced spin density on that carbon

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[10] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.*, 1962, *A*, **263**, 385

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[12] M. Karplus, D. H. Anderson, T. C. Farrer, and H. S. Gutowsky, *J. Chem. Phys.*, 1957, **27**, 597.

atom and/or (*b*) to include the second term in equation (4).

TABLE 2

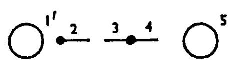
Coupling constants in butadiene and in benzene (c./sec.)

Butadiene	$J_{1.3}$	$J_{2.3}$	$J_{1.4}$	$J_{2.4}$	$J_{1.5}$	$J_{1.6}$
Calc.	11·1	18·4	0	1·6	0·7	1·4
Obs.[14]	11	16	−1·3	−0·7	0·5	1·5

Benzene	J_{ortho}	J_{meta}	J_{para}
Calc.	8·8	1·5	2·3
Obs.[13]	8—9	2—3	0·5

Acetylene. The coupling constant predicted for acetylene, 1·3 c./sec., is much smaller than the experimental value of 9·1 c./sec. Several reasons for this discrepancy suggest themselves; first, we might expect appreciable interaction of the protons *via* the π-electron system[15] (involving configurational interaction);

(I)



(II)

secondly, the interactions 1—3, 1—4, etc., may be important; and thirdly, in our approximation the coupling energy varies as the fourth power of γ and is therefore extremely sensitive to that parameter. At this point it is not worthwhile trying to make a " better " choice.

Coupling between methyl protons. When methyl groups are separated by an odd number of carbon atoms the above theory leads to zero or near-zero coupling; we might therefore expect the splittings to be negative, as is observed.[13b] When the methyl groups are separated by an odd number of double or triple bonds we need to know further parameters which can be found from those whose values have been given already. The problems are solved in much the same way as those above and the method is illustrated below for the case when two protons are in the most favourable position for coupling and are separated by one multiple bond

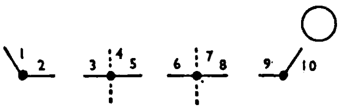
TABLE 3

Long range coupling of methyl protons

	$\mathrm{Me_2C{:}CH_2}$	$\mathrm{MeCH{:}CHMe}$	$\mathrm{Me(CH{:}CH)_2Me}$
Calc. (c./sec.) ...	0	1·7	0·8
Obs. (c./sec.)[13]	?	1·2	?

	$\mathrm{Me(CH{:}CH)_3Me}$	$\mathrm{CH_2{:}C{:}Me_2}$	$\mathrm{MeC{\vdots}CMe}$
Calc. (c./sec.) ...	0·3	2·5	2·5
Obs. (c./sec.)[13]	?	3·0	2·7

	$\mathrm{Me(C{\vdots}C)_2Me}$	$\mathrm{Me(C{\vdots}C)_3Me}$
Calc. (c./sec.) ...	0·9	0·3
Obs. (c./sec.)[13]	1·3	0·4



$$\beta_{1.4} = \gamma\pi' = 0{\cdot}305$$

$$\beta\pi = \beta_{4.7} = \begin{cases} 0{\cdot}5 \text{ (ethylene)} \\ 0{\cdot}61 \text{ (acetylene)} \end{cases}$$

$$c_4/c_1 = 0;\ c_7/c_1 = -\gamma\pi'/\beta\pi;\ c_{11}/c_1 = (\gamma\pi'/\beta\pi)\gamma\pi'$$

DISCUSSION AND CONCLUSION

From the above Tables we can see that the agreement between theory and experiment is generally rather good. The most useful point we can make is that we can expect good order of magnitude predictions whenever coupling constants are largely determined by the π-interactions of carbon hybrid orbitals. In other cases it is apparently necessary to include configurational interactions, especially when the nuclei are separated by an even number of σ-bonds or by multiple bonds. The main problem which remains unsolved is that the calculated coupling constant for *para*-protons in benzene is wrong by nearly an order of magnitude. On semi-quantitative grounds one might expect a splitting of 2—3 c./sec. by comparison with the δ-coupling constants in butadiene derivatives. Sensible variations in the parameters and more extended calculations[5a,16] all lead to similar estimates, which are much higher than observed splittings by *para*-protons. It may be that interaction with the π-electrons leads to negative, rather than positive contributions to the induced spin density at the *para*-position. This problem is not, apparently, one which will be resolved in simple molecular orbital terms.

Finally, we might summarise some of the more interesting points about the simple MO theory given above. (i) Numerical predictions are often good. (ii) It is easy to arrive at explicit expressions for spin densities in radicals or proton–proton coupling constants in hydrocarbons. (iii) It gives us some idea as to how effects may be transmitted through σ-electron systems, *i.e.*, effectively by means of hyperconjugation; retaining the idea of σ-bonds being very strongly localised. (iv) It provides us with a useful picture of a complex phenomenon, the indirect coupling of protons in molecules; that is, the C–H bond is spin polarised by the magnetic moment of the proton so that a certain spin orientation is preferred near the carbon atom. This spin density (opposite in sign to that around the proton) is then delocalised to a certain extent around the rest of the molecule, leading to interactions with other magnetic nuclei.

[7/212 *Received, February* 21*st*, 1967]

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THE ROLE OF SIGMA ELECTRONS IN AROMATIC SUBSTITUTION

by W.T.Dixon
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(Received in UK 10 September 1967)

The recent development of generalised Huckel

PERGAMON PRESS
OXFORD NEW YORK LONDON PARIS

Tetrahedron Letters No.2, pp. 189-192, 1968. Pergamon Press Ltd. Printed in Great Britain.

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The recent development of generalised Huckel theories, e.g. that of Hoffmann (1), and their application to the changes which take place during molecular interactions, e.g. by Fukui et al. (2), promises to increase our understanding of many chemical reactions. Unfortunately, the results obtained from computors for specific problems take time to be digested and the important factors determining the course of a reaction are still liable to remain obscure. For this reason a rather simplified approach has been developed in which direct computation of energies is avoided and in which we only have to estimate the coefficients of a single non-bonding orbital (3). In this letter we hope to demonstrate the part which sigma electrons play in electrophilic substitution reactions of aromatic molecules.

In our model we imagine that an electrophile Y^+, with only one empty molecular/atomic orbital available for bonding, approaches the carbon atom C1 of an aromatic ring, from a direction approximately at right-angles to the molecular plane. In this case we can assume that the direct interaction involves only the $2p_\pi$ and 2s orbitals of C1. For simplicity we take the same value for all coulomb integrals of the orbitals involved in which case the charge distribution is given by a non-bonding orbital, mainly localised on Y, as long as the separation is large enough. We are, of course, considering the first part of the reaction. Both π- and σ- type atomic orbitals appear in the non-bonding orbital and their coefficients can be calculated easily, and more or less separately, because the diagonal terms of the secular equations are approximately zero.

We define the problem in terms of the usual carbon sp^2 and $2p_\pi$ atomic orbitals and one atomic orbital for the attacking agent and each substituent (see diagram).

FIG I

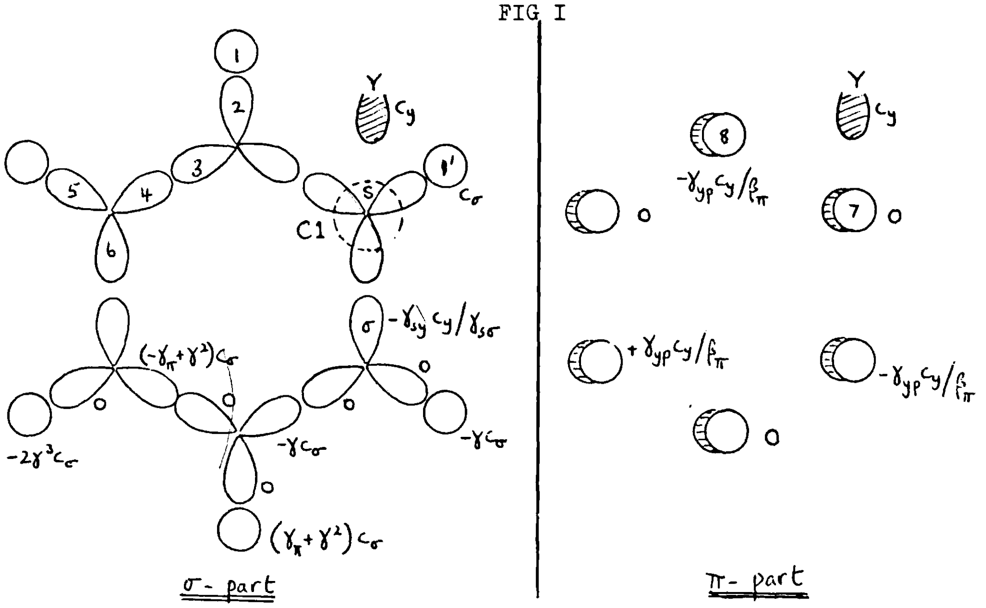

FIG I : Diagram of the atomic orbitals involved in the non-bonding orbital with approximate expressions for their coefficients.

The non-zero resonance integrals which, from results of nuclear spin-spin coupling constant calculations (4), should be sufficient for determining the coefficients of these orbitals, are of the following types:- $\beta_{12} = \beta_{34} = 1$; $\beta_{13} = \gamma$; $\beta_{25} = -\beta_{26} \approx \frac{1}{2}\beta_{78} = \gamma_\pi$; $\beta_{7\delta} = \beta_\pi$; $\beta_{y7} = \gamma_{yp}$; $\beta_{ys} = \gamma_y$
approximate expressions for the coefficients are shown in FIG I.

Looking at the π- part first, if there is a halogen atom attached to the carbon atoms ortho or para with respect to Cl, then the positive charge transmitted to these positions (as shown) will tend to counterbalance the negative charge there arising from the partial sharing of the lone pair(s) of the halogen. We would expect this to lower the energy compared with the situation in benzene itself, or when the attack is meta with respect to the substituent. As with more 'static' (5) theories of these reactions we therefore expect preferential attack on the ortho and para positions.

Now the charge distribution is given by the squared coefficients of atomic orbitals in the lowest unoccupied orbital of the system of two reactants. It is interesting to note that in the carbon $2p_{\pi}$ orbitals, the relative distriution ortho: meta: para remains approximately constant as Y^+ approaches, right up until the σ-complex intermediate has been formed.

However, we have to consider also the drift of positive charge into the sigma skeleton of the original molecule, more particularly on to the substituents. Confining ourselves only to the sigma part, if any substituents are more electronegative than hydrogen, then their atomic orbitals will accomodate this positive charge less easily than a hydrogen 1s orbital, and the situation will be less favourable than that in benzene. Presumably the greater the tendency is for concentrating (partial) positive charge in a more electronegative orbital, the higher will be the energy, and therefore we expect the attack to be most favoured when the least positive charge is transmitted on to these electronegative substituents. From calculations of coupling constants in magnetic resonance spectra (4) the following orders of magnitude are found for the parameters γ_{π} and γ :

$$\gamma_{\pi} \approx 1/4 > \gamma$$

From the coefficients given in the diagram we therefore obtain the following order for the charges in the σ atomic orbitals :

$$c_{1'}^{2} \gg c_{meta}^{2} > c_{ortho}^{2} > c_{para}^{2}$$

We expect then, that the most favourable position for electrophilic attack will be para to a strongly electronegative substituent.

Now we must reintroduce the π-type atomic orbitals for the non-bonding orbital is a linear combination :

$$\Psi_{NBO} = \sum c_i \psi_{\sigma i} + \sum c_r \psi_{\pi r} + c_y \psi_y$$

Where $\psi_{\sigma i}$, $\psi_{\pi i}$ are the i^{th} σ-type, π-type atomic orbitals, respectively, of the original aromatic molecule. These are effectively linked by the electrophile Y^+.

Combining the activating influence in the π-system with the deactivating effect in the σ-electron system we arrive at the following order of expected reactivity in electrophilic substitution (or addition) reactions :

zeroth (C1) $<$ meta $\ll$ ortho $<$ para

This is the order which is generally observed (6) in 'activated' benzene derivatives and does not appear to have been explained very well before.

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4. W.T.Dixon, *J.Chem.Soc.*, in the press
5. see J.N.Murrell, S.F.A.Kettle and J.M.Tedder, *Valence Theory*, Ch.17, Wiley (1965)
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TRANSFERENCE OF CHARGE IN ORGANIC REACTIONS—I

MODELS FOR SIMPLE ABSTRACTION REACTIONS

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Abstract—A simple MO model is proposed for calculating the charge or spin delocalization at the beginning of an abstraction reaction in which a single MO of some attacking agent, B^- say, interacts with one of the atomic orbitals, say ψ_{H*}, of the molecule RH*. According to the model there should be a direct proportionality between the distribution of 'extra' charge or spin induced in RH* at the start of the reaction, and the hyperfine coupling of proton H* with other magnetic nuclei in RH*.

By assuming that increased delocalization in R— or in RH*—B^-, as measured by the coefficients of their non-bonding orbitals, will decrease the R—H* bond strength and also will increase the ease of forming the B—H* bond, some empirical correlations between NMR coupling constants and reactivities can be explained.

THE rate of a chemical reaction is determined by two main factors; one is the probability that the reactants will collide in a favourable way and the other, the activation energy of the slowest step. We shall only be concerned with the second of these factors.

To determine the height of the energy barrier which has to be overcome in a reaction, we could ideally apply the methods of quantum mechanics to a large number of static configurations of the nuclei involved, calculate the energy of each configuration, plot potential energy surfaces and finally measure the height of the lowest pass connecting the valley associated with the reactants with that associated with the products. In practice, of course, this ideal situation is not realised and we have to be content with semi-empirical theories of questionable validity.[1,2] Though often crude, such theories have greatly added to our insight into chemical behaviour, and can be classified into three types: First, the sites open to attack are considered in terms of the electron distribution in the isolated molecule,[3] Fukui's frontier orbital theory[4] is an example of this; secondly, the energy of an intermediate or transition state is either calculated or estimated,[5] the "localization energy" model[6] is an example; and thirdly, the changes in MO energies occurring as the reaction proceeds are examined in terms of perturbation theory[7,8]

Into the third category comes also the application of symmetry principles to show how the course of a reaction may be determined.[9] The advantage of this approach is that, apart from finding the order of the energy levels, one does not have to actually calculate energies, so that the method leads to predictions which are relatively insensitive to the choice of parameters. This is an important point when we are using simple MO theory, for calculated energies are very sensitive to the values chosen for the various integrals.

In this paper we, too, shall avoid explicit calculation of energies and shall examine instead how the electrons get delocalized as the reactants come together. The main question to which we shall try to find a reliable answer will be: What has to happen in a reaction involving the initial abstraction of an H atom?

Charge delocalization in a model E2 reaction. We start our investigation with a convenient example—a base-catalysed E2 reaction of a substituted ethylene. Suppose a single MO of base B^- interacts with the hydrogen ls orbital of olefine CHZ:CXY (Fig. 1).

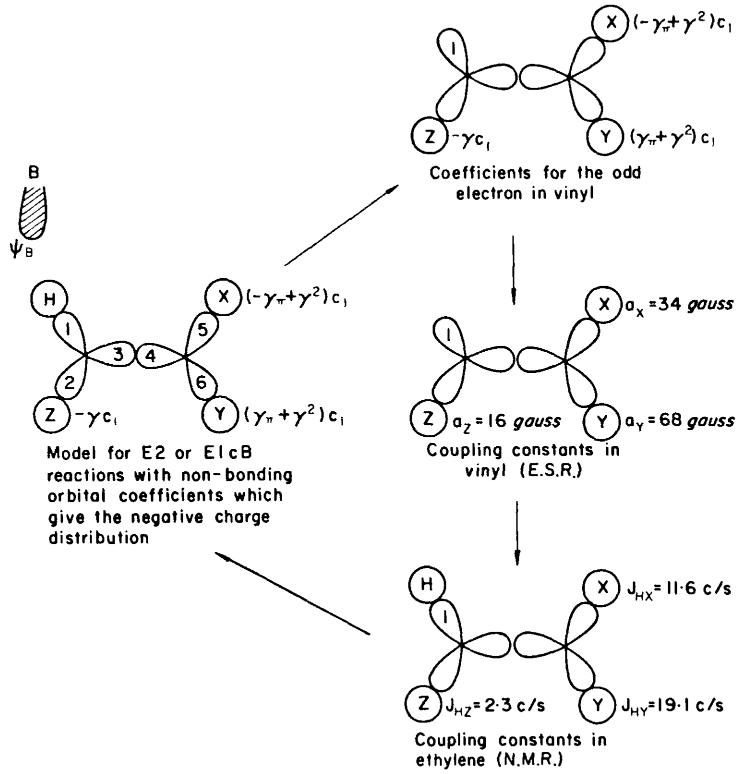


FIG. 1 Model for elimination reactions and the connection with NMR coupling constants. Parameters as in text, except that for simplicity we equate β_{34}, β_{1H}, etc., with our unit of energy.

If we equate all coulomb integrals, i.e. $\alpha_B = \alpha_H = \alpha_1 =$ etc, then the distribution of negative charge is given by the squares of the coefficients of the non-bonding orbital $E = \alpha_B$. A convenient parameterization[10–12] which has been found adequate for calculating proton spin-spin coupling constants is: for the resonance integrals, $\beta_{15} = -\beta_{16} = \gamma_\pi$, $\beta_{12} = \gamma$; usually we shall equate the resonance integrals of types, β_{1H}, β_{34} and shall let them be our unit of energy. Other "non-bonded" interactions are neglected apart from β_{BH}. For simplicity we shall neglect overlap since this makes no difference to relative charge densities in the atomic orbitals. Since the carbon orbitals in this case are sp^2 hybrids γ is one third of the difference in coulomb energy of carbon 2s and 2p atomic orbitals.[10]

It is easy to calculate the coefficients of the non-bonding orbital because the diagonal terms of the secular equations are zero; for example, from appropriate rows we find immediately that coefficients c_H, c_2, c_3, c_5, and c_6 are all zero.

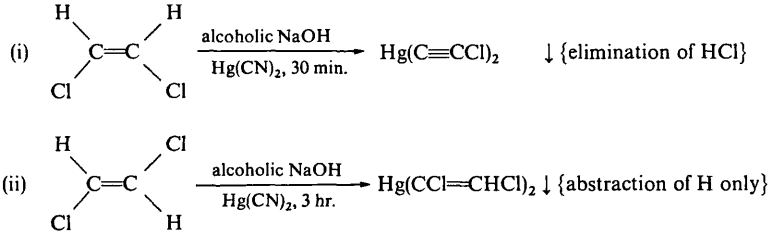
The other coefficients are as follows:

$$c_1 = -(\beta_{BH}/\beta_{1H})c_B; \quad c_2 = -(\gamma/\beta_{2Z})c_1; \quad c_4 = -(\gamma/\beta_{34})c_1;$$
$$c_X = (-\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{5X}; \quad c_Y = (+\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{6Y}. \qquad (1)$$

The most important point to observe here is that since all of the resonance integrals have the same sign, i.e. all our parameters are negative, more negative charge drifts on to a substituent when it is *trans* than when it is *cis* with respect to the attacked hydrogen. Another point of interest is that delocalization is favoured by weak bonds, i.e. small β's, in particular, the amount of negative charge which accumulates on say, substituent X, varies with the resonance integral β_{5X}.

Connection with reaction rates. In order to translate our discussion about charge densities into energetic terms we have to make some further assumptions. We shall assume that the more easily the negative charge on B^- is transferred to the molecule, the faster will be the abstraction, and also that the situation is most favourable when this charge is concentrated in the most electronegative orbitals, i.e. in the attacked molecule. For example, in the case of vinyl chloride, *trans* elimination of HCl is preferred because more negative charge is transmitted to the chlorine when it is *trans* than when it is *cis* with respect to the eliminated H atom.

Another point to consider is that for there to be synchronous loss of HCl, there needs to be sufficient accumulation of negative charge on the halogen atom in the perturbed molecule. The presence of other electronegative groups in the molecule will increase the total ability of a vinyl residue for holding negative charge, but also will decrease the concentration of charge in any particular orbital. This would appear to be the explanation of the ways in which *cis*- and *trans*-dichloroacetylenes behave when reacting with base in the presence of mercuric ions;[13]



Apparently the α-Cl atom reduces the excess negative charge on the vicinal chlorine in reaction (ii) so much that elimination of HCl is no longer an effectively synchronous process.

Connection with nuclear magnetic resonance. In view of the apparent connection with certain abstraction reactions, it would be very useful if we had some way of measuring the efficiency of negative charge transfer when a hydrogen atom is attacked by base. Fortunately such a measure is available from NMR spectra and this comes about in the following way:

Consider the fragment left when an H atom is removed from ethylene and the other nuclei are fixed in their original positions. The spin densities in the atomic orbitals of this vinyl radical are given by the squares of appropriate coefficients, which are: $c_2 = c_3 = c_5 = c_6 = 0$;

$$c_Z = -(\gamma/\beta_{2Z})c_1; \quad c_4 = -(\gamma/\beta_{34})c_1;$$

$$c_X = (-\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{5X}; \quad c_Y = (+\gamma_\pi + \gamma^2/\beta_{34})c_1/\beta_{6Y}$$

The relative spin densities in this radical fragment are exactly the same as the negative charge densities induced when the base B^- approached in our model reaction. Since the spin density in a hydrogen atomic orbital is proportional to the coupling constant between its nucleus and the odd electron, we arrive at the following results: First, the relative magnitudes of coupling constants in σ-radical will tell us the way in which negative charge from a base is distributed over the complete molecule; and secondly, the absolute value of the coupling constants give a measure of the total delocalization of the negative charge, i.e. away from the incoming base.

By itself, this connection with ESR spectra is not very useful because very few σ-radicals have been observed. We can, however, use data from NMR spectra instead, since the proton spin-spin coupling constant J_{12} between protons H_1, H_2 in molecule RH_1, is proportional to the splitting a_2 of the electron spin resonance spectrum of the σ-radical R— by proton H_2[10,14,15]; i.e. if $R \equiv CX{:}CH_2H_3$, splittings in ESR spectrum are a_2, a_3; coupling constants in NMR spectrum of RH_1 are J_{12}, J_{13}, then $a_2/J_{12} = a_3/J_{13}$. (Fig. 1).

Using this relationship, then, we can use relatively accessible data from NMR spectra for estimating degrees of delocalizability.

Example (a): in ethylene, $J_{cis} = 11{\cdot}6$ c/s, $J_{trans} = 19{\cdot}1$ c/s; we therefore expect base attack on a hydrogen *trans* with respect halogen to be the most effective, i.e. by the same argument as that above.

Example (b): In vinyl chlorine, $J_{cis} = 7{\cdot}3$ c/s, $J_{trans} = 14{\cdot}6$ c/s[16]. If attack is on the proton *trans* with respect to the chlorine degree of delocalization relative to ethylene is $11{\cdot}6/7{\cdot}3 = 1{\cdot}59$. If attack is *cis*, degree of delocalization $= 19{\cdot}1/14{\cdot}6 = 1{\cdot}31$. We conclude that elimination should be *trans*, as in example (a) but now there are two reasons; one that more negative charge goes onto the Cl atom when it is *trans*, and two, that the total degree of delocalization is then greater.

The above relationship between ESR and NMR is only expected to apply when the nuclei in question are joined by an odd number of bonds; in other cases there is often

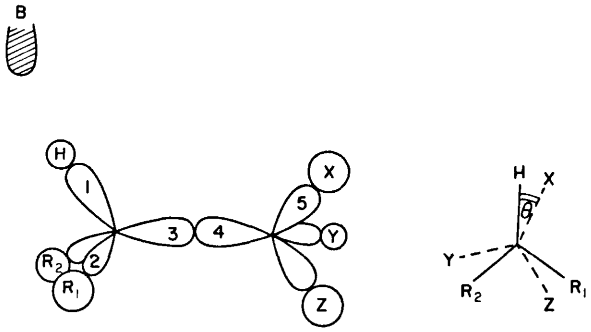


FIG. 2 Model for base-catalysed 1:2 eliminations in saturated systems.

a large negative contribution to consider also.[10] Also for nuclei other than hydrogen the situation becomes rather complicated and usually we would not expect any obvious simple connections between coupling constants and reactivities except perhaps when the H atom is bonded directly to a magnetic nucleus.

Extension to alkane/cycloalkane systems. In simple olefine systems the situation is simplified by the nuclear planarity; in saturated compounds, on the other hand, we have to consider a 3-dimensional problem. Let the dihedral angle of the bonds connecting the eliminated groups to the molecule be θ (Fig. 2).
The coefficient of orbital X in the non-bonding orbital is:

$$c_X = (-\gamma_\pi \cos\theta + \gamma'^2/\beta_{34})c_1/\beta_{5X}$$

where γ_π is approximately the same as before[10] and $\gamma' = \frac{3}{4}\gamma$, assuming that the C atoms are tetrahedrally hybridized. Two orientations give maximum transference of charge on to X;

$$\text{(i)}\ \theta = 0, \quad C_X/c_1 = (-\gamma_\pi + \gamma'^2/\beta_{34})/\beta_{5X}$$

$$\text{(ii)}\ \theta = 180, \ c_X/c_1 = (+\gamma_\pi + \gamma'^2/\beta_{34})\beta_{5X}$$

Using the principles put forward in the previous section we can see from Fig. 3 why it is that elimination is unlikely when atoms are *gauche* with respect to each other.

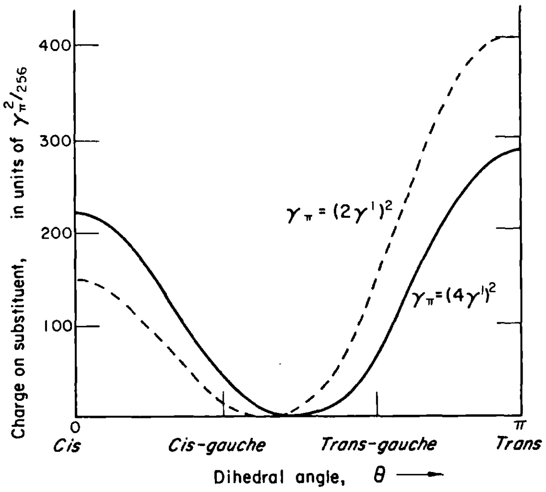


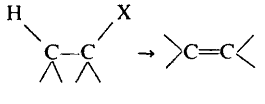
FIG. 3 Variation of induced charge on a vicinal substituent with dihedral angle. (Most probable relationship between γ_π and γ' is $\gamma_\pi \approx (4\gamma')^2$).

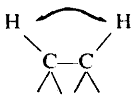
When there is relatively free rotation about the C—C bond it will be most improbable that the atoms will ever be in eclipsing positions for a significant length of time, hence we expect facile removal of a proton only when there is a strongly electronegative group *trans* with respect to it. This is due to the low degree of charge transfer on to *gauche* substituents. When substituents are held in eclipsing positions as in cyclopentyl derivatives, aromatic halides, etc, *cis* elimination will occur, i.e. according to our approach.

Once again we expect a direct connection with NMR coupling constants and this is shown in Table 1.

TABLE 1. STEREOCHEMISTRY OF SOME ELIMINATION REACTIONS AND THE CONNECTION WITH NMR DATA

Reaction is:



	Coupling constants			
Product	J_{trans}	J_{cis}	J_{gauche}	Elimination[11]
Cyclohexene	~ 12 c/s	—	~4 c/s	*trans*
Cyclopentene	—	~9 c/s	~5 c/s	*cis*
Benzyne	—	9 c/s	—	*cis*
Acetylene	19·1 c/s	11·6 c/s	—	*trans*

Effects of substituents. Until now we have been concerned with determining which proton in a given molecule is that most likely to be removed by base. Now we shall briefly discuss the effects of replacing H atoms by Me groups in various types of molecules and their reactions.

Using either of our previous models (Figs 1 and 2) the total charge delocalization as the base approaches will increase by an amount $\frac{3}{2}\gamma_\pi^2 c_1^2$ when we replace an α-H by Me, due to the "extra" transference of charge on to the Me protons. We also expect that the average coupling constant between an α-proton and one of these Me protons, will be proportional to c_1^2, so that this coupling constant will give us a measure of total delocalization.

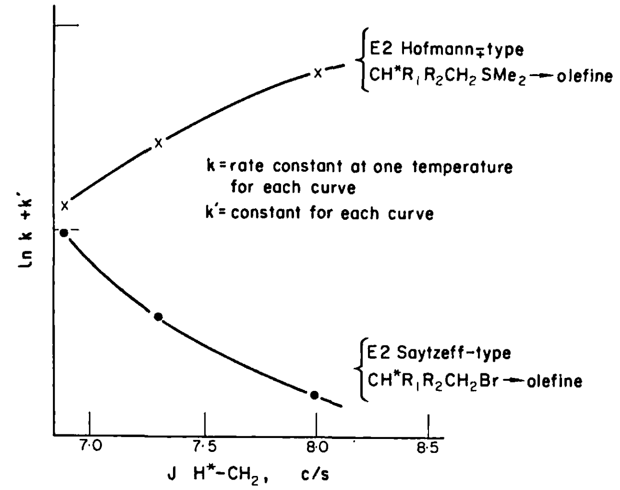
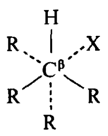


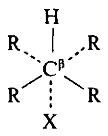
FIG. 4 Effect of β-substituents on rates of base-catalysed E2 reactions and the connection with NMR.

The curves shown in Fig. 4 show that Me substituents generally increase rates of elimination and the correlation with the NMR data indicates that this arises from increased delocalization of negative charge, i.e. the Me groups are acting as electron acceptors! This direct connection between reaction rates and proton–proton hyperfine interactions is also found in gas phase El reactions[1] and in various radical abstraction reactions.[11] A similar[20] correlation has been observed between C^{13}—H coupling constants and rates of hydrogen abstraction from molecules of type $M(CH_3)_4$.

Effects of steric repulsions. We have deliberately limited ourselves to considering a single orbital of the attacking species in order to keep the theory simple. Interactions of other orbitals of the two reactants come broadly under the heading of "steric effects". In most of the cases cited above it appears that the way in which the charge of the incoming group is transferred to the attacked molecule often determines, or at least, is directly connected to, the course of the reaction. In some cases, however, e.g. in Hofmann-type eliminations, the rates are governed by something else. In this connection we have to consider two factors; the size of the attacking group and the size of the leaving group. In the former case it is obvious that if the incoming base or radical is large enough, attack will be preferred on the least hindered H atom; and in the latter case, the ease of attaining a favourable conformation for transference of charge may be determined by the size of the leaving group. Consider as an example Hofmann-type eliminations ($X = NR_3$, SR_2, etc.). In these cases the group X is large and the reaction rates depend on how easy it is to achieve the favourable conformation of type (a),[2] which has a smaller probability when there are substituents on the site of attack. Apparently in these instances the steric repulsions of methyl groups outweigh their ability to delocalize charge.



(a)



(b)

Abstraction of negative groups. We shall now examine the three main ways whereby substituents can affect the rate of loss of X^- from RX, that is apart from steric repulsions. First we could set up a model in exactly the same way as we did in Fig. 1, replacing the base B^- by an acid A^+, which normally would be a solvent molecule. As this acid approaches X its positive charge becomes delocalized around the fragment R— and as before, a measure of the degree of delocalization is given by the coupling of protons in R— with H* in RH*. Substituents which increase the degree of delocalization, e.g. α-Me groups, according to the NMR data, do, in fact, also increase the rates of reactions involving loss of X^-.

The second and third ways are related to the first and depend on the strength of the C—X bond, which is weaker when there is more delocalization around the fragment R—.[21] Since the carbonium ion $R^+_{(\pi)}$ is stabilized by delocalization of the positive charge, a group such as Me should favour dissociation in the equilibrium

$$RX \rightleftharpoons R^+_{(\pi)} + X^-$$

i.e. as in El and S_N1 reactions.

The third way, by means of which loss of X^- could be affected by substituents, is that if the C—X bond is weakened in some way, its length could increase and the associated resonance integral decrease. From formula (1) this could increase the transference of any positive charge from the acid to the group R—.

All of these effects act in the same direction and so, if any/all of them is important, we would expect a correlation between the degree of delocalization in the fragment R—, as measured by the coupling constants in the NMR spectrum of RH*, and the rates of reactions involving breakage of the C—X bond. Such a correlation certainly exists, as we can see from Fig. 5, indicating that the stretching of the C—X bond is important even when the reaction depends on the attack on a proton by a suitable base. Steric factors appear to have little effect on the reactions considered, when we change only the α-substituents in going from one reactant to another.[18]

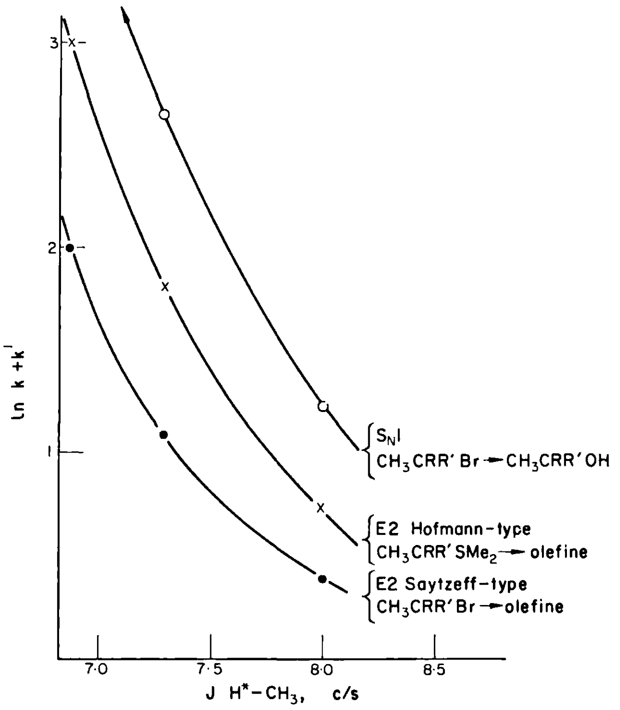


FIG. 5 Effect of α-substituents on reactivities of $CH_3CRR'X$ and the connection with the NMR spectrum of $CH_3CRR'H^*$[3].

RESULTS AND DISCUSSION

We have tried to make three main points in this paper. The first is that the transference of charge/spin, initially associated with a single orbital ψ_B of the attacking species B, to a molecule RH, occurs largely via a non-bonding orbital. The coefficients of this non-bonding orbital tell us how this "extra" charge/spin is distributed around R, and are found by substituting $E = \alpha_B$ directly into the secular equations.

The second point is that the activation energy of the abstraction reaction is determined by the ease of forming the new bond B—H and of breaking the old one R—H, say, and that both of these processes are favoured by a large tendency for charge/spin delocalization around the fragment R— in these reactions.

The third point is that this tendency, as well as the extra charge/spin distribution in the initial stages of these reactions, can be measured by the values of certain coupling constants in the NMR spectrum of RH.

The whole model and the connection with NMR are only expected to be valid, at least in the simple form described above, when the coulomb integral to be associated with the attacking agent is not too different (i.e. by more than ~ 1½ eV) from that of appropriate carbon hybrid orbitals. In view of all the correlations given, it would appear that this condition is satisfied. We can justify it in the case of base-catalysed E2 reactions because the O atoms are then negatively charged at the start and are therefore less electronegative than when they are in neutral molecules, i.e. we can use a lower coulomb energy.

What we have tried to do, then, is to simplify the approach to some abstraction reactions in order better to correlate reactivities with either a simple theory or some properties of the reactant molecules. As a final example of our approach we shall compare 1:2 and 1:4 eliminations:[22, 18]

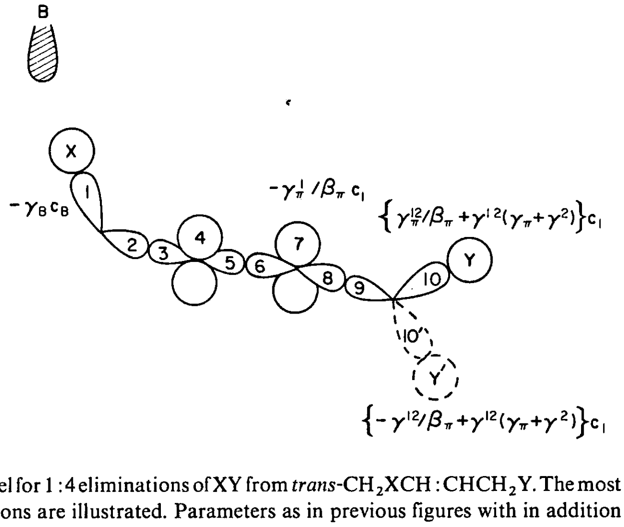


FIG. 6 Model for 1:4 eliminations of XY from *trans*-$CH_2XCH:CHCH_2Y$. The most favourable conformations are illustrated. Parameters as in previous figures with in addition: $\beta_{47} = \beta_{\pi}$, $\beta_{14} = \gamma'_{\pi}$.

The important differences between the situation in 1:4 eliminations as shown in Fig. 6, and that in 1:2 eliminations are:

(i) Even in the most favourable conformation less charge is transmitted to the leaving group Y.

(ii) Delocalized charge from the base collects on a C atom rather than on a leaving group.

(iii) One would not expect any particularly preferred conformation of the original molecule, whereas in $C_2H_4I_2$, for example, the I atoms would tend to be *trans* with respect to each other.

(iv) Because γ,γ' are small, some stereospecificity of the elimination will be lost, in fact *cis* elimination would be expected to be preferred over *trans*. Gauche elimination should not occur, however.

Summing up these factors, we have to balance them against the greater delocalization of charge to estimate whether 1:4 E2 reactions should be more or less fast than corresponding 1:2 reactions. On the whole we would expect points (i) and (ii) to be the most important effects and therefore 1:4 eliminations to be the slower ones.

This example illustrates the approach and we show later how it can be applied to reactions involving initial addition, e.g. as in aromatic substitution.[12]

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Reprinted from American Journal of Physics, Vol. 38, No. 9, 1162, September 1970
Printed in U. S. A.

A Classical Derivation of Spin–Orbit Coupling Energy

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(Received 10 December 1969)

The correct formula for the spin–orbit coupling energy term is usually assumed to be obtainable only from relativistic theories such as those of Dirac,[1] Thomas,[2] and Frenkel.[3] These explanations of the spin–orbit interaction are, in a sense, incomplete, because they apply only to cases when the moving particle has a magnetogyric ratio of q/mc, where q is its charge, m its mass, and c is the velocity of light. We can, in fact, derive a more general formula and also avoid "embarrassing" transformations between noninertial frames of reference by measuring everything from a frame at rest with respect to the nucleus N, which we take to be stationary.

We are interested only in the effects of the magnetic moment $\boldsymbol{\mu}$ of the moving particle, usually an electron, so we shall not consider its charge explicitly. Now the field at the nucleus due to the magnetic moment of the moving particle will be changing, and therefore a "back emf" will act on the nuclear charge q_N according to Faraday's induction law, i.e.,

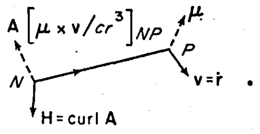
$$\mathbf{F}_N = -(q_N/c)\partial\mathbf{A}/\partial t,$$

where $\mathbf{A}$ is the vector potential generating the magnetic field, and is given by the formula $\mathbf{A} = -\boldsymbol{\mu}\times\mathbf{r}/r^3$, $\mathbf{r}$ being the vector distance $\mathbf{NP}$:

The force acting on the nuclear charge due to the motion of the magnetic dipole is therefore given by the following:

$$\mathbf{F}_N = (q_N/c)[(\dot{\boldsymbol{\mu}}\times\mathbf{r}/r^3) + (\boldsymbol{\mu}\times\mathbf{v}/r^3) - (3v\boldsymbol{\mu}\times\mathbf{r}/r^4)].$$

In order to calculate the potential energy associated with this force, we imagine a similar nucleus in an electrostatic field which is given by an expression identical to that for an instantaneous force field $\mathbf{F}_N/q_N$. In this electrostatic field . , $\boldsymbol{\mu}$, and $\mathbf{v}$ will simply be constants. Presumably the potential energy of the nucleus in this electrostatic field is the same as that when it is experiencing the same force in the moving system.



In the electrostatic system, however, it is comparatively easy to calculate the energy required to bring up the nucleus to its appropriate position from infinity since this is the same for all paths. We choose the easiest path, i.e., along the line of N and P. The work done during this process is the potential energy and is given by

$$-\int_{\infty\,(\text{constant time})}^{\mathbf{r}} \mathbf{F}_N\cdot d\mathbf{r} = -(q_N/c)\int_{\infty}^{\mathbf{r}} \boldsymbol{\mu}\times\mathbf{v}\cdot d\mathbf{r}/r^3$$

($d\mathbf{r}$ is parallel to $\mathbf{r}$)

$$= +(q_N/c)\boldsymbol{\mu}\times\mathbf{v}\cdot\mathbf{r}/2r^3$$

$$= -(1/2c)\boldsymbol{\mu}\cdot\mathbf{E}\times\mathbf{v},$$

where $\mathbf{E}$ is the electrostatic field, due to the nucleus, at P. This is the correct expression for the spin–orbit coupling, and it is worthwhile observing that it does not depend on the magnetogyric ratio; in fact the moving particle does not even have to be charged!

Another interesting point is that if we replace the moving particle by a continuous "classical" current, the field at the nucleus would remain constant, and therefore, there would be no energy of interaction between the "smeared out" moving dipole and the nuclear charge.

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Symmetry Effects in Aromatic Substitution

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Reprinted from

Chemical Communications 1969

The Chemical Society, Burlington House, London W1V 0BN

Symmetry Effects in Aromatic Substitution

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Two main processes are involved in aromatic substitution reactions, the first being addition, say, of an electrophile, leading to the formation of a σ-complex; and the second, loss of a proton.

The first step usually controls the rate of the reaction but the second has to compete with a possible further attack, this time by a nucleophile, leading to overall addition. Now we would expect that the greater the positive charge on the aliphatic proton, H_a, [see Figure, (a)] the more acidic it would be, *i.e.*, the more easily could it leave the σ-complex as a proton. We can estimate the charge density on H_a quite easily using simple molecular orbital, theory, and from there we can try to predict whether substitution will compete favourably with addition.

For example, let us compare a typical $4n$ system, cyclobutadiene, with a typical $4n + 2$ system, benzene, in relation to their expected behaviour after electrophilic attack.

For simplicity, take orbital 1 to be the appropriate antisymmetric combination of two hydrogen atomic orbitals, as in hyperconjugation theory;[1] let all resonance integrals be unity except $\beta_{12} = \gamma$, equate all coulomb integrals, and finally, neglect non-nearest-neighbour interactions.

The charge distributions in these species are both given by the coefficients of the non-bonding orbitals[2,3] and are shown in the Figure.

One important feature immediately emerges; in the $4n$ system the non-bonding orbital is antisymmetric with respect to reflection through the plane of symmetry and has a node through the aliphatic carbon and its substituents. On the other hand, in the benzyl-like adduct, the non-bonding orbital is symmetrical about the plane of symmetry and in this case appreciable positive charge can accumulate on the aliphatic proton.

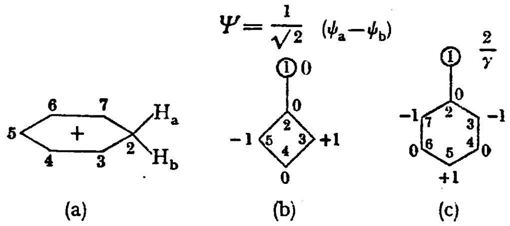

FIGURE. *Adducts of* H^+ *with* C_4H_4, C_6H_6, *and the un-normalised coefficients of the non-bonding orbitals.*

This gives us yet another contrast between the properties of rings containing $4n$ and $4n + 2$ carbon atoms, and the result is quite general within the framework of simple MO theory and does not depend on our particular simplifications.

It is interesting to note that a measure of the tendency towards substitution (and perhaps of aromatic character) is given by the methylene proton coupling constants in the e.s.r. spectra of the radical adducts (*e.g.* in cyclohexadienyl they are 47·72 G[4]). In adducts of $4n$ atom rings such coupling constants (and ease of substitution compared with addition) are expected to be low.

(*Received, March* 19*th*, 1969; *Com.* 393.)

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Competition between Aromatic Substitution and Addition

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Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION B
Physical Organic Chemistry

1970

Competition between Aromatic Substitution and Addition

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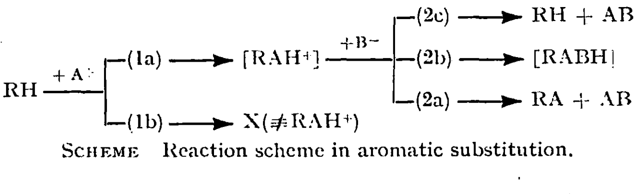
One of the criteria of aromatic character is the ability to undergo substitution reactions with certain reagents. Whether overall substitution or addition occurs depends on the reactions of the so-called σ-complex intermediate. With some simple assumptions about the relationship between charge/spin density and reactivity, it is possible, from simple MO theory, to predict whether substitution should occur to a significant extent and to calculate indices for the ' aromaticity ' or ' aromatic character ' of a molecule.

ONE of the most characteristic properties of benzene, and of aromatic compounds in general, is the ability to undergo substitution reactions with certain electrophilic, radical, or even, on occasion, nucleophilic reagents.[1-3] Along with certain physical properties such as heats of formation, diamagnetism, and proton chemical shifts, this chemical property is one of the criteria which are considered when deciding whether or not to describe a given compound by the term ' aromatic.'

Although a chemist's intuitive test for ' aromaticity ' or ' aromatic character ' would probably be to see whether the compound in question undergoes electrophilic, or perhaps radical substitution, this approach has not been used directly as a measure of ' aromaticity ' until now, largely because the theory of such reactions has not been developed sufficiently. In contrast, the π-electron theories of ' resonance ' and ' delocalisation ' energies have been well developed. For benzene and other monocyclic $(4n + 2)$ systems the idea of ring currents is useful in trying to explain the low field chemical shifts of the ring protons. However, both of these static approaches suffer from the disadvantage of defining aromaticity relative to a compound (ethylene) in which the bond lengths and σ framework are markedly different from those of most aromatic compounds.

In order to avoid the ambiguities associated with these methods, especially the difficulty of interpreting the effects of substituents, fused rings *etc.*, we shall investigate the possibility of defining aromaticity in terms of the tendency of a molecule to undergo substitution, rather than addition, with certain reagents.

Empirical Model.—In order to interpret, and perhaps predict experimental results from a simple theoretical model, we shall consider those situations in which electrophilic attack leads to a σ-complex,[4] *i.e.* a carbonium ion, which reacts with a nucleophile to give either overall substitution or addition (see Scheme).



SCHEME Reaction scheme in aromatic substitution.

The theory applies equally to radical attack and even to nucleophilic substitutions, but we shall talk, for convenience, only in terms of the rather better known, electrophilic substitution reactions.[5,6]

We are concerned primarily with kinetic rather than thermodynamic stabilities, for we wish to define aromaticity in terms of the relative rates of reactions (2a) and the other possibilities (2b), (2c). This is what differentiates benzene from the linear polyenes for example. The feasibility of step (1a) differentiates saturated from unsaturated hydrocarbons. From the rate constants of step (1a) and (2a) compared with those of the other paths we could define a numerical measure of the tendency towards substitution, *i.e.* the aromaticity of a compound. However the experimental difficulties are liable to be great, the first being to establish the existence of the σ-complex at all. In view of the labour involved, such an empirical definition would not be very useful, though it would be meaningful. For a term or concept to be of much practical value, we need to be able to use it to predict properties from some experiment or calculation which is relatively easy to carry out, *e.g.* the observation of a chemical shift in a n.m.r. spectrum or calculations of π-electron energies.

It turns out that it is not difficult to approach the

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[1] G. M. Badger, ' Aromaticity and Aromatic Character,' 1969, Cambridge University Press.

[2] M. E. Vol'pin, *Uspekhi Khim.*, 1960, **29**, 129.

[3] *Chem. Soc. Special Publ.*, 1967, No. 21.

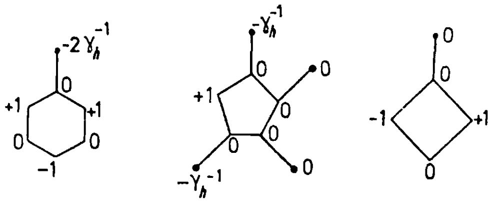
[4] G. W. Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.

[5] R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' 1965, Elsevier, London.

[6] A. Streitwieser, ' Molecular Orbital Theory for Organic Chemists,' 1961, John Wiley, New York.

subject of substitution *versus* addition by way of simple MO theory.

Molecular Orbital Model.—We shall bypass the first step (1a) for the moment, and simply consider the path from the carbonium ion to the substituted species, and the competing reactions. It is convenient to begin by looking at the distribution of charge in three types of σ-complex (see Figure 1).



$c_h^2 = 4/(3\gamma_h^2 + 4)$ Addition to $(4n + 2)$ system

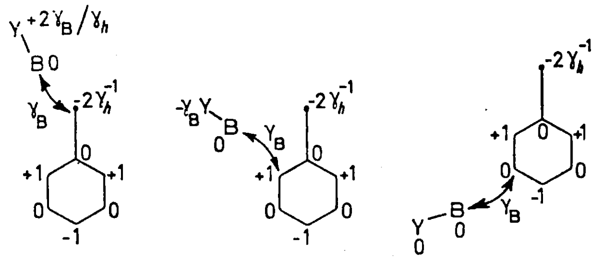
$c_h^2 = 1/(\gamma_h^2 + 2)$ Addition to alkene

$c_h^2 = 0$ Addition to $4n$ system

FIGURE 1 Electron systems of some σ-complexes, with un-normalised coefficients of the nonbonding orbitals

In order to keep the algebra as simple as possible we take the orbital h to be the composite orbital of π-symmetry, familiar from hyperconjugation theory,[7] *i.e.* $\psi_h = \frac{1}{\sqrt{2}}[\psi(H_1) - \psi(H_2)]$, we take all coulomb integrals to be the same,† and for the resonance integrals $\beta_\pi(C - C) = 1$ for adjacent carbon atoms, $\beta_\pi(C - H) = \gamma_h$. An approximately planar alkene is chosen so as not to complicate the comparisons with the cyclic alternant systems. The distribution of charge is given in each case by the coefficients of a nonbonding orbital.[8,9]

Now we would expect that the greater the positive charge in the orbital h, the easier it should be to remove hydrogen as a proton. Similarly the higher the charge density in one of the carbon p_π orbitals, the greater the chance of nucleophilic addition occurring.



$\frac{4\gamma_B^2}{3\gamma_h^2 + 4}$ $\frac{\gamma_B^2\gamma_h^2}{3\gamma_h^2 + 4}$ Zero

FIGURE 2 Charge on Y as B–Y approaches various sites on the σ-complex

We can justify these statements by means of a simple model reaction scheme for steps (2) in the Scheme. Treating B–Y as a two orbital system, the rate at which charge accumulates on Y, as B–Y approaches the ion, is proportional to the charge density at the point of attack (see Figure 2).

This follows from the properties of non-bonding orbitals.

Thus, from Figure 1 we can see that substitution is more favoured with benzene than with cyclopentene and that substitution is not helped at all by a drift of the positive charge onto the aliphatic protons in the cation from cyclobutadiene. These arise from the different symmetries of the nonbonding orbitals,[10] *i.e.* with $(4n + 2)$ conjugated rings, the NBO is symmetric about a plane through the aliphatic carbon, whereas in $4n$ rings, the NBO is antisymmetric, giving zero charge on the aliphatic substituents.

Definitions of Aromaticity.—We are now in a position to investigate the possibilities of finding numbers which correspond to the tendency towards substitution compared with that for addition. When substitution is more favoured, then the molecule is defined to be more aromatic. A measure of the relative rate of proton loss, leading to overall substitution, is given by the charge density in group orbital h. The rate of the competing process, leading to overall addition, is determined similarly by the maximum charge density in a carbon p_π atomic orbital.

One measure of the favourability of substitution compared with addition is given by the ratio of these charge densities, say R, *i.e.* $R = \frac{\text{charge density on protons}}{\text{max charge density in ring}} = C_h^2/C_r^2$ (max). Thus we have for a $(4n + 2)$ system (in units of γ_h^{-2}): $R(4n + 2) = 4$, $R(4n) = 0$, $R(\text{alkene}) = 1$. This number R does seem to express the aromatic character of the molecules considered rather well. Thus, if benzene is aromatic and ethylene nonaromatic, cyclobutadiene would naturally be classified as antiaromatic.

We can check some of these numbers by means of e.s.r. measurements on cycloalkyl and cyclohexadienyl radicals.[11] If the spin density (negative) on an α-proton is proportional to that in the p_π orbital of the α-carbon, then apart from a constant factor

$$R(C_6H_6) = \frac{47\cdot72}{13\cdot04} = 3\cdot7\ (\textit{para}),$$

$$R(C_6H_6) = \frac{47\cdot72}{8\cdot9} = 5\cdot4\ (\textit{ortho}), R\left(\frac{\text{cyclo-}}{C_5H_9}\right) = \frac{35\cdot2}{21\cdot5} = 1\cdot7.$$

In view of the simplifying assumptions of the Hückel treatment and of the simplified geometry, the agreement between theory and experiment is as good as can reasonably be expected.

There are some unsatisfactory features about R as a measure of aromaticity and one is that the rates of the reactions we are considering should vary exponentially with the charge densities, rather as in the simplified localisation energy theory of reactivities. Also proton

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† It is this assumption which enables us to deal with more general systems and which essentially defines the MO model.

[7] R. S. Mulliken, *Tetrahedron*, 1959, **6**, 68.

[8] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, 1940, **36**, 193.

[9] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

[10] W. T. Dixon, *Chem. Comm.*, 1969, 559.

[11] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2141.

loss occurs most readily when there is less extensive delocalisation of charge (see Figure 2).

If we wish to base our idea of aromaticity on reaction rates, we have to take these points into account, so we define another number $\mathscr{A} = \frac{\lambda C^2{}_h - C_m{}^2(\max)}{\sum C_r{}^2}$, Where λ is some parameter to be chosen, which takes into account that further addition and proton loss are different types of reaction, C_r are the coefficients of the carbon p_π orbitals and C_m the largest of these.

It is convenient to take $\lambda = 1$, since this leads to ' unit aromaticity ' for benzene. Values of R and $\mathscr{A}$, calculated for a selection of alternant hydrocarbons, are given in the Table. Both R and $\mathscr{A}$ correlate consistently with the usual ideas about aromatic character. However, as with chemical shifts, each position in a molecule has its own values of these quantities.

$\mathscr{A}$ is particularly attractive as an index, since it is negative for cyclic $4n$ systems (antiaromatic), zero for alkenes (nonaromatic), and positive for what are generally regarded as aromatic molecules.

Another desirable feature about $\mathscr{A}$ is that the factor in the denominator is the same as that which occurs to the power 1/2 in Dewar's localisation theory of reactivities.[12] Thus when $\mathscr{A}$ is small, the localisation energy tends to be small also, and hence the position in question tends to be relatively reactive.

TABLE

Some representative values of R and $\mathscr{A}$ together with corresponding values of localisation energies, E_L in units of ' β '

	Cyclo($C_{4n}H_{4n}$)	Linear polyenes $C_{2n}H_{2n+2}$	Cyclo($C_{4n+2}H_{4n+2}$)	Styrene Double bond	*o*-/*p*-	*m*-
R	0	1	4	1	4	4
$\mathscr{A}$	$-1/2n$	0	$+3/(2n+1)$	0	3/4	1
E_L	0	$1/\sqrt{n}$	$2/\sqrt{n+1}$	$2/\sqrt{7}$	1	$2/\sqrt{3}$

	Naphthalene		Phenanthrene		Anthracene			Pyrene	
Positions	1	2	9	4	9	1	2	3	4
	9/4	9/4	25/16	25/9	1	16/9	16/9	4	4
	5/11	5/8	9/31	14/29	0	7/26	7/18	3/7	1
E_L	$3/\sqrt{11}$	$3/2\sqrt{2}$	$5/\sqrt{31}$	$5/\sqrt{29}$	$2/\sqrt{10}$	$4/\sqrt{26}$	$4/\sqrt{18}$	$2/\sqrt{7}$	$2/\sqrt{3}$

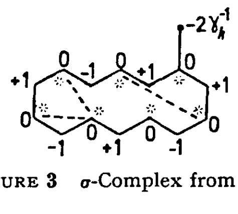
A large value (*i.e.* positive) of $\mathscr{A}$ for a hydrocarbon is associated with chemical inertness as well as with a large driving force to reform the original ' aromatic ' skeleton after addition of an electrophile (or radical *etc.*).

Applications to Polycyclic Systems.—In this section we shall prove some general theorems, about fused ring systems, which can be used to estimate the magnitude and sign of the two factors R and $\mathscr{A}$ together with the corresponding localisation energy. These numbers should enable us to predict reactivities and whether substitution or addition should occur. In the first place we shall call a molecule aromatic if $R > 1$, $\mathscr{A} > 0$ and antiaromatic if $R < 1$, $\mathscr{A} < 0$ for the most reactive position in that molecule. As we have seen for the systems treated in the previous section (see Table), this makes benzene the most aromatic molecule. Alkenes are said to be nonaromatic corresponding to $R = 1$, $\mathscr{A} = 0$.

We consider only those systems formed from simple alternant rings by the introduction of bonds between the various carbon atoms.

Bicyclic Systems.—Theorem 1. Any bicyclic system, formed by joining atoms separated by an even number of bonds in a conjugated ring of $(4n + 2)$ atoms, should be at least as reactive and at most as aromatic as the parent compound.

Proof:

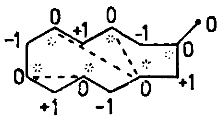


$R = 4$
$\mathscr{A} = 3/(2n + 1)$
$E_L = 2/\sqrt{2n+1}$

FIGURE 3 σ-Complex from a typical $(4n + 2)$ system

When one of the starred atoms is attacked (see diagram, Figure 3), the NBO coefficients are unchanged if any of the other starred atoms are joined, hence the localisation energy and aromaticity parameters, R and $\mathscr{A}$ are unchanged also. Hence the molecule will be at least as reactive as before and if some positions are more reactive, then R and $\mathscr{A}$ will be correspondingly less positive (example azulene).

Theorem 2. Any bicyclic system formed from a $4n$ atom ring by joining atoms separated by an even number of bonds will be antiaromatic ($\mathscr{A}$ negative) and highly reactive. The proof is the same as above (see Figure 4) (example: pentalene).



$R = 0$
$\mathscr{A} = -\frac{1}{2}n$
$E_L = 0$

FIGURE 4 σ-Complex from a typical $4n$ system

Once again attack on other positions is only significant if they are faster than this.

Corollary to Theorems 1 *and* 2. These theorems can be generalised to any network formed by joining one of the sets of alternate atoms, providing that the

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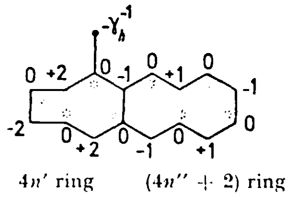
[12] M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

original bond distances are not drastically changed and that the system remains planar. These fused ring systems are all nonalternants, a consequence of joining two atoms of the same class (*e.g.* starred), and are, therefore, not so easy to discuss very fully, in a theoretical way, as the alternants which we consider next.

Alternant Bicyclic Systems.—In order to arrive at alternant polycyclic hydrocarbons from simple rings, we have to join starred to unstarred atoms only. The σ-complexes formed from alternants all have nonbonding orbitals and thus attack at all sites can be discussed with relative ease.

Theorem 3. Bicyclic systems containing $4n$ atoms are antiaromatic



$R = \frac{1}{4}$
$\mathscr{A} = -3/(8n' + 2n'' - 3)$
$E_L = 1/\sqrt{8n' + 2n'' - 3}$
$(n', n'' > 0)$

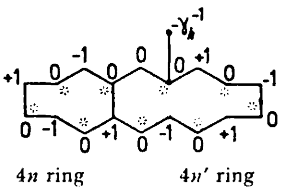
FIGURE 5 σ-Complex from an alternant, bicyclic system of $4N$ atoms

We have already shown that this is true for the class of molecules covered by theorem 2. In the case of alternants there will be one ring of $4n'$ and one of $4n'' + 2$ (see Figure 5) sharing a bond. Attack at the most reactive site (adjacent to $4n'' + 2$ ring) leads to the situation shown in Figure 5, *i.e.* according to our definition the compound is antiaromatic, hence the theorem is proved for all cases. However, the alternant systems will not have a localisation energy of zero and hence should be less reactive then the parent compounds (and less antiaromatic).

Theorem 4. Alternant bicyclic systems containing $(4n + 2)$ atoms are more reactive and less aromatic than the corresponding simple rings.

There are two sorts of system to consider.

(*a*) $(4n - 4n')$ Rings sharing a bond. From Figure 6



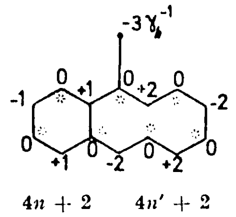
$R = 1$
$\mathscr{A} = 0$
$E_L = 1/\sqrt{2N}$

FIGURE 6 σ-Complex from an alternant, bicyclic $4N + 2$ system, consisting of two $4n$-type rings

we can see that whichever position is attacked the molecule behaves like a 'linear' polyene, *i.e.* is nonaromatic and more reactive than the original ring.

(*b*) $(4n + 2)$, $(4n' + 2)$ Rings sharing a bond. The most reactive site is that adjacent to the smaller ring (see Figure 7), evidently the molecule is still aromatic and more reactive than the simple ring.

We can extend theorem 1 to include these two cases. It would appear that mono- or bi-cyclic $(4n + 2)$ systems



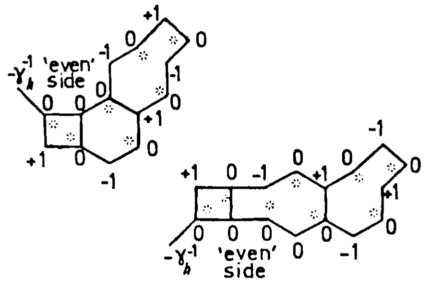
$R = 9/4$
$\mathscr{A} = 5/(8n' + 2n + 1)$
$E_L = 3/\sqrt{8n' + 2n + 1}$
$(n' > n)$

FIGURE 7 σ-Complex from an alternant, bicyclic $4N + 2$ system, each ring being of the $4n + 2$ type

are never antiaromatic, though we have not actually proved this generally for nonalternants.

Tricyclic Alternants.—It is convenient to classify tricyclic systems in which a bond is shared by at most two rings, according to the number of atoms in the component rings and their relative configurations.

Theorem 5. When two $4n$ rings are separated by an *odd* number of bonds, the system is *nonaromatic* and should behave as a linear polyene. When attack is on the central ring, *i.e.* that sharing a side with the other two, the coefficients on the 'even side' are zero, due to alternation of signs around the $4n$ ring on that side (see Figure 8).



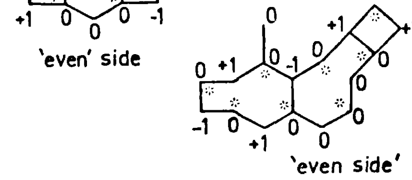
$R = 1$
$\mathscr{A} = 0$
$E_L = 1/\sqrt{N - n^*}$

Total number of carbon atoms = $2N$
Minimum number of bonds between the outer $4n$ rings = $2n^* - 1$

FIGURE 8 σ-Complexes from alternant, tricyclic systems of the type $4n$ — (odd number of bonds) — $4n$

When attack is on an outer ring coefficients on the 'even side' of the site of attack are zero. Hence in all cases $R = 1$ $\mathscr{A} = 0$. The most reactive position is that on a $4n$ ring adjacent to the central ring.

Theorem 6. When two $4n$ rings are separated by an *even* number of bonds the system is *antiaromatic*. Consider attack on one of the outer rings then coefficients of the atomic orbitals of the central ring on the 'even' side (see Figure 9) of point of attack



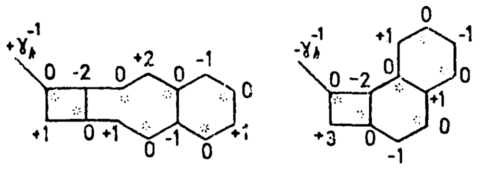
$R = 0$
$\mathscr{A} = -1/(N - n^*)$
$E_L = 0$

Total number of atoms = $2N$
Minimum number of bonds between rings = $2n^*$

FIGURE 9 σ-Complexes from alternant, tricyclic systems of type $4n$ — (even number of bonds) — $4n$

are all zero hence coefficients adjacent to this point have opposite signs.

Theorem 7. When $4n$ and $(4n + 2)$ rings are separated by an *odd* number of bonds, the tricyclic system is antiaromatic.



$R = 1/4$ $\mathcal{A} = -3/\Sigma C_r^2$ $L = 1/\sqrt{\Sigma C_r^2}$

$R = 1/9$ $\mathcal{A} = -8/\Sigma C_r^2$ $L = 1/\sqrt{\Sigma C_r^2}$

FIGURE 10 σ-Complexes of $4n$ — (odd number of bonds) — $(4n + 2)$ types

Theorem 8. When $4n$ and $(4n + 2)$ rings are separated by an *even* number of bonds the system is nonaromatic if the total number of atoms is $4n$ and antiaromatic if it is $(4n + 2)$.

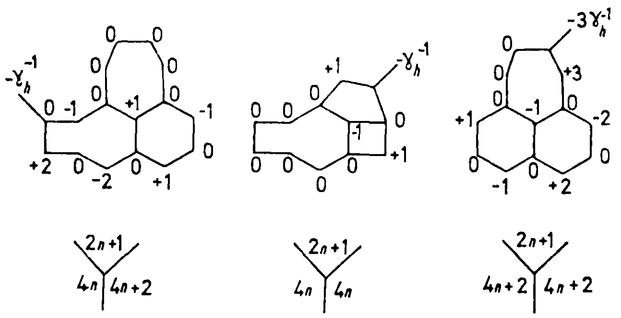
Theorem 9. When two $(4n + 2)$ rings are separated by an even number of bonds, the system is antiaromatic if the total number of atoms is $4n$ and aromatic/nonaromatic if it is $(4n + 2)$ [the nonaromatic case is when the number of linking bonds is $(4n + 2)$, *e.g.* anthracene].

Theorem 10. When two $(4n + 2)$ rings are separated by an odd number of bonds the system is aromatic if the total number of atoms is $4n + 2$ (*e.g.* phenanthrene) and antiaromatic when it is $4n$ except when $n = 1$ (biphenylene). We can formulate similar rules to theorems 1 and 2 for more general nonalternant fused systems by starting from an appropriate 'parent' alternant hydrocarbon. Some convenient rules for tricyclic systems are:

$(4n + 3) - (4n + 3) - (4n + 2)$ $(4n + 1) - (4n + 1) - (4n + 2)$	($4N$ total atoms)	anti-aromatic
$(4n + 3) - (4n + 3) - 4n$ $(4n + 1) - (4n + 1) - 4n$	($4N + 2$ total atoms)	non-aromatic
$(4n + 3) - (4n + 1) - 4n$	($4N$ atoms)	non-aromatic
$(4n + 3) - 4n + 1) - (4n + 2)$	{total $4N + 2$ atoms}	aromatic

The rules for more highly condensed systems increase in complexity with size and it seems, at the moment, that it is more practical to look at the individual cases as they arise rather than to derive general formulae.

It is, however, worthwhile mentioning the class of tricyclic systems in which each of three bonds are shared between two rings (see Figure 11).



$R = 1/4$ $\mathcal{A} < 0$

$R = 1$ $\mathcal{A} = 0$

$R = 1$ $\mathcal{A} = 0$

FIGURE 11 σ-Complexes from some nonalternant, tricyclic systems

We consider here only the cases when there are two even-membered rings sharing one side which is adjacent to the sides they share with the odd-membered ring.

If the two even rings are of the same class [*i.e.* both $4n$ or both $(4n + 2)$ types] the molecule is nonaromatic (*e.g.* acenaphthylene).

If the two even rings are not of the same class [*i.e.* one has $4n$, the other $(4n' + 2)$ atoms] the molecule is antiaromatic.

CONCLUSIONS

We have effectively introduced a theoretical treatment of the competition between substitution and addition reactions of unsaturated organic compounds. We have shown how to apply it to various classes of molecules and are able, at least to say, whether their reactions are expected to be of the aromatic type. In order to preserve simplicity we have not attempted to calculate charge distributions in σ-complexes which do not have nonbonding coefficients, but the theory is, of course, applicable to such cases.

Combined with the localisation energy approach to reactivity we can use the criteria put forward for evaluating the competition between substitution and addition (the indices R and $\mathcal{A}$) and we can now, in principle, follow the path of aromatic substitution rather more closely than before and widen our concept of aromaticity.

[9/962 *Received, June 5th*, 1969]

Methyl Proton Resonance in Nuclear Magnetic Resonance Spectra of 2,2′- and 8,8′-Dimethyl-1,1′-binaphthyls. The Optical Stability of (+)-2,2′-Dimethyl-1,1′-binaphthyl

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Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION B
Physical Organic Chemistry

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Methyl Proton Resonance in Nuclear Magnetic Resonance Spectra of 2,2'- and 8,8'-Dimethyl-1,1'-binaphthyls. The Optical Stability of (+)-2,2'-Dimethyl-1,1'-binaphthyl

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(+)-2,2'-Dimethyl-1,1'-binaphthyl has resisted racemisation in solution. This contrasts with 8,8'-dimethyl-1,1'-binaphthyl which is optically labile. Methyl proton signals in the n.m.r. spectra of these compounds can be used to throw light on their conformations in the ground state.

A RECENT study of the molecular structure of crystalline 1,1'-binaphthyl, m.p. 145 °C,[1a] has shown that the dimensions of the two naphthalene rings are not significantly different from those of naphthalene itself; in the crystal, the dihedral angle between the two naphthalene systems (which deviate somewhat from planarity, but can be considered as planar for this definition) on the diad axis is 68°, in a *cis*-conformation: this angle is probably different when the molecule is in solution.[1b]

1,1'-Binaphthyl[2] and 8,8'-dimethyl-,[3] 8-methyl-,[4] and 2,2'-dimethyl-1,1'-binaphthyl[5] have all been obtained in the optically active state. The low optical stability of the 8,8'-dimethyl and 8-methyl compounds has been

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[1] (*a*) K. Ann Kerr and J. Monteath Robertson, *J. Chem. Soc.* (*B*), 1969, 1146; see also W. A. C. Brown, J. Trotter, and J. Monteath Robertson, *Proc. Chem. Soc.*, 1961, 115, and H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Letters*, 1968, **1**, 97; (*b*) R. J. W. Le Fevre, (Mrs.) A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.* ,1963, 3180.

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[4] Ann S. Cooke and Margaret M. Harris, *J. Chem. Soc.* (*C*), 1967, 988.

[5] D. D. Fitts, M. Siegel, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 480.

attributed to distortions in the ground state, arising from *peri*-repulsions, which would be favourable to attaining the transition state for racemisation. There is crystallographic evidence from related compounds for the possibility of such distortions.[6] In contrast to this, 2,2′-dimethyl-1,1′-binaphthyl, which is not di-*peri*-substituted, may be presumed to be much closer to 1,1′-binaphthyl itself in its geometry, and therefore to have a lower ground-state energy and consequently a higher energy of activation for racemisation.

We have now attempted to racemise optically active 2,2′-dimethyl-1,1′-binaphthyl and failed to do so at temperatures below those at which it decomposes. Its specific rotation is unaltered after 40 h in 1-methylnaphthalene solution at 240 °C; at 290 °C decomposition sets in, but the recovered undecomposed material retains its optical rotation fully. This is a marked difference from the 8,8′-dimethyl compound, where the activation energy for racemisation in solution, 27·5 kcal mol^{-1}, is only 5 kcal mol^{-1} greater than that for the racemisation of 1,1′-binaphthyl itself.[3]

Interest in the ground state of these two molecules has led us to look at the methyl proton signals of their n.m.r. spectra, together with those of a set of reference compounds; these are listed in Table 1. (4,4′-Dimethyl-1,1′-binaphthyl was prepared, albeit in very small yield, by an Ullmann reaction on 4-bromo-1-methylnaphthalene; Fichter and Herszbein[7] described a compound, m.p. 147 °C, as one of several products isolated from the electrolytic oxidation of 1-methylnaphthalene and tentatively assigned the structure 4,4′-dimethyl-1,1′-binaphthyl to it; we consider that our synthesis confirms this assignment.)

TABLE 1

Methyl proton signals in n.m.r. spectra in CCl_4 at 60 MHz with tetramethylsilane as internal standard

	τ		τ
2,2′-Dimethyl-1,1′-binaphthyl	8·05 [a]	1-Methylnaphthalene	7·47 [a,c]
8,8′-Dimethyl-1,1′-binaphthyl	8·25 [a]	2-Methylnaphthalene	7·63 [a]
8-Methyl-1,1′-binaphthyl	8·32 [a]	2,3-Dimethylnaphthalene	7·75 [a,d]
4,4′-Dimethyl-1,1′-binaphthyl	7·26 [a]	2,6-Dimethylnaphthalene	7·60 [a,d]
2,2′-Dimethylbiphenyl	7·99 [a]	2,7-Dimethylnaphthalene	7·65 [a,d]
3,3′-Dimethylbiphenyl	7·75 [a]	1,4-Dimethylnaphthalene	7·50 [a,d]
4,4′-Dimethylbiphenyl	7·65 [a]	1,5-Dimethylnaphthalene	7·45 [a,d]
Toluene	7·66 [c]	1,8-Dimethylnaphthalene	7·26 [a,d]
		2,2′-Di-t-butylbiphenyl	8·88 [a,e]

[a] Present work. [b] Ref. 10. [c] G. Cum, P. B. D. de la Mare, and M. D. Johnson, *J. Chem. Soc.* (*C*), 1967, 1590 report τ 7·44 in $CDCl_3$. [d] C. MacLean and E. L. Mackor, *Mol. Phys.*, 1960, **3**, 223, reported figures for solvent CS_2, 50 MHz, H_2O–D_2O external indicator; conversion by use of established factors shows excellent agreement with the figures here. [e] We thank Dr. M. S. Lesslie for a specimen of this compound.

Table 1 shows that high τ values are given by the 2,2′- and 8,8′-dimethyl-1,1′-binaphthyls, by 8-methyl-1,1′-binaphthyl, by 2,2′-dimethylbiphenyl, and by 2,2′-di-t-butylbiphenyl. At room temperature they each gave one sharp signal for methyl protons. In all of this set of biaryls, the methyl protons are shielded by an aromatic system. Since each signal is sharp, either each compound exists in one conformation or interchange between conformers is rapid: it can be assumed that the methyl groups *per se* rotate fairly freely, and that the conformations to be considered as those of the aromatic frameworks and their attached substituents; the energy barriers to racemisation are all sufficiently high for it to be unnecessary to consider eclipsed conformations.

If we make an initial assumption (later to be modified) that the geometry of 2,2′-dimethyl- and 8,8′-dimethyl-1,1′-binaphthyl can be correctly described by taking 1,1′-binaphthyl and substituting appropriate hydrogen atoms by methyl groups, participants in the statistical average may then be represented as in Figure 1, where the intersection of the lines marks the diad axis; alternatively, plans of the two dimethyl-1,1′-binaphthyls can be drawn (Figure 2) in which the arc of travel (represented by a dotted line) of a methyl group in the 2-position can be seen to differ from that of one in the 8-position, relative to the second aromatic system. In the diagrams, the whole sweep of 180° is shown, but in fact van der Waals touching distances would limit movement to a small proportion of the arc, near to the orthogonal position. Interannular conjugation must be very small

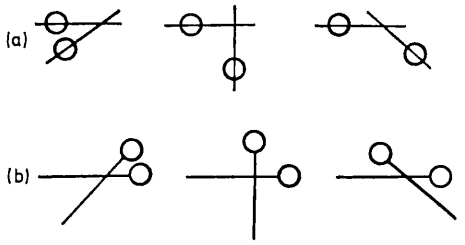
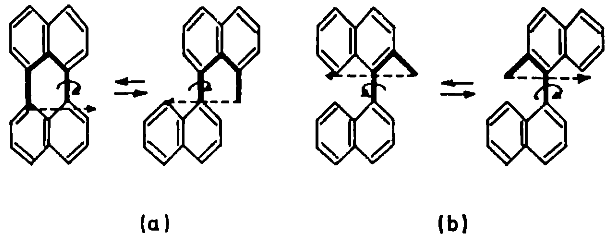


FIGURE 1 Cisoid, orthogonal, and transoid conformations of undistorted 1,1′-binaphthyls; (a) 8,8′-dimethyl-1,1′-binaphthyl; (b) 2,2′-dimethyl-1,1′-binaphthyl; ○ represents methyl



(a) (b)

FIGURE 2 Plans of undistorted molecular models to show path of one methyl group relative to the second naphthalene system: (a) 8-methyl-; (b) 2-methyl-1,1′-binaphthyl

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[6] M. B. Jameson and B. R. Penfold, *J. Chem. Soc.*, 1965, 528.

[7] F. Fichter and S. Herszbein, *Helv. Chim. Acta*, 1928, **11**, 1265.

at these high interplanar angles,[8] therefore resonance energy can play little part in forming an energy barrier between conformations.

Interpretation of the N.m.r. Data.—The chemical shifts of protons relative to those in alkenes can be calculated, by use of the point-dipole approximation for the magnetic effects of the ring current induced by the applied field. Our model differs from that used previously[9] in that the current is regarded as flowing along the bonds rather than in a circle over the carbon nuclei; the induced moment is therefore rather smaller. Good agreement is found, for aromatic and for methyl protons, between the chemical shifts calculated from this model, and those observed for benzene, naphthalene, toluene, and the methylnaphthalenes. The agreement gives confidence in the method of calculation.

TABLE 2

Comparison between some calculated and observed chemical shifts

Aryl protons; standard, cyclohexadiene

		Naphthalene	
Compound	Benzene	α	β
Chemical shift (calc.)	−1·45	−2·00	−1·65
Chemical shift (obs.)	−1·41	−1·95	−1·60

Methyl protons; standard, propene

Compound	Toluene	α-Me-naphthalene	β-Me-naphthalene
Chemical shift (calc.)	−0·56	−0·90	−0·70
Chemical shift (obs.)	−0·65	−0·95	−0·75

The next objective is to see what the comparison of calculated and observed chemical shifts reveals about the molecules under discussion; the interest now lies chiefly in the effects of induced ring currents in the second aromatic fragment, since at the high dihedral angles required by the allowed conformations there will be shielding effects on protons of methyl groups attached to the first aryl group. A simple approach is to consider idealised, undistorted biaryl models in which each aromatic moiety is planar and the positions 4, 1, 1′, and 4′ are collinear (as in Figures 1 and 2) and from the observed chemical shifts to calculate dihedral angles which would correspond with them.

We can regard the average field acting on the three methyl protons as being not significantly different from that at their centre of gravity. Bond distances were taken to be C(1)–C(2), 1·4 Å; C(1)–C(1′), 1·5 Å; C(2)–Me, 1·5 Å; C–H, 1·08 Å. These are grossly simplified, but the results of the calculations were relatively insensitive to the exact values of the various bond angles and distances, provided that they were within reasonable limits, *except for* the elevation of the point in question above the plane of the 'second' ring, *i.e.*, the dihedral angle.

If the undistorted model of the 8,8′-dimethyl compound is taken in its orthogonal position (dihedral angle 90°), the shielding effect calculated by the present method is of the order of 3 p.p.m. A similar result is obtained if the method put forward by Johnson and Bovey[10] is employed. The discrepancy between 3 p.p.m. and the observed 0·8 p.p.m. is wide, and hence it can be concluded that the undistorted orthogonal conformation is unlikely for this compound.

Dihedral angles which are compatible with the observed chemical shifts in models of undistorted geometry are given in Table 3; these we have considered in conjunction with molecular models which incorporate the van der Waals radii of the constituent atoms (Leybold models). It is then evident that the result for the 2,2′-disubstituted compound is reasonable. The ground-state geometry can be satisfactorily represented by the near-orthogonal conformation of relatively undistorted rings. This conclusion for 2,2′-dimethyl-1,1′-binaphthyl is in agreement with spectroscopic evidence for a related compound; the u.v. spectrum of 2,2′,7,7′-tetramethyl-1,1′-binaphthyl is closely similar to that of naphthalene.[11]

TABLE 3

Results of calculations of average dihedral angles, from models of undistorted geometry

Biaryl	Reference	Observed high-field chemical shift $\tau - \tau_r$	Calculated average dihedral angle
2,2′-Dimethylbiphenyl, τ 7·99	4,4′-Dimethylbiphenyl, τ 7·65	$0{\cdot}3_5$	85—90°
2,2′-Dimethyl-1,1′-binaphthyl, τ 8·05	2-Methyl-, 2,6-dimethyl-, 2,7-dimethyl-naphthalene, τ 7·65	0·4	85—90
8,8′-Dimethyl-1,1′-binaphthyl, τ 8·25	1-Methyl-, 1,4-dimethyl-, 1,5-dimethyl-naphthalene, τ 7·47;	0·8	55
	1,8-dimethylnaphthalene, τ 7·26	1·0	60

On the other hand, the dihedral angle calculated for 8,8′-dimethyl-1,1′-binaphthyl from the n.m.r. data is shown by the models to be a sterically impossible one *unless* distortions are introduced which can increase the distance between the 8-methyl group and the second ring considerably. Small angular distortions spread over the whole molecule, such as have been found in crystalline 3-bromo-1,8-dimethylnaphthalene,[6] would not have too large an energy requirement.[12] The n.m.r. evidence is thus in accord with the distortion hypothesis previously advanced to explain the low optical stability of 8,8′-dimethyl-1,1′-binaphthyl.

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[8] G. H. Beaven and E. A. Johnson, Conference on Molecular Spectroscopy, Pergamon Press, 1959, p. 78.

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, 1959, p. 180.

[10] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[11] R. A. Friedel, M. Orchin, and L. Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

[12] C. A. Coulson and S. Senent, *J. Chem. Soc.*, 1955, 1819.

EXPERIMENTAL

(±)-2,2′-*Dimethyl*-1,1′-*binaphthyl*.—2,2′-Bisbromomethyl-1,1′-binaphthyl[13] (10 g) in sodium-dried ether (500 ml) was added to lithium aluminium hydride (12 g) and heated under reflux for 2·5 h. Normal working up gave a viscous oil which crystallised from ethanol to give (±)2,2′-*dimethyl*-1,1′-*binaphthyl*, 4·5 g, m.p. 70—71° (Found: C, 93·4; H, 6·35. $C_{22}H_{18}$ requires C, 93·6; H, 6·4%).

(+)- *and* (—)-2,2′-*Dimethyl*-1,1′-*binaphthyl*.—Reduction of (—)-2,2′-bisbromomethyl-1,1′-binaphthyl {$[\alpha]_{578}^{22}$ −155·9° in benzene (lit.,[5,13] $[\alpha]_{579}^{23}$ −169·4° in benzene and $[\alpha]_{546}^{29}$ −200° in benzene)} gave (+)-2,2′-dimethyl-1,1′-binaphthyl, m.p. 70—71°, $[\alpha]_{578}^{22\cdot5}$ +21·0° in methanol (lit.,[5] m.p. 64—67°, $[\alpha]_{578}^{22}$ +19° in ethanol).

Similar treatment of the (+)-bisbromomethyl compound gave (—)-2,2′-dimethyl-1,1′-binaphthyl, m.p. 69—70°, $[\alpha]_{578}^{22\cdot5}$ −21·0° in methanol.

Attempted Racemisation of (+)-2,2′-*Dimethyl*-1,1′-*binaphthyl*.—A portion of the material of $[\alpha]_{578}^{25}$ +21·0° was dissolved in *m*-xylene and heated at 136 °C for 9 h; another portion was dissolved in 1-methylnaphthalene and heated at 240 °C for 15 h. In neither case was there any loss of optical activity. On heating at 290 °C a similar solution darkened; the i.r. spectrum showed that some change had occurred; purification gave the original hydrocarbon, $[\alpha]_{578}^{20}$ +21·0°, *i.e.*, the undecomposed material had not racemised.

4,4′-*Dimethyl*-1,1′-*binaphthyl*.— 4-Bromo-1-methylnaphthalene (22·6 g) was heated to 230 °C with a trace of iodine and copper bronze (24 g) added gradually during 4—5 h, the temperature being raised to 270 °C and 1-methylnaphthalene added when the mixture became very viscous. Steam distillation left a tarry mass which was extracted with chloroform and filtered through diatomaceous earth; addition of light petroleum (b.p. 40—60°) precipitated some tar which was filtered off and the solution purified on an alumina column, with elution with light petroleum (b.p. 40—60°). Removal of the solvent gave an oil: the part which distilled below 130°/1 mm was rejected; the residue crystallised from acetone in colourless needles, m.p. 143—144·5° (yield, *ca*. 0·5 g). Its molecular weight was 282 (by mass spectroscopy).

N.m.r. spectra were determined on a Varian A-60 instrument in CCl_4 solution with tetramethylsilane as internal standard.

We thank the Rockefeller Foundation for a maintenance grant and Makere University College, Kampala, for study leave (R. Z. M.), and West Ham College of Technology and the School of Pharmacy and Queen Elizabeth College, University of London, for preliminary n.m.r. spectra. We thank Mr. J. Pragnell for help in the preparation of 4,4′-dimethyl-1,1′-binaphthyl.

[0/1598 *Received, September* 17*th*, 1970]

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[13] D. Muriel Hall and E. E. Turner, *J. Chem. Soc.*, 1955, 1242.

Secondary Radicals in the Autoxidation of Hydroquinones

By P. Ashworth and W. T. Dixon*
(*Bedford College, Regents Park, London* N.W.1)

Reprinted from

Chemical Communications 1971

The Chemical Society, Burlington House, London W1V 0BN

Secondary Radicals in the Autoxidation of Hydroquinones

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(*Bedford College, Regents Park, London* N.W.1)

Summary Strongly alkaline solutions of hydroquinones, shaken in air, may give e.s.r. spectra corresponding to radicals other than the expected semiquinones; secondary or even tertiary stages of the autoxidation may thus be observed.

THE autoxidation of hydroquinones in alkaline solution is well known to be a radical process involving initial formation of *p*-semiquinone radicals,[1] which are short-lived in aqueous solution, but can be kept for much longer periods in strongly alcoholic media. The relative stability of these 'primary' radicals in alcoholic solution[2] has, to a certain extent, precluded further investigation of what appears to be a complex autoxidation process.

The autoxidation of 4-methylcatechol in aqueous alkali has been found to give a secondary radical, in which an additional oxygen is bonded to the aromatic ring.[3] This extends our knowledge of the autoxidation process in that particular case, and now, using e.s.r. spectroscopy, we have found rather similar results for some substituted hydroquinones and *p*-quinones.

In contrast to the situation in ethanolic solutions, more than one type of radical may be observed in largely aqueous solutions of certain hydroquinones or *p*-quinones, depending on the conditions. For example, in 1% sodium hydroxide solution, simple *p*-semiquinone radicals are usually observed, but after a relatively short time, their e.s.r. spectra disappear. In more concentrated alkali (5—20% NaOH), totally different e.s.r. spectra are obtained (apart from cases where we might expect strong steric hindrance), corresponding to 'secondary' radicals. These arise from substitution of an aromatic hydrogen, probably by hydroxyl, to give radicals derived from the 1,2,4-trihydroxybenzene system.

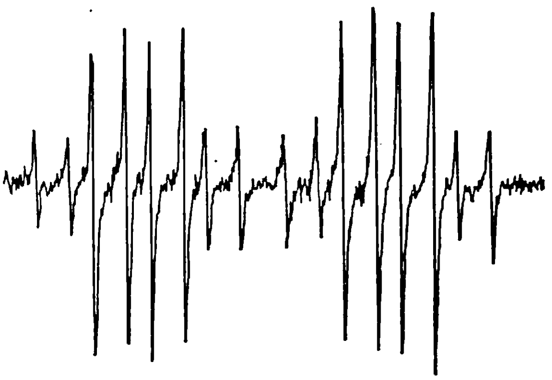


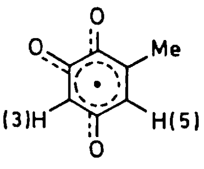
FIGURE. *E.s.r. spectrum of secondary radical from methylhydroquinone.*

Coupling constants in the e.s.r. spectra of the observed radicals

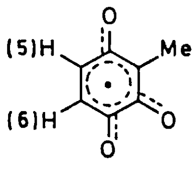
Hydroquinone or p-quinone	Proton	Coupling Constants (Gauss)						
		Primary (weak alkali)	Secondary (strong alkali)					
	2	2·38 [a]						
Unsubstituted	3	2·38						
	5	2·38						
	6	2·38						
			A		B		C	
	2	2·12 [b]		[a]			[a]	
2-Methyl-	3	1·75	0·55 (H)		0·95 (Me)	0·56 (H)		0·66 (H)
	5	2·54		4·15 (H)			5·18 (Me)	
	6	2·45	0·95 (Me)		0·55 (H)	0·66 (H)		0·56 (H)
	2	2·32 [c]		[d]				
2,5-Dimethyl-	3	1·84	0·98 (Me)		0·88 (Me)			
	5	2·32		4·31 (H)				
	6	1·84	0·88 (Me)		0·98 (Me)			
	2	2·15 [c]						
2,6-Dimethyl-	3	1·98		0·97 (Me)				
	5	1·98		5·20 (Me)				
	6	2·15		0·72 (H)				
	2	[b]						
2,5-Di-t-butyl	3	2·09						
	5							
	6	2·09						

[a] Aqueous solution. [b] 1 : 1 H_2O–EtOH. [c] 1 : 1 H_2O–DMF. [d] 3 : 1 H_2O–DMF.

One characteristic of the ensuing radical is that the coupling constants of methyl or aromatic protons *para* to an oxygen atom (*i.e.* on C-5), are much larger than in the original *p*-semiquinone radical (Table).



A



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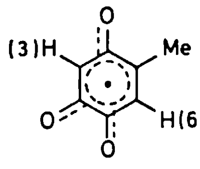
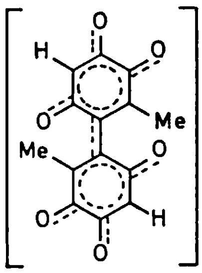


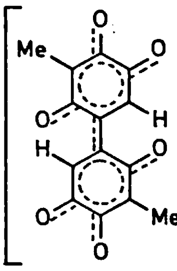
C

It is clear that competing reactions in these solutions are finely balanced, for changes of solvent have a marked effect on the ease of formation and lifetimes of the observed radicals and also, in one case, that of methylhydroquinone, at least two secondary radicals can be observed depending on the conditions (A—C).

(*a*) In cold sodium hydroxide (5—20%) radical A (or radical B, which would be expected to have similar coupling constants) was observed (Figure); (*b*) in hot, strong alkali radical C, the same as that observed by Stone and Waters from 4-methylcatechol, was obtained; and (*c*) in mildly



D



E

alkaline aqueous DMF a spectrum corresponded to a mixture of both radicals was obtained.

In the case of methylhydroquinone a 'tertiary' radical was obtained in very strong, cold alkali (30% NaOH). The resulting spectrum appears to correspond to a biphenyl derivative, D or E, where there is conjugation between the two rings, the coupling constants being approximately half those in the secondary radical (A or B) from which it would be formed.

The formation of this dimer is apparently favoured by the high spin-density on the position *para* to an oxygen (*i.e.* on C-5), and the presence of a replaceable hydrogen at that position.

P. A. thanks the S.R.C. for a research grant.

(*Received, July 20th,* 1971; *Com.* 1258)

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[1] G. K. Fraenkel and B. Venkataraman, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.

[2] G. K. Fraenkel and B. Venkataraman, *J. Chem. Phys.*, 1959, **30**, 1006.

[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.

Secondary Radicals in the Autoxidation of Hydroquinones and Quinones

By **P. Ashworth** and **W. T. Dixon,*** Bedford College, Regents Park, London N.W.1

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS II

1972

Secondary Radicals in the Autoxidation of Hydroquinones and Quinones

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The autoxidation of hydroquinones and quinones in strongly alkaline solution gives rise to radical intermediates other than the expected semiquinones. These 'secondary' radicals, which are derived from 1,2,4-trihydroxybenzene, can be characterised by means of e.s.r. spectroscopy. Different isomeric radicals may be formed, depending on the solvent, and apparently these may reduce any excess of quinone present to the corresponding semiquinone.

SEMIQUINONES were among the first radicals to be investigated by means of e.s.r. spectroscopy because they are easily produced and can generally be obtained in relatively high concentrations. A wide range of *ortho*-, *meta*-, and *para*-semiquinones have been studied.[1-4] However, the formation of semiquinones is only the first stage in the autoxidation of dihydric phenols in alkaline solution. Further stages can profitably be followed by changes in the e.s.r. spectra of the solutions. For example, Stone and Waters[4] have observed semiquinones of trihydroxybenzenes in the autoxidation of some substituted catechols. It is surprising that this has not been reported before, in any detail, in relation to the autoxidation of hydroquinones, since slight variations in alkalinity, concentration, and in the composition of the solvent lead to radicals derived from 1,2,4-trihydroxybenzenes rather than the expected *p*-semiquinones.[5] These 'secondary' radicals can be characterised from their e.s.r. spectra which are frequently well defined and easily resolved.

High concentrations of semiquinones can be obtained just as easily from quinones as from the corresponding hydroquinones,[5,6] in spite of the fact that in the latter

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[1] G. K. Fraenkel and B. Venkataraman, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.

[2] R. Hoskins, *J. Chem. Phys.*, 1955, **23**, 1975.

[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302.

[4] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.

[5] P. Ashworth and W. T. Dixon, *Chem. Comm.*, 1971, 1150.

[6] D. C. Reitz, J. R. Hollahan, F. Dravnieks, and J. E. Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

case there is aerial oxidation, and in the former an overall reduction. This apparent paradox can be resolved by postulating intermediates capable of reducing quinones and it seems that these may well be the secondary radicals which we have been investigating. Under certain conditions we observed spectra which appear to arise from products of coupling reactions and we will refer to these as ' tertiary ' radicals.

The radicals we obtained and their e.s.r. coupling constants are shown in the Table. In practice the observation of each secondary radical was favoured by certain conditions. A working guide for producing the radicals is as follows.

Primary Radicals.—These are produced in even faintly alkaline solutions of hydroquinones and quinones and are more stable in alcoholic media. The spectra are best observed by use of a flow system and in this case a solution of the hydroquinone (0·005M) in ethanol was allowed to flow against 1% sodium hydroxide solution.

Secondary Radicals.—Although these are formed in dilute alkali, more concentrated alkali is usually required to obtain good e.s.r. spectra. Different isomeric radicals may be obtained depending on the solvent (see Table) and sometimes mixtures of these radicals are observed. The techniques used for obtaining e.s.r. spectra of the secondary radicals were as follows. (*a*) A solution of the hydroquinone (*ca.* 0·01M) in the appropriate solvent was added to 10% sodium hydroxide solution. This technique was particularly effective for the monosubstituted and the 2,3-dimethylhydroquinones. (*b*) The hydroquinone or quinone (*ca.* 0·005M) was left in 1% sodium hydroxide solution for *ca.* 1 h and then an equal volume of 10% sodium hydroxide was added. This was effective for the disubstituted compounds where method (*a*) gave only primary radicals. (*c*) A solution of the quinone (*ca.* 0·01M) was added dropwise to an excess of alkali (5% NaOH).

The solutions were immediately transferred to an aqueous cell in the cavity of an e.s.r. spectrometer. The spectra observed were then normally uncontaminated by the presence of other radicals and subsequent interpretation was made easier. The exact values of the coupling constants of the secondary radicals were found to depend on the nature of the solvent, as observed for primary radicals.[7]

Coupling constants of primary (as I) and secondary (as II) radicals

	Coupling constants/G								
	Primary radical (in 50% aq. EtOH)					Secondary radical			
Parent hydroquinone:	a_2	a_3	a_5	a_6		a_3	a_5	a_6	Solvent
Hydroquinone	◄—2·37—►					0·60	4·98	1·34	Water
Methyl	2·12 (Me) (quartet)	1·76	2·61	2·41	A	0·58	5·12 (Me)	0·69	50% aq. EtOH
					B	0·55	4·15	0·95 (Me)	Water
Ethyl	2·02 (Et) (triplet)	1·74	2·53	2·53	A	0·54	4·56 (Et)	0·71	50% aq. EtOH
					B	0·56	4·14	1·08 (Et)	Water
t-Butyl		1·65	2·89	2·12	A	0·52	0·16 * (Bu^t) (septet)	0·84	Water
					B	0·66	4·02		Water
2,3-Dimethyl	1·74 (Me)	1·74 (Me)	2·62	2·62		0·55	4·70 (Me)	0·55 (Me)	Water
2,6-Dimethyl	2·09 (Me)	1·93	1·93	2·09 (Me)		0·97 (Me)	5·20 (Me)	0·72	50% aq. DMF †
2,5-Dimethyl	2·34 (Me)	1·80	2·34 (Me)	1·80		0·88 (Me)	4·20	0·98 (Me)	50% aq. DMF †
5-Isopropyl-2-methyl	2·18 (Me)	1·76	1·92 (Pr^i) (doublet)	1·46		0·92 (Me)	4·20	0·75 (Pr^i) (doublet)	Water

* Splitting from 6 equivalent protons showing that the t-butyl group is not freely-rotating (C. Trapp, C. A. Tyson, and G. Giacometti, *J. Amer. Chem. Soc.*, 1968, **90**, 1394). † Dimethylformamide.

Characterisation of the Radicals.—We felt that the e.s.r. spectra alone did not enable us to deduce with certainty the nature of the secondary radicals, so we tried to gather supporting evidence. The most obvious method was to synthesise the 1,2,4-trihydroxybenzene derivatives which on autoxidation should give semiquinones which correspond to the secondary radicals. We did this for three hydroquinones by means of the sequence[8] (1). When R = H we observed the same eight-line spectrum (from three doublet splittings) as that ascribed to the secondary radical of hydroquinone

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[7] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **36**, 1944.
[8] E. B. Vliet, *Org. Synth.*, Coll. Vol. I, 317.

(see Figure 2). When R = Me we observed the same spectrum as that of radical A from 2,5-dihydroxytoluene. When R = Bu^t we observed the same spectrum as that of radical A from 1,4-dihydroxy-2-t-butylbenzene. The three radicals just discussed were also reproduced by adding solutions of catechol and the 4-substituted catechols (0·01M) dropwise to 5% sodium hydroxide. If 5% alkali is added to a more concentrated solution of catechol (0·05M) a different type of radical is observed along with the *o*-semiquinone, *i.e.*, the dimer observed by Stone and Waters.[9]

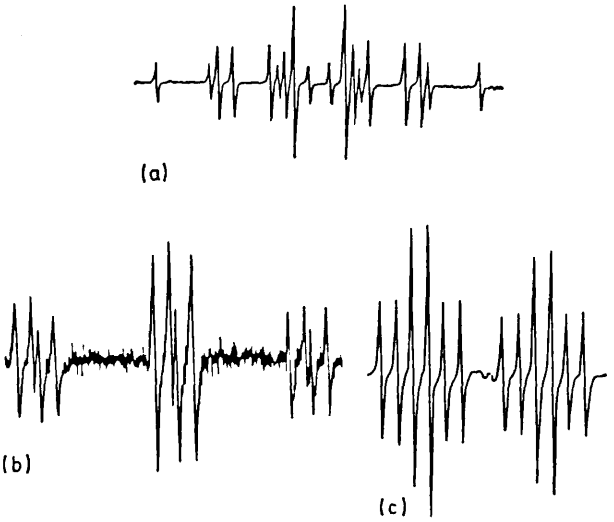


FIGURE 1 The e.s.r. spectra obtained from alkaline solutions of ethylhydroquinone: (a) primary radical in 50% ethanol, 1% NaOH; (b) secondary radical A in 50% ethanol, 10% NaOH; (c) secondary radical B in 10% NaOH

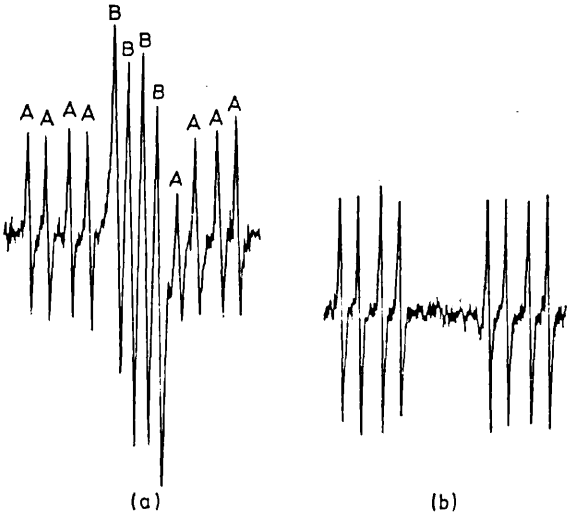
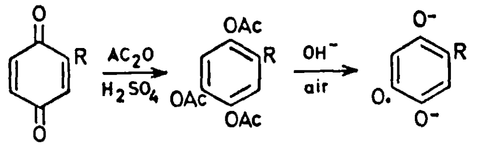


FIGURE 2 (a) Spectrum from hydroquinone (0·001M) in 5% NaOH; lines A due to secondary radical; lines B due to tertiary radical, (b) spectrum from 1,2,4-triacetoxybenzene in 5% NaOH



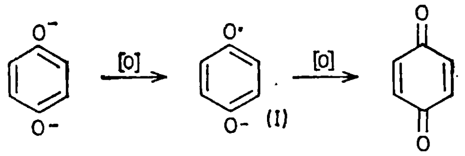
(1)

Having thus proved the identity of these three radicals we reasonably infer the structure of other secondary radicals on the basis of their e.s.r. spectra and a knowledge of the starting material. The following rules seem to apply: (i) Spin densities *para* with respect to oxygen atoms are high (proton coupling constants *ca.* 4—5 G); (ii) methyl proton coupling constants tend to be slightly higher than corresponding aromatic proton splittings; (iii) spin densities on ring carbon atoms between those attached to two oxygen atoms are apparently lower than those on carbon atoms adjacent to only one carbon–oxygen linkage.

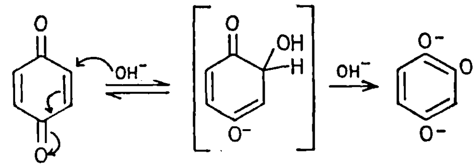
On the basis of these empirical rules we could consistently account for the observed hyperfine splittings. Our assignments imply that hydroxyl is introduced into the ring at the least hindered position, as expected.

DISCUSSION

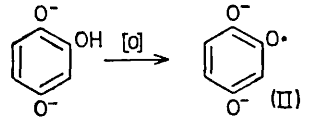
Since our secondary radicals are derived from 1,2,4-trihydroxybenzenes, we now ask how they arise. It is of interest that both hydroquinones and quinones can be used as starting materials.



(2)



(3)



(4)

It is not difficult to arrive at a feasible reaction scheme. The first steps (2) in the autoxidation of hydroquinone lead to benzoquinone. We are not concerned here with coupling products so the next stage is the introduction of a further oxygen atom into the ring. Here we are helped by two well established reactions in which no overall oxidation of the quinone takes place. First, there is addition of HCl to give chloroquinol,[10] and secondly there is the Thiele acetylation[8,11] discussed above. We might, therefore, expect a base-catalysed addition (3) of the elements of water. If this is so there

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[9] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 408.

[10] J. B. Conant and L. F. Fieser, *J. Amer. Chem. Soc.*, 1923, **45**, 2194.

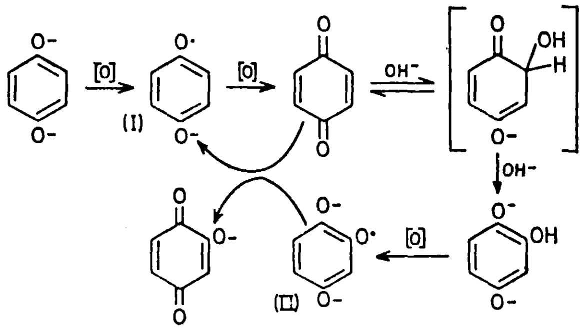
[11] J. Thiele and E. Winter, *Annalen*, 1900, **311**, 341.

must then be further attack by oxygen (4) to give the semiquinone of trihydroxybenzene.

We can now rationalise the observed reduction of quinones when their alkaline solutions are shaken in air. It appears that they are reduced by the corresponding secondary radicals. This possibility is strengthened by our experiments on quinones. When the quinone is always present in high concentration (*e.g.*, 0·01M), the primary radical is observed in alkaline solution, whereas if the concentration of the quinone is kept low (*i.e.*, by adding a 0·01M solution dropwise to alkali) a secondary radical is observed.

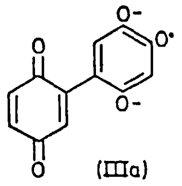
Similarly when an alkaline solution of benzoquinone (*ca.* 0·01M) is left, the signal due to the semiquinone decays. After *ca.* 1 h, addition of fresh alkali leads to the secondary radical, showing that the trihydroxybenzene derivative must have replaced the quinone.

Therefore, we suggest the Scheme for the cycle of reactions leading to the formation of primary and secondary radicals.[12] Both primary and secondary radicals may be destroyed by further oxidation, by dimerisation, or by coupling with, for example, benzoquinone. The further oxidation stage was demonstrated by an experiment in which a solution of t-butylhydroquinone in 5% sodium hydroxide was left open to the air for a day. When the mixture was allowed to flow against dithionite the spectrum of a mixture of both secondary radicals (see Table) was observed showing that the hydroxyquinone derivatives must have been formed. There was no trace of the spectrum of t-butylsemiquinone.

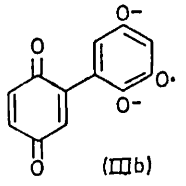


SCHEME

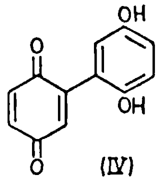
We have obtained a number of well defined spectra which are probably due to coupled products of the reaction. For example the quartet which appears in the secondary spectrum from hydroquinone or benzoquinone (Figure 2) appears to arise from radical (IIIa) in which there is no delocalisation around the second ring. The coupling constants, 0·90 and 0·45 G, are similar to those obtained by Reitz *et al.*[6] starting from the quinol (IV) but they apparently saw a further splitting of 0·1 G. We did not observe this small splitting but we feel justified in our assignment because, first, the magnitudes of the coupling constants are just those expected for a trihydroxy-compound and not for a substituted semiquinone (*cf.* radical A from t-butylhydroquinone in the Table). Secondly, under the conditions of their experiment (10% NaOH), we would expect a secondary-type radical.



(IIIa)



(IIIb)



(IV)

If we add 10% sodium hydroxide to a solution of benzoquinone in 50% dimethylformamide we observe a different quartet (splittings 4·52 G, 0·70 G) which we ascribe to the isomeric radical (IIIb). However, the situation with regard to these tertiary radicals is still not clear and further study is required.

EXPERIMENTAL

E.s.r. spectra were obtained with a Varian E-4 instrument by use of both flow and static methods.

Quinones could be obtained by oxidation of the corresponding hydroquinones with chromic anhydride in 60% acetic acid. The reverse process was effected by reducing the quinone with zinc and 25% hydrochloric acid.

When neither the quinone nor the hydroquinone were available the corresponding phenol was oxidised to the quinone by use of Frémy's salt, according to the method of Tauber and Rau.[13] 4-Substituted catechols were prepared analogously,[14] the *o*-quinones so produced being reduced by zinc and hydrochloric acid.

Triacetoxybenzene derivatives were prepared by the Thiele acetylation [8] and were used directly since the acetyl groups were hydrolysed off by the alkaline medium.

We thank the S.R.C. for a grant (to P. A.) and Miss J. E. Finch for assistance in preparing the typescript.

[2/116 *Received, 19th January*, 1972.]

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[12] M. Eigen and P. Matthies, *Chem. Ber.*, 1961, **94**, 3309.

[13] H.-J. Teuber and W. Rau, *Chem. Ber.*, 1953, **86**, 1036.

[14] H.-J. Teuber and G. Staiger, *Chem. Ber.*, 1955, **88**, 802.

Electron Spin Resonance Spectra of Radicals derived from Arylhydroquinones

By **P. Ashworth** and **W. T. Dixon,*** Bedford College, Regents Park, London N.W.1

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PERKIN TRANSACTIONS II

1972

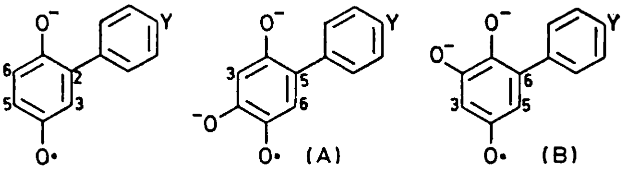
Electron Spin Resonance Spectra of Radicals derived from Arylhydroquinones

By **P. Ashworth** and **W. T. Dixon,*** Bedford College, Regents Park, London N.W.1

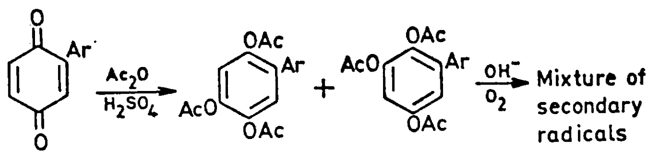
The e.s.r. spectra of radicals formed in the autoxidation of arylhydroquinones show hyperfine splitting from protons attached to the aryl group, showing that the odd electron is delocalised over both rings. Substituents on the phenyl group influence the various proton coupling constants in a way which is related to their electron-donating or electron-withdrawing properties.

We have reported how several different types of radical intermediate can be observed during the autoxidation of alkylhydroquinones and quinones.[1,2] In addition to semiquinones, radicals derived from 1,2,4-trihydroxybenzenes can be seen by means of e.s.r. spectroscopy. A parallel series of radicals are formed during the autoxidation of arylhydroquinones, showing that the aryl groups have little effect on the reactivity of the quinone nucleus, although the hyperfine splittings of aryl protons indicate that the odd electron is delocalised on to the second ring to some extent. Substituents on the aryl group have only a small effect on the coupling constants although the trends are reasonably definite.

The parent quinones were made by direct arylation of *p*-benzoquinone *via* the diazonium salts,[3] and the ease with which this reaction could be made to yield the arylquinone varied somewhat from one case to another. The primary radicals were generated easily in dilute alkaline solutions and the secondary radicals from more concentrated alkali. The latter were always obtained initially as a mixture of two isomeric radicals, (A) and (B). This contrasts with the behaviour of alkylhydroquinones which could be made to yield one or other isomer depending on the conditions. However, when the solutions were left the (B)-type radical decayed, often leaving a pure spectrum from type (A). Improved spectra of the secondary radicals could be obtained by acetylating the arylquinones followed by alkaline hydrolysis (Scheme 1). The e.s.r. spectra were in general well resolved and although there was a mixture of secondary radicals both spectra could be analysed because the overlap between them was minimal (see Figure 1). Difficulties arise in a few cases because the smaller splittings are of the same



Primary radical Secondary radicals



Scheme 1

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[1] P. Ashworth and W. T. Dixon, *Chem. Comm.*, 1971, 1150.

[2] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[3] P. Brassard and P. L. Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

order as the line-widths, and since we observe the first derivative of the absorption spectrum, overlapping of maxima and minima can lead to reductions of apparent intensity or even total annihilation of some lines. This leads, in the case of *p*-nitrophenylsemiquinone to some uncertainty in the smaller coupling constants (see Figure 2).

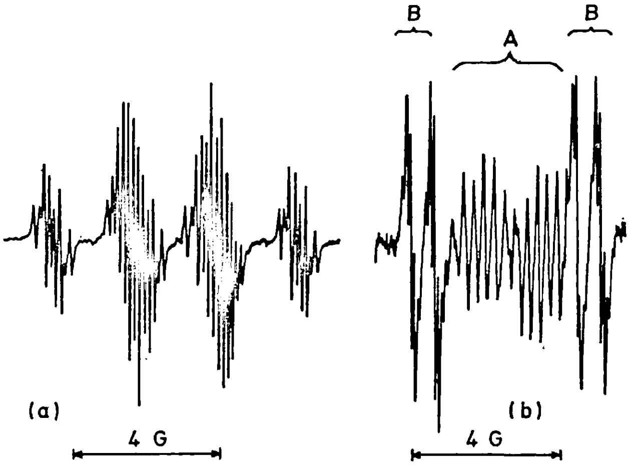


FIGURE 1 E.s.r. spectra of radicals from *m*-chlorophenylhydroquinone, (a) primary radical (in 50% aqueous ethanol, 0·5% sodium hydroxide; (b) secondary radicals (in 7·5% sodium hydroxide)

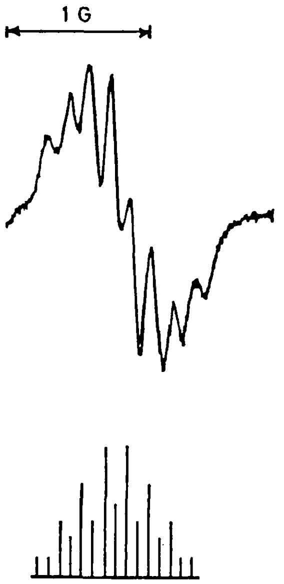


FIGURE 2 One of the side bands of the e.s.r. spectrum of *p*-nitrophenylsemiquinone, with the reconstructed 'stick' spectrum (alternate lines are 'missing')

The assignments given in Tables 1 and 2 are based on the rules adopted in our previous paper [2] on alkyl semiquinones and which are in agreement with the results of previous workers.[4-6] These rules may be summarised thus: (1) coupling constants of protons *para* to a substituent on the semiquinone nucleus are large; (2) coupling constants of protons *ortho* to an electron-donating substituent are small. As an example, consider structure (I). Position 5 is *para* to X; positions 5 and 6 are *ortho* to O$^-$; position 3 is *ortho* to O$^-$ and to X. Hence $a_3 < a_6 < a_5$; (3) the influence of the group X decreases along the series O$^-$ $\gg$ Bu^t > Me > Ph > Cl > H.

TABLE 1

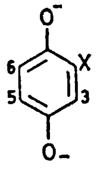
Coupling constants of primary radicals

	Coupling constants/G				
	a_2				
Aryl group	a_{ortho} a_{para}	a_{meta}	a_3	a_5	a_6
Ph	0·27	0·16	1·99	2·56	2·12
p-OH	0·32	0·14	1·38	2·53	2·33
p-OMe	0·30	0·15	1·85	2·56	2·16
p-Me	0·28	0·16	1·88	2·55	2·13
p-Ph	0·28	0·20	1·98	2·58	2·10
m-Cl	0·27	0·15	2·00	2·52	2·13
p-Cl	0·28	0·16	2·10	2·54	2·10
p-CO_2H	0·27	0·17	2·10	2·56	2·10
p-CO_2Me	0·29	0·18	2·26	2·56	1·95
p-NO_2	0·30	0·15	2·38	2·50	1·92
	a_N = 0·75				
2,5-Diphenyl	0·25	0·14	2·20		2·20
2,5-Di-*p*-Cl	0·31	0·16	1·78		1·78

TABLE 2

Coupling constants/G of secondary radicals

	Secondary radical (A)				Secondary radical (B)			
		a_5					a_6	
Aryl group	a_3	a_{ortho} a_{para}	a_{meta}	a_6	a_3	a_5	a_{ortho} a_{para}	a_{meta}
Ph	0·50	0·54	0·31	1·08	0·67	4·52	0·12	0·12
p-OH	0·53	0·65	0·27	0·53	0·63	4·00	0·14	0·10
p-OMe	0·53	0·59	0·29	0·90	0·65	4·40	0·12	0·12
p-Me	0·50	0·58	0·31	0·90	0·67	4·42	0·13	0·13
p-Ph	0·50	0·58	0·33	1·12	0·66	4·52	0·12	0·12
m-Cl	0·52	0·54	0·29	1·19	0·67	4·62	0·12	0·12
p-Cl	0·48	0·59	0·31	1·16	0·68	4·58	0·12	0·12
p-CO_2H	0·48	0·58	0·32	1·17	0·67	4·66	0·12	0·12
p-NO_2	0·45	a_{ortho} = 0·60 a_{para} a_N = 0·15	0·30	1·48	0·70	4·86	0·12	0·12



(I)

In the case of primary radicals we expect substitution into the phenyl ring to affect H-3 more than H-5, and we

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[4] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

[5] A. Fairbourn and E. A. A. Lucken, *J. Chem. Soc.*, 1963, 258.

[6] K. A. K. Lott, E. L. Short, and D. N. Waters, *J. Chem. Soc. (B)*, 1969, 1232.

assign the larger splitting to H-3 in two cases: (a) Y = NO_2 and (b) Y = CO_2Me (see Table 1).

The coupling constants of protons on the phenyl ring were assigned by reference to unambiguous cases (*e.g.*, *m*-chlorophenyl) and in the primary radicals and the secondary radicals of type (A) the *ortho*- and *para*-proton splittings were of the order of twice the *meta*-proton coupling constants.

Trends in the Coupling Constants.—There seems to be a small but definite relationship between the electron-donating power of the substituent on the phenyl ring and the coupling constants of the various protons. For example, the rules applying to the protons attached to the original quinone nucleus are as follows. For protons *ortho* to the aryl group, the coupling constants decrease with increasing electron-donating power of Y, as shown in Table 3. Protons *meta* to the aryl group have coupling constants which increase with increasing electron-donating power of Y, as shown in Table 4. Protons *para* to the aryl group are little affected by the substituent Y, if anything the trend is similar to that for *ortho*-substituents, as shown in Table 5. When the overall spin density in the aryl ring is large the *ortho*- and *para*-proton coupling constants are of the order of twice those of the *meta*-protons, but as this overall coupling decreases the splittings become more equal. The difference between the coupling constants of the *ortho*- and *meta*-protons is apparently increased somewhat by electron-donating substituents in the *para*-position, as shown in Table 6. Addition of the proton coupling constants gives us a measure of the amount of spin associated with carbon atoms attached to hydrogen, provided that the splittings all have the same sign. If this is the case, then it appears that electron-donating substituents on the phenyl ring tend to decrease the probability of the odd electron being on carbon atoms attached to hydrogen. It, therefore, appears to be probable that the >C–Y group tends to ' attract ' spin density more when Y releases electrons more easily. We can rationalise this in terms of valence-bond approach to radicals in which the odd electron is largely associated with oxygen. The only canonical structures which have reasonably low energies and can lead to delocalisation of the odd electron are those having a double bond to, or a negative change on, the oxygen, *i.e.*, for phenoxyl or semiquinone radicals the main canonical structures are of types (i), (ii), and (iii). The odd electron density will be greater on positions which yield electrons more easily, for the canonical structures in which the odd electron is associated with these positions will have higher probabilities owing to contributions of canonical structures of type (II). The delocalisation of the odd electron to the phenyl group must occur largely through structures such as (II)—(IV) and that explains why the spin density on the *ortho*- and *para*-positions is generally greater than that on the *meta*-positions.

TABLE 3

Y	O^-	OMe	Me	H	Cl	CO_2Me	NO_2
a_{ortho}							
Primary	1·38	1·85	1·88	1·99	2·10	2·26	2·38
Secondary (A)	0·53	0·90	0·90	1·08	1·16		1·48
Secondary (B)	4·00	4·40	4·42	4·52	4·58		4·86

TABLE 4

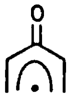
Y	O^-	OMe	Me	H	Cl	CO_2Me	NO_2
a_{meta}							
Primary	2·33	2·16	2·13	2·12	2·10	1·95	1·92
Secondary (A)	0·53	0·53	0·50	0·50	0·48		0·45

TABLE 5

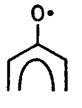
Y	O^-	OMe	Me	H	Cl	CO_2Me	NO_2
a_{para}							
Primary	2·53	2·56	2·55	2·56	2·54	2·56	2·50
Secondary (B)	0·63	0·65	0·67	0·67	0·68		0·70

TABLE 6

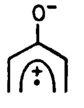
	Primary		(A)		(B)	
Y	O^-	Cl	O^-	Cl	O^-	Cl
a_{ortho}	0·32	0·28	0·65	0·59	0·14	0·12
a_{meta}	0·14	0·16	0·27	0·31	0·10	0·12



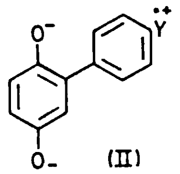
(i)



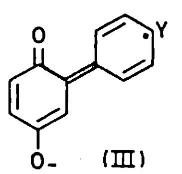
(ii)



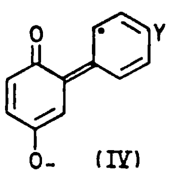
(iii)



(II)



(III)



(IV)

Similarly on the hydroquinone nucleus, the trends of the coupling constants of protons *meta* to phenyl substituents probably arises from the lack of conjugation between the two positions and also, perhaps, from the influence of the phenyl group on the adjacent oxygen atom.

By difference, these trends are opposite to those at the *ortho*- and *para*-positions, which, from the usual valence-bond viewpoint, are more directly affected by the substituents, although the observed changes at the *para*-position are very small.

Finally the extra stability of the radicals of type (A) compared with corresponding radicals (B) is probably due not so much to the fact that there is greater delocalisation of the odd electron in type (A), but more to the availability of a position of high spin density for further attack in the type (B) radicals.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E4 instrument. To obtain the primary radicals a solution of the arylhydroquinone (0·01M) in ethanol was mixed with an equal volume of 1% sodium hydroxide solution, both flow and static methods being used. The secondary radicals were obtained by adding an aqueous solution of the hydroquinone (0·05M) to an equal volume of 15% sodium hydroxide solution.

Materials.—The arylquinones were obtained by direct arylation of *p*-benzoquinone *via* the diazonium salts according to the method of Brassard and L'Écuyer.[3] In certain cases, where appreciable amounts of the diarylquinone tended to be formed, it was convenient to use a large excess of the *p*-benzoquinone. The arylquinone was much easier to separate from the excess of starting material than from the diaryl compound. Reaction of the arylquinone in aqueous acetone with further diazonium salt produced the 2,5-diaryl compound in moderate yield.[3]

The triacetoxy-derivatives were prepared by heating the quinone with acetic anhydride and a little concentrated sulphuric acid at 80 °C.

[2/1215 *Received*, 31*st May*, 1972]

Steric Effects observed in the Electron Spin Resonance Spectra of Some Arylsemiquinones

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Steric Effects observed in the Electron Spin Resonance Spectra of Some Arylsemiquinones

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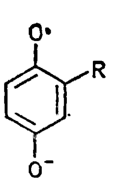
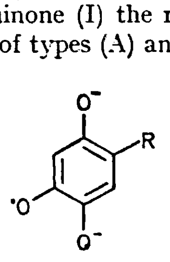
The e.s.r. spectra of radicals derived from arylhydroquinones are discussed with particular reference to how the conformations of the radicals vary with increasing *ortho*-substitution on the aryl group. With two *ortho*-substituents the dihedral angle becomes close to 90° so that the major splitting from the aryl group is from the *meta*-protons. The results are rationalised in terms of two contributions to the coupling constants of protons associated with the aryl group, one from the π electron system and the other from delocalisation through the σ bond framework.

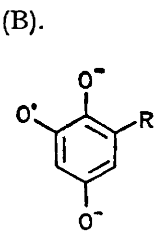
THE mechanism of the initial stages in the autoxidation of hydroquinones has recently been elucidated by means of e.s.r. spectroscopy.[1] After initial formation of the appropriate semiquinone (I) the reaction later involves secondary radicals of types (A) and (B).



(I)



(A)



(B)

The e.s.r. spectra of these three species are related to each other in a simple way and so it is useful to be able to obtain three spectra from each starting material, since they corroborate each other and aid us in the assignments of coupling constants. In a previous paper we discussed radicals from *para*-substituted arylhydroquinones.[2] Trends were pointed out both in the hyperfine splittings of protons attached to the semiquinone ring, and in those of protons in the aryl fragment. The results indicated that delocalisation of spin density *away* from the semiquinone ring is facilitated by electron-donating groups in the *para*-position of the attached aryl group.

Other things being equal, we would have expected similar trends when the substituents were in an *ortho*- instead of the *para*-position.

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[1] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.
[2] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 2264.

RESULTS

However, as regards the coupling constants on the semiquinone ring, the effects of *ortho*-substituents in the aryl group are much smaller than when those substituents are in the *para*-position, and are roughly the same as in the corresponding *meta*-derivatives (see Tables 1 and 2).

This last observation can be coupled with the more striking result, that the coupling constants of the aryl protons are about twice as large when a substituent is either in the *meta*- or *para*-position than when it is *ortho* with respect to the bond joining the two rings.

TABLE 1

(a) Coupling constants of primary radicals from mono-substituted arylsemiquinones

	Coupling constants (G)						
				Aryl group splittings			
Aryl group	a_3	a_5	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituent}}$
Ph	1·99	2·56	2·12	0·27	0·16	0·27	
o-FC_6H_4	2·07	2·52	2·21	0·16	0·16	0·16	$a_F = 0·56$
m-FC_6H_4	2·02	2·56	2·13	0·28	0·15	0·28	$a_F \approx 0·04$ *
p-FC_6H_4	2·01	2·54	2·12	0·28	0·15		$a_F = 0·57$
o-ClC_6H_4	2·12	2·52	2·22	†			
o-BrC_6H_4	2·10	2·50	2·20	0·10	0·10	0·10	
p-BrC_6H_4	2·04	2·48	2·04	0·28	0·16		
o-MeC_6H_4	2·09	2·51	2·20	0·13	0·13	0·13	$a_{Me} \approx 0·05$ *
m-MeC_6H_4	1·96	2·58	2·14	0·27	0·18	0·27	$a_{Me} = 0·09$
o-$OMeC_6H_4$	2·05	2·63	2·17	0·15	0·15	0·15	
m-$OMeC_6H_4$	2·02	2·54	2·05	0·26	0·15	0·26	
o-OHC_6H_4	1·82	2·65	2·28	0·14	0·14	0·14	
m-OHC_6H_4	1·81	2·57	2·17	0·26	0·15	0·26	
p-OHC_6H_4	1·38	2·53	2·33	0·32	0·14		
o-$NO_2C_6H_4$	2·10	2·56	2·10	0·16	0·16	0·16	$a_N \approx 0·06$ *
m-$NO_2C_6H_4$	2·26	2·44	1·94	0·27	0·17	0·27	$a_N \approx 0·04$ *
p-$NO_2C_6H_4$	2·38	2·50	1·92	0·30	0·15		$a_N = 0·07$
o-PhC_6H_4	2·06	2·60	2·06	†			

* Unresolved splitting, estimated from observed splitting in secondary (A). † Aryl group splittings not resolved.

(b) Coupling constants of secondary radicals from monosubstituted arylsemiquinones

	Coupling constants (G)											
	Secondary radical (A)						Secondary radical (B)					
			Aryl group splittings						Aryl group splittings			
Aryl group	a_3	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituent}}$	a_3	a_5	a_o(H)	a_m(H)	a_p(H)	$a_{\text{substituent}}$
Ph	0·50	1·08	0·54	0·31	0·54		0·67	4·52	0·12	0·12	0·12	
o-FC_6H_4	*						0·68	4·72	†			$a_F = 0·40$
m-FC_6H_4	0·53	1·15	0·53	0·28	0·53	$a_F = 0·08$	0·66	4·64	0·12	0·12	0·12	
p-FC_6H_4	0·51	1·09	0·58	0·30		$a_F = 1·09$	0·66	4·48	0·12	0·12		$a_F = 0·24$
o-ClC_6H_4	0·50	1·27	0·25	0·25	0·20		0·65	4·72	†			
o-BrC_6H_4	0·48	1·23	0·24	0·24	0·17		0·64	4·74	†			
p-BrC_6H_4	0·49	1·13	0·59	0·31			0·67	4·56	0·12	0·12		
o-MeC_6H_4	0·51	0·96	0·28	0·28	0·28	$a_{Me} = 0·11$	0·64	4·56	†			
m-MeC_6H_4	0·52	1·06	0·52	0·32	0·52	$a_{Me} = 0·16$	0·65	4·45	0·12	0·12	0·12	
o-$OMeC_6H_4$	0·52	1·12	0·26	0·26	0·26		0·67	4·65	†			
m-$OMeC_6H_4$	0·54	1·08	0·54	0·29	0·54		0·68	4·56	0·12	0·12	0·12	
o-OHC_6H_4	0·49	0·82	0·24	0·24	0·30		0·64	4·16	†			
m-OHC_6H_4	0·51	0·96	0·51	0·27	0·51		0·66	4·36	0·12	0·12	0·12	
p-OHC_6H_4	0·53	0·53	0·65	0·27			0·63	4·00	0·14	0·10		
o-$NO_2C_6H_4$	*					$a_N = 0·13$	‡					
m-$NO_2C_6H_4$	0·43	1·42	0·60	0·30	0·60	$a_N = 0·09$	‡					
p-$NO_2C_6H_4$	0·45	1·48	0·60	0·30		$a_N = 0·15$	0·70	4·86	0·12	0·12		
o-PhC_6H_4	0·48	1·04	0·30	0·30	0·20	0·10 (2 protons)	0·64	4·44	†			

* Spectra not analysed. † Aryl group splittings not resolved. ‡ Spectra not obtained.

These two broad generalisations have led us to investigate more closely how changes in the dihedral angle affect the coupling constants of protons in the system which give a measure of the conjugation between the two rings.

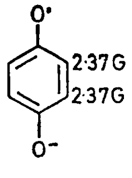
A number of additional points arise from the results given in Tables 1 and 2 and require explanation. (1) Whereas the *meta*-proton coupling constants seem to remain constant with increasing *ortho*-substitution on the aryl group, the *ortho*- and *para*-splittings decrease sharply. (2) For methyl substituents on the aryl group (i) *p*-methyl proton splittings are about the same as those of *p*-hydrogens, (ii) *o*-methyl proton splittings are less than those of *o*-hydrogens, and (iii) *m*-methyl proton splittings are about half those of *m*-hydrogens. (3) Related to points in (2), when the aryl group has two *o*-methyl groups, a *p*-chloro or -methyl group does not affect the resolution. On the other hand in the *o*-chlorophenylsemiquinone the aryl proton splittings are not resolved (due probably to broadening by hyperfine coupling with ^{35}Cl and ^{37}Cl nuclei). (4) In the primary radicals (I), *no* splitting is observed from *o*-methyl protons, from *o*-nitro nitrogen nuclei, or from ^{19}F on the *meta*-position.

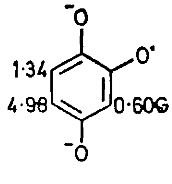
Most of these points can be explained in terms of the increase in dihedral angle between the two rings when the number of *ortho*-substituents is increased.

THEORY

It is not difficult to find a relatively simple, satisfactory model for the situation presented by two rings joined together. In the first place it seems that the coupling constants in the three types of radical bear a simple relationship to each other, *i.e.* the hyperfine splittings of methyl or aryl protons which are associated with the aryl substituents vary in the same way for all three types of radical, as far as one can detect. These splittings in radicals of type (B) are about half those in the corresponding primary radicals which in turn are about half those in the radicals of type (A).

This suggests first that the dihedral angle is probably the same in all three cases and secondly, that the splittings in the aryl group are roughly proportional to the spin density on the carbon atom to which they are attached. Support





for this second possibility comes from the coupling constants in semiquinone itself and the radical from 1,2,4-trihydroxybenzene, *i.e.* expected ratios of aryl proton splittings are type (B) : type (I) : type (A) : : 1·34 : 2·37 : 4·98, *i.e. ca.* 1 : 2 : 4 as observed.

Molecular Orbital Model.—We can consider the delocalisation of the odd electron on to the aryl substituent as being similar to that in benzyl. Thus we look at the fragment consisting of the aryl group and the carbon atom to which it is attached. This problem, together with the variation of spin densities with the angle of twist about the carbon–aryl bond has already been discussed at various levels of sophistication.[3,4] However some understanding is to be gained using simple molecular orbital theory. If the dihedral angle is θ (see Figure 1) then we can resolve the

TABLE 2

(a) Coupling constants of primary radicals from polysubstituted arylsemiquinones

Aryl group	Coupling constants (G)						
				Aryl group splittings			
	a_3	a_5	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{substituents}$
α-Naphthyl	2·16	2·52	2·16			0·10 (2 protons) 0·16 (1 proton)	
2-Me, 3-ClC$_6$H$_3$	2·20	2·52	2·20	*			
2,3-Me$_2$C$_6$H$_3$	2·05	2·52	2·18	0·12	0·12	0·12	
2,4-Me$_2$C$_6$H$_3$	2·05	2·55	2·18	0·13	0·13		$a_{Me(o)}$ = 0·13
2,5-Me$_2$C$_6$H$_3$	2·05	2·55	2·17	0·12	0·12	0·12	
2,6-Me$_2$C$_6$H$_3$	2·10	2·50	2·26		0·15		$a_{Me(o)}$ ~ 0·05 †
2-Me,6-ClC$_6$H$_3$	2·14	2·50	2·18		0·13		
2,6-Cl$_2$C$_6$H$_3$	2·10	2·50	2·42		~0·10		
2,6-Me$_2$,4-ClC$_6$H$_2$	2·20	2·48	2·20		0·15		$a_{Me(o)}$ ~ 0·05 †
2,6-Me$_2$,4-BrC$_6$H$_2$	2·20	2·49	2·20		0·14		$a_{Me(o)}$ ~ 0·05 †
2,4,6-Me$_3$C$_6$H$_2$	2·11	2·54	2·26		0·16		$a_{Me(o)}$ ~ 0·04 †
2,4,6-Me$_3$, 3-BrC$_6$H	2·16	2·50	2·16		0·11		

* Aryl group splittings not resolved. † Unresolved splitting, estimated from observed splitting in secondary (A).

(b) Coupling constants of secondary radicals from polysubstituted arylsemiquinones

Aryl group	Coupling constants (G)											
	Secondary radical (A)						Secondary radical (B)					
			Aryl group splittings						Aryl group splittings			
	a_3	a_6	a_o(H)	a_m(H)	a_p(H)	$a_{substituent}$	a_3	a_5	a_o(H)	a_m(H)	a_p(H)	$a_{substituent}$
α-Naphthyl	0·53	1·16				0·23 (2 protons) 0·34 (1 proton)	0·64	1·60	†			
2-Me, 3-ClC$_6$H$_3$	*						0·64	4·64	†			
2,3-Me$_2$C$_6$H$_3$	0·48	1·10	0·24	0·24	0·24		0·64	4·48	†			
2,4-Me$_2$C$_6$H$_3$	*					$a_{Me(o)}$ = 0·10	0·64	4·52	†			
2,5-Me$_2$C$_6$H$_3$	*						0·64	4·52				
2,6-Me$_2$C$_6$H$_3$	0·51	1·08		0·31		$a_{Me(o)}$ = 0·09	0·63	4·52		0·08		
2-Me, 6-ClC$_6$H$_3$	0·54	1·18		0·30			0·56	5·86	†			
2,6-Cl$_2$C$_6$H$_3$	0·54	1·38		0·27			1·20	5·16	†			
2,6-Me$_2$, 4-ClC$_6$H$_2$	0·51	1·08		0·30		$a_{Me(o)}$ = 0·09	0·63	4·62	†			
2,6-Me$_2$, 4-BrC$_6$H$_2$	0·50	1·09		0·30		a_{Me} = 0·09	0·64	4·62	†			
2,4,6-Me$_3$C$_6$H$_2$	0·49	1·00		0·32		$a_{Me(o)}$ = 0·08 $a_{Me(p)}$ ~ 0·00	0·65	4·52		0·09		
2,4,6-Me$_3$, 3-BrC$_6$H	*						0·64	4·60	†			

* Spectra not analysed or resolved. † Aryl group splittings not resolved.

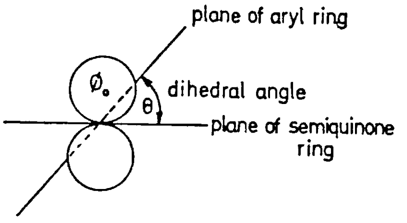


FIGURE 1

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[3] J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725.

[4] W. J. Van den Moek, B. A. C. Rousseeuw, J. Smidt, W. G. B. Huysmans, and W. J. Mijs, *Chem. Phys. Letters*, 1972, **13**, 429.

$2p$- orbital of the adjacent carbon atom in the semiquinone ring into two parts, one, $\phi_0 \cos\theta$, which has the same symmetry as the π orbitals of the aryl substituent, and the other, $\phi_0 \sin\theta$, which has interactions only with the σ orbitals of the aryl group (see Figure 2). Spin density is therefore transmitted effectively *via* two distinct routes and we can write the hyperfine splittings as a simple sum of two terms [equation (1)].

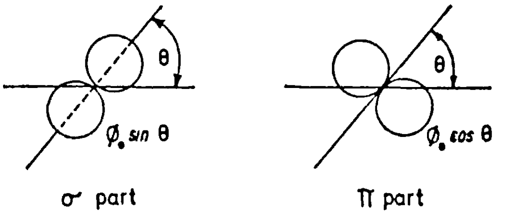

FIGURE 2

$$\begin{aligned} a(\theta) &= a_\pi(\theta) + a_\sigma(\theta) \\ &= a_\pi(0)\cos^2\theta + a_\sigma(90^\circ)\sin^2\theta \qquad (1) \end{aligned}$$

We are interested in calculating the order of magnitude of the splittings and can estimate $a_\pi(0)$ and $a_\sigma(90^\circ)$ either empirically, or theoretically using the parameters shown in Figure 3, which have been shown to account for a variety of coupling constants in n.m.r. spectra[5] and for certain effects in elimination reactions.[6] In both cases it is π interactions between bonds on adjacent atoms which are mainly responsible for the spin delocalisation. If we neglect differences in coulomb integrals the odd electron goes into a non-bonding orbital.

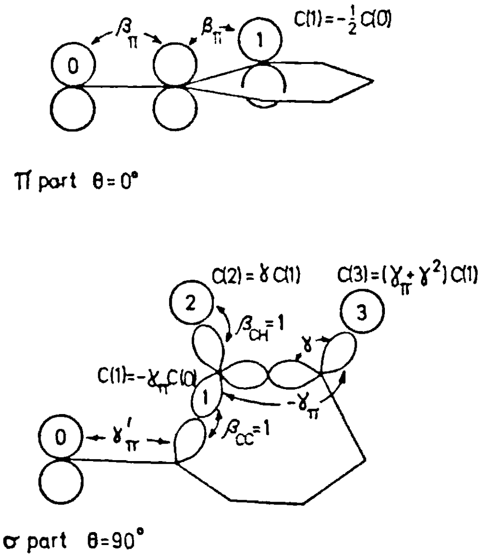

FIGURE 3 Some of the orbitals involved in extreme conformations, with the appropriate resonance integrals and coefficients

It has been found that values $\gamma_\pi \approx 1/4$, $\gamma \approx 1/4\sqrt{2}$, for the resonance integrals, roughly reproduce the coupling constants in vinyl and in phenyl (in the case of the *ortho*- and *meta*-protons). We use formula (2) for the splitting

$$a_H(\sigma) = 508\rho_H \qquad (2)$$

where ρ_H = spin density in the hydrogen 1s orbital.

This corresponds to an effective atomic number of hydrogen of unity. In the case of the π system we get the same formula as for benzyl [$a_{CH_2} = 16{\cdot}5$, $a_o(H) = 4{\cdot}9$, $a_m(H) = 1{\cdot}5$, $a_p(H) = 6{\cdot}1$ G], *i.e.* $a^\pi(H) = -28\rho_C$ where ρ_C = spin density in adjacent carbon p_π orbital. To be realistic we shall use the coupling constants in free benzyl to give us the π contribution and for the various kinds of proton we get the relationships (3)—(8) for the dependence on dihedral angle, for a given spin density ' ρ ' on the ' benzylic ' carbon.

for the π part:

$$\textit{ortho:}\ a_o^\pi(H) = -8{\cdot}75\,\rho\cos^2\sigma \approx -a_o^\pi(CH_3) \qquad (3)$$

$$\textit{meta:}\ a_m^\pi(H) = +2{\cdot}6\,\rho\cos^2\theta \approx -a_m^\pi(CH_3) \qquad (4)$$

$$\textit{para:}\ a_p^\pi(H) = -10{\cdot}5\,\rho\cos^2\theta \approx -a_p^\pi(CH_3) \qquad (5)$$

for the σ part:

$$a_o^\sigma(H) = +0{\cdot}95\,\rho\sin^2\theta \approx +a_o^\sigma(CH_3) \qquad (6)$$

$$a_m^\sigma(H) = +2{\cdot}54\,\rho\sin^2\theta \qquad (7)$$

$$a_p^\sigma(H) = 0 \approx a_m^\sigma(CH_3) \approx a_p^\sigma(CH_3) \qquad (8)$$

Only the value of ρ is different for the three types of radicals and to estimate it we use the coupling constants in the corresponding methyl substituted radicals[1] using $Q_{CH_3} \approx 30$ G, *i.e.* from methylsemiquinone in primary (I) $a(CH_3) = 2{\cdot}12$, in secondary ' (A) ', $a(CH_3) = 5{\cdot}12$, and in secondary ' (B) ', $a(CH_3) = 0{\cdot}95$ G.

For our purposes, changes in ' ρ ' with the substituent in the aryl ring are small, and for obtaining orders of magnitude, we can equate $a(H)$ with $a(CH_3)$. We shall go through with the calculation only for secondary radicals type ' (A) ', since these have the largest splittings.

The variation of proton splittings within the aryl group in the type (A) radicals is therefore given by equations (9)—(13). One might have expected the dihedral angle in phenylsemiquinone to be of the order of 45°, that in the mono-*ortho*-substituted phenylsemiquinones to be 60° or more, and that in the 2,6-disubstituted phenylsemiquinones to be close to 90°. It is interesting therefore to compare the predicted couplings for these angles with those observed for the type (A) radicals when the aryl substituent is one of the methyl phenyl groups.

$$a_o(H) = -1{\cdot}4\cos^2\theta + 0{\cdot}16\sin^2\theta \qquad (9)$$

$$a_o(CH_3) = +1{\cdot}4\cos^2\theta + 0{\cdot}16\sin^2\theta \qquad (10)$$

$$a_m(H) = 0{\cdot}44\cos^2\theta + 0{\cdot}42\sin^2\theta \qquad (11)$$

$$a_m(CH_3) = -0{\cdot}44\cos^2\theta \qquad (12)$$

$$a_p(H) = a_p(CH_3) = -1{\cdot}75\cos^2\theta \qquad (13)$$

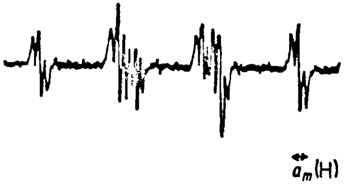

FIGURE 4 E.s.r. spectrum of the primary radical 2,6-dimethylphenylsemiquinone in 50% aqueous EtOH

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[5] W. T. Dixon, *J. Chem. Soc.* (*A*), 1967, 1879.
[6] W. T. Dixon, *Tetrahedron*, 1968, **24**, 5509.

DISCUSSION

From Table 3 we can see that the theory does account quite well for the variation of the various coupling constants, the most significant deviations from predicted behaviour being that of *o*-methyl proton coupling constants. This might have been expected since distortion is most likely to occur at the *ortho*-position[7] (bond bending of C–CH_3). From the theoretical point of view this simple approach gives much the same variations with dihedral angle as do more sophisticated theories. ' σ Spin delocalisation ', responsible for coupling constants when the angle is 90°, arises mainly from π type interactions involving the carbon hybrid orbitals each of which has 2/3 *p* character which can be resolved into part along the adjacent C–C bond and part perpendicular to it. In fact the π interactions between carbon sp^2 hybrid orbitals in ethylene are half the magnitude of the resonance integral assigned to the π bond, so they are by no means negligible.

TABLE 3

Comparison of calculated coupling constants of protons associated with aryl substituents with some of those observed for secondary radicals type (A) (in gauss)

	θ = 45°	Ar ≡ *p*-MeC_6H_4	Ar ≡ *m*-MeC_6H_4	θ = 60°	Ar ≡ *o*-MeC_6H_4	θ = 90°	Ar ≡ 2,6-$Me_2C_6H_3$	Ar ≡ 2,4,6-Me_3C_6H
a-(H)	(−) 0·62	0·58	0·52	(−) 0·23	0·28	(+) 0·16		
a-(CH_3)	(+) 0·78			(+) 0·47	0·11	(+) 0·16	0·09	0·08
a–(H)	(+) 0·43	0·31	0·32	(+) 0·42	0·28	(+) 0·42	0·31	0·32
a–(CH_3)	(−) 0·22		0·16	(−) 0·11		0		
a-(H)	(−) 0·87		0·52	(−) 0·45	0·28	0	0	
a-(CH_3)	(+) 0·87	0·58		(+) 0·45		0		0

meta-*Proton Splittings*.—Out of the theory and also from the results comes the fact that the *meta*-proton splittings are remarkably constant throughout the various series of aryl substituents studied. This has also been observed in aryl nitroxide radicals.[8] This proves that the coupling constant must have the same *sign* at all dihedral angles. Since in the near perpendicular conformations these splittings arise effectively from hyperconjugation, *i.e.* direct transmission of spin density, the sign should be *positive*. This means that if we accept the spin polarisation mechanism in π type radicals we are led to confirm empirically that the spin density in the *meta*-carbon $2p_\pi$ orbital must be *negative*.

Dihedral Angles.—The disappearance of hyperfine splitting due to *ortho*- or *para*-protons or methyl protons, in the primary and secondary type (B) radicals, together with appropriately low values in the secondary type (A) radicals, confirms that when there is a 2,6-disubstituted aryl ring, the dihedral angle between the two rings is close to 90°. Similarly when there is no *ortho*-substituent on the aryl ring, the angle, by comparison with theory, is apparently of the order of 45°. With a single *ortho*-substituent the situation is intermediate between these two.

Substituent Effects.—When substituents are in the *para*-position, quite definite effects are observed in the coupling constants of protons attached to the original semiquinone ring. When the same substituents are in either the *ortho*- or in the *meta*-positions of the aryl ring, they have very little effect on the spin densities around the semiquinone ring. This is because, in the latter case, there is insufficient conjugation and in the former, presumably, there is less conjugation due to an increased dihedral angle. The most obvious case is that when the substituent on the aryl group is hydroxy (see Table 1) but other cases (*e.g.* NO_2) show similar relationships. The direction of effects induced by substituents on the aryl ring have been discussed already but what is important in the light of the present evidence is that the effects of a given substituent must be largely determined by the relative configuration of the π electron system, *i.e.* the effects of substituents are transmitted *only by the π electron system*. This point is usually assumed but seldom proved so directly. The reason why transmission of polar effects or of spin density is inefficient in the σ framework is because the σ bonds are so strong that they effectively damp out the effects of different polar groups.

^{19}F *Splittings*.—Two points stand out here; first the ^{19}F splitting in the *o*-fluoro-derivative is unexpectedly large, compared with either the *p*-fluoro case, or with the *o*-proton splitting which in other systems is usually about half the corresponding ^{19}F coupling constant. Secondly, the coupling of a *m*-fluorine nucleus could only be resolved in the secondary type (A) radical spectrum. Both of these points can be explained by the fact that when fluorine is attached to a π system, the ^{19}F coupling constants are thought to be of opposite sign to corresponding proton splittings[9] and has been proved in some cases, *e.g.* by n.m.r. contact shifts in stable nitroxide radicals.[10] This is so because spin density can get directly onto the fluorine atom *via* the F($2p_\pi$) orbital. Similarly in the case of β-fluorine coupling[10,11] spin density is transmitted onto a F($2p_\sigma$) orbital, presumably also giving rise to a *positive* contribution to the hyperfine splitting. The result of these two effects is that $a_\pi(^{19}F)$ and $a_\sigma(^{19}F)$ have the same sign

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[7] W. T. Dixon, M. M. Harris, and R. Z. Mazengo, *J. Chem. Soc.* (*B*), 1971, 775.

[8] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

[9] A. Hudson and J. E. W. Lewis, *Mol. Phys.*, 1970, **19**, 241.

[10] H. J. Jakobsen, T. E. Peterson, and K. Torssell, *Tetrahedron Letters*, 1971, 2913.

[11] D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 4486.

for *o*-fluorine but have opposite signs in the case of *m*-fluorine nuclei, because in the π part there is negative spin density derived from the *m*-carbon $2p_\pi$ orbital. From our calculations above $a_\pi{}^m$ and $a_\sigma{}^m$ are approximately equal for hydrogen nuclei and of the same sign, *i.e.* for an angle of *ca.* 45°. For fluorine nuclei in the *meta*-position these two contributions would be expected also to have the same magnitude (*i.e.* about twice the proton splittings) but of opposite sign, so they cancel so effectively that the resultant splitting can be resolved only in the spectrum from the secondary radical type (A).

For *o*-fluorine, the two contributions are both positive and add to each other giving a comparatively large coupling constant.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E4 instrument. To obtain the primary radicals a solution of the arylhydroquinone (0·01M) in ethanol was mixed with an equal volume of 1% sodium hydroxide solution, both flow and static methods being used. The secondary radicals were obtained by adding an aqueous solution of the hydroquinone (0·05M) to an equal volume of 15% sodium hydroxide. A mixture of the two secondary radicals was initially obtained, but on leaving the solutions the spectra from the type (B) radical decayed leaving a pure spectrum from type (A). Since the overlap of the spectra from (A) and (B) was, at the most, very small, both could be analysed.

Materials.—The arylquinones, some of which were new compounds, were obtained by direct arylation of *p*-benzoquinone via the diazonium salts according to the method of Brassard and L'Écuyer.[12]

The extra steric strain in the *ortho*-substituted arylquinones lowered the m.p. in these compounds and they were initially produced as oils. They were obtained pure by repeated crystallization from light petroleum (at *ca.* −50 °C) until their m.p.s were sharp and the e.s.r. spectra did not reveal impurities.

[3/512 *Received*, 12*th March*, 1973]

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[12] P. Brassard and P. L. L'Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

The Electron Spin Resonance Spectra of Naphthoxyl Radicals

By **William T. Dixon,*** **Wendy E. J. Foster**, and **David Murphy**, Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

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PERKIN TRANSACTIONS II

1973

The Electron Spin Resonance Spectra of Naphthoxyl Radicals

By **William T. Dixon,* Wendy E. J. Foster,** and **David Murphy,** Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

The e.s.r. spectra of α- and of β-naphthoxyl radicals have been obtained and analysed. Unambiguous assignments of the coupling constants have been found by getting spectra from a number of substituted naphthols and these have been confirmed by generating radicals from the dihydroxynaphthalenes in acid solution and analysing the corresponding e.s.r. spectra.

THE e.s.r. parameters of α- and of β-naphthoxyl radicals are of intrinsic interest because they indicate features about the electronic structure of these species which are simple extensions of phenoxyl or, for that matter, of benzyl radicals. However the e.s.r. spectra of neither α- nor of β-naphthoxyl have until now been obtained in resolvable form so the two sets of proton coupling constants have not been available. The e.s.r. spectra of both radicals were obtained by Stone and Waters[1] in 1964 but the signal-to-noise ratio was unfavourable and analysis was not possible. Using essentially the same technique (*i.e.* the oxidation of naphthols by ceric ion) we have been able to increase the intensity of these two spectra by a factor of 10 or more and have thus been able to resolve and to analyse them. We achieved this by modifying the coaxial mixing device[2] so that the reactant

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[1] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.
[2] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

solutions mixed virtually inside the cavity of our Varian E4 spectrometer. We estimate a 'dead time' of *ca.* 1 ms. The signals were largest at the maximum flow rate we could achieve (*ca.* 15 ml s^{-1}) so it appears that naphthoxyl radicals are at least as unstable as phenoxyl radicals and the second ring contributes little towards their stability under the conditions used

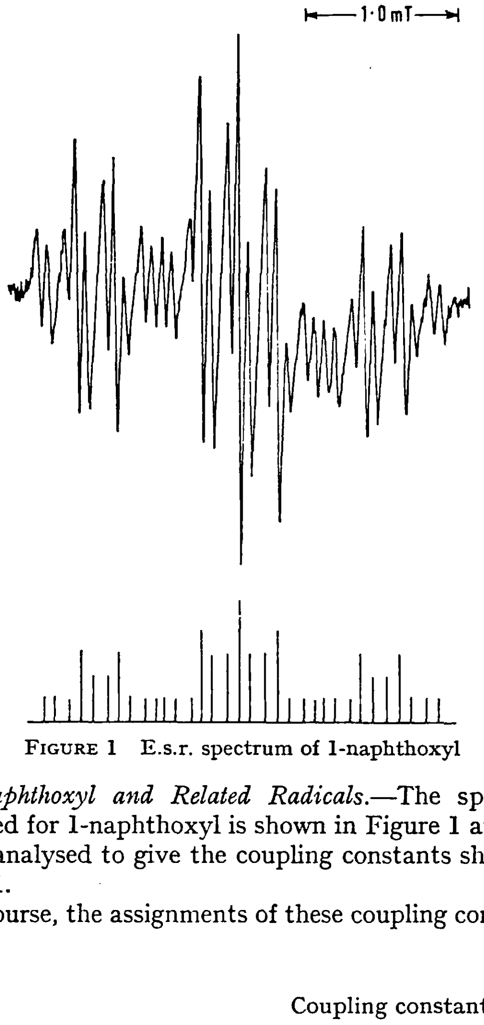

FIGURE 1 E.s.r. spectrum of 1-naphthoxyl

1-*Naphthoxyl and Related Radicals.*—The spectrum obtained for 1-naphthoxyl is shown in Figure 1 and was easily analysed to give the coupling constants shown in Table 1.

Of course, the assignments of these coupling constants to particular protons is ambiguous in the first instance, but can be tentatively made by comparison with the simple Huckel theory for the corresponding benzyl-type radical, or, since most of the odd electron density is on the rings and not on the oxygen (from the magnitude of the coupling constants) by comparison with the π electron radical formed by eliminating C-1. In either case the predicted odd electron densities are in the same ratios. A rough rule for getting negative spin densities which more or less inevitably appear when Huckel theory leads to predictions of zeros, is: the negative spin density at a position where the simple theory predicts zero, is approximately proportional to the adjacent positive spin density. By comparison then with the *meta*-splittings in phenoxyl we are led to the assignment shown, with some ambiguity in the 6- and 8-positions.

TABLE 1

Coupling constants (in mT) in α-naphthoxyl radicals

Substituents in starting material	1-OH	1-OH 2-CO_2H	1-OH 5-CO_2H [b]	1-OH 7-CO_2H [b]	1-OH 5-OMe [c]	1-OH 4-SO_3^-	1-OH 8-SO_3^- [d]	Assigned positions	Huckel MO spin density
Observed coupling constants	1·075	1·04	1·075	1·10	1·10		1·075	4	4*x*
	0·825		0·825	0·85	0·725	0·875	0·875	2	4*x*
	0·25	0·29	0·25		0·275	0·25	0·20	7	*x*
	0·25	0·29		0·25		0·25	0·20	5	*x*
	0·175	0·09	0·21	0·20	0·15	0·25	0·20	3	0
	0·065	0·09	0·09	0·05	0	0·075	0	6	0
	0 [a]	0	0·06	0·05	0	0		8	0

[a] Limit of resolution ~0·04 mT. [b] Ref. 4. [c] Ref. 5. [d] Ref. 6.

Although the agreement with such a simplified theory is in many ways very satisfactory, we felt it necessary to confirm the assignments empirically, the more so since the splittings bear almost no relationship with those observed in nitroxyl radicals containing naphthyl groups.[3] The results from a number of substituted 1-naphthols which gave rise to well resolved e.s.r. spectra are shown in Table 1 and evidently confirm the picture we have given.

A point of interest here is that the substituent groups do not seem to alter the general odd electron density very much.

2-*Naphthoxyl and Related Radicals.*—A similar exercise was undergone for 2-naphthoxyl and some of its derivatives, and though in general the spectra were not quite well resolved as in the 1-naphthoxyl, they could be analysed easily to give a consistent set of results leading to the assignments shown.

Once again the substituents did not seem to affect the odd electron density very much. The main deviations from what might be expected from a simplified molecular orbital model such as that used for 1-naphthoxyl are that the coupling constants of protons on 6- and 8-positions are rather large and the splitting of the 3-proton is rather small. We might attribute this to the relative fixation of double bonds across C-1 and -2 and across similar pairs of carbon atoms, in the naphthalene skeleton. The 6-position which is furthest from the oxygen atom has the highest spin density, apart from that on the 1-position, and this can be explained from simple molecular orbital theory in terms of the short C-7–C-8 bond (resonance integral β), *i.e.* in the non-bonding orbital $\beta\text{C-8} + \beta'\text{C-6} = 0$. But the C-7–C-8 bond is shorter

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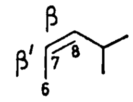
[3] J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J.C.S. Perkin II*, 1973, 718.

[4] F. A. Royle and J. A. Schedler, *J. Chem. Soc.*, 1923, 1641.

[5] C. A. Naylor and J. H. Gardner, *J. Amer. Chem. Soc.*, 1931, **53**, 4109.

[6] G. Heller, *Z. anorg. Chem.*, 1928, **41**, 171.

than the C-6–C-7 bond implying that β > β′ and hence that $(C\text{-}6)^2 > (C\text{-}8)^2$.



Radicals from Dihydroxynaphthalenes.—Some further interesting points come out of the study of radicals formed by the oxidation of dihydroxynaphthalenes by ceric ion. In most cases good e.s.r. spectra were obtained, but it is clear that the radicals are not particularly stabilised and that they were just as transient in the acidic oxidation conditions as were the naphthoxyl radicals themselves.

TABLE 2

Coupling constants (in mT) in β-naphthoxyl radicals

Substituents in starting material	2-OH	2-OH 1-CO_2H	2-OH 3-CO_2H	2-OH 3-OMe[a]	2-OH 6-OMe[b]	2-OH 7-OMe[a]	2-OH 1-SO_3^-	2-OH 6-SO_3^-	2-OH 7-SO_3^-	2-OH 6-SO_4^- 8-SO_3^-	Assigned positions	Huckel MO spin densities
Observed coupling constants	1·075		1·04	0·95	0·975	1·05		1·1	1·075	1·065	1	$4x$
	0·54	0·55	0·52	0·55		0·525	0·55		0·55		6	x
	0·43	0·425	0·44	0·45	0·375	0·4	0·45	0·425	0·425		8	x
	0·145	0·15			0·25	0·15	0·15	0·15	0·15	0·2	3	x
	0·145	0·15	0·16	0·10	0·125	0·125	0·15	0·15	0·125	0·15	5	0
	0·12	0·125	0·08	0·05	0·125		0·125	0·15		0·15	7	0
	0	0	0·08	0·05	0	0	0	0	0	0·05	4	0

[a] Ref. 7. [b] Ref. 8.

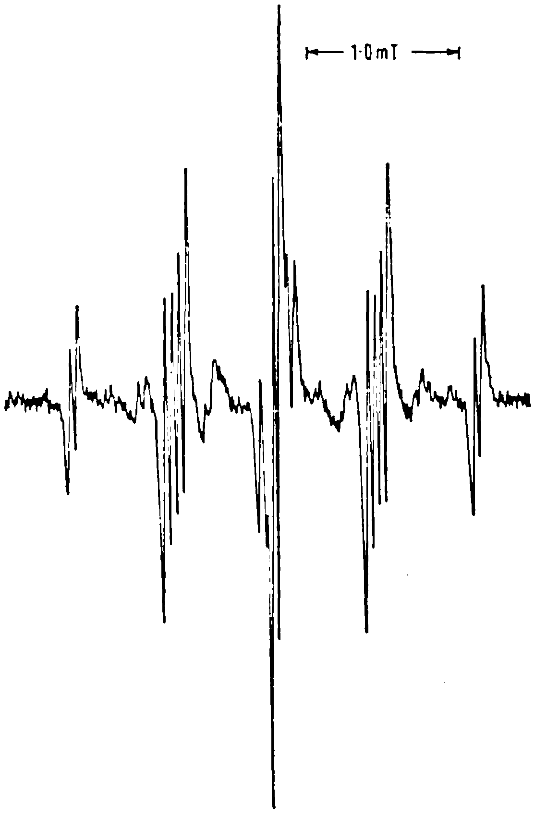


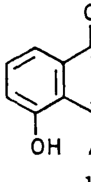
FIGURE 2 E.s.r. spectrum of radical from 4,5-dihydroxynaphthalene-2,7-disulphonic acid

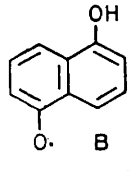
In most cases spectra indicating a rather smoothed out odd electron density were obtained (see Figure 2) showing a change similar to that in going from phenoxyl to semiquinone.

In Table 3 we see that when the two hydroxy-groups are conjugated with each other (*i.e.* one can draw quinonoid structures) the coupling constants are relatively small whereas in the other cases larger couplings may appear.

In three cases the results appear to be anomalous, *i.e.* when starting from 2,3-, 1,6-, and 1,7-dihydroxynaphthalenes, in the sense that the coupling constants lack the expected symmetry. With the 1,6- and 1,7-isomers one can justify the result to some extent by suggesting that in each case there is competition between oxidations at a 1- or a 2-position and that the former is favoured. The second hydroxy-group can then be regarded as simply a perturbing substituent. We can rationalise the spectrum from the 2,3-isomer in an analogous way although here the oxygen atoms seem to be in identical positions.

Connection between Radicals from Mono- and Dihydroxynaphthalenes.—Tables 1—3 contain further information which throw light on the apparent anomalies just discussed. In the acidic conditions we would expect the hydroxy-groups to be protonated so that on oxidation say, of 1,5-dihydroxynaphthalene, the initial radical formed would be either A or B.


A


B

Once these naphthoxyl radicals are formed we would expect rapid proton exchange with the acidic medium, leading to rapid equilibration of the two isomers. The result of this is that an average coupling constant would be observed for each proton (see Figure 3). This type of

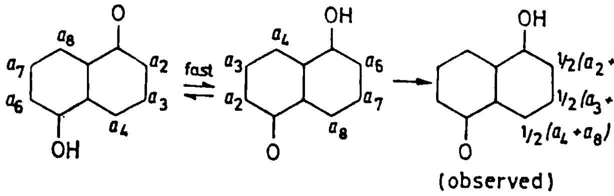


FIGURE 3 Averaging of coupling constants due to rapid proton exchange

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[7] P. Friedlaender, *Monatsh.*, 1902, **23**, 513.

[8] D. F. Downing and D. Woodcock, *J. Chem. Soc.*, 1958, 531.

situation has been observed in the case of *ortho*- and *para*-semiquinones.[12]

As we have seen from Tables 1 and 2, substituents have but little effect on coupling constants so we might use the coupling constants in the two parent naphthoxyl radicals to estimate the average. These are compared with the splittings observed in Table 4 and the agreement is very convincing.

The so-called anomalous cases can now be seen in a different light. An obvious possibility is that the proton exchange is relatively slow in these cases and that the β-oxygen atoms are effectively protonated for a long time, on the scale of the e.s.r. experiment. What factors are involved here we cannot say exactly at the moment but in the case of the 2,3-isomer it is likely that some sort of complexing takes place with the metal ion present influencing the proton exchange rate. In the other cases, the radicals from 1,6- or 1,7-dihydroxynaphthalene, it appears that an α-naphthoxyl type of radical is preferred. The presence of a 3-sulphonate group does not change this tendency.

The excellent agreement between calculated and observed splittings shown in Table 4 reinforces our confidence in the assignments of the coupling constants in α- and β-naphthoxyl both from the point of view of their magnitudes and of their signs.

TABLE 3

Coupling constants (in mT) in spectra from dihydroxynaphthalenes

1-OH [a] 2-OH	1-OH 2-OH 4-SO_3^-	1-OH 3-OH	2-OH 3-OH	1-OH 4-OH	1-OH 5-OH	1-OH 6-OH	1-OH 7-OH [b]	1-OH 7-OH 3-SO_3^- [c]	1-OH 8-OH	1-OH, 8-OH 3-SO_3^- 6-SO_3^-	2-OH 6-OH	2-OH 7-OH
	0·20	1·19	0·95	0·325	0·54	1·075	0·95	0·925	0·70	0·70	0·41	0·74
	0·125	0·47	0·475	0·325	0·54	0·875	0·675	0·70	0·70	0·70	0·41	0·74
	0·125	0·36	0·525	0·081	0·35	0·30	0·225	0·25	0·575	0·613	0·24	0·32
	0·05	0·36	0·125	0·081	0·35	0·20	0·10		0·575	0·613	0·24	0·32
		0·11	0·125		0·06	0·20	0·10	0·10	0·125			0·07
			0·125		0·06		0·10	0·10	0·125			0·07
									0·05 [d]	0·05 [d]		

[a] Spectrum very poor. [b] Ref. 9. [c] Ref. 10. [d] Coupling with H-bonded proton characteristic of 1,8-derivatives.[11]

TABLE 4

Comparison of observed and calculated spectra for radicals from some dihydroxynaphthalenes (in mT)

1,3			1,4			1,5		
Calc.	Obs.	Position	Calc.	Obs.	Position	Calc.	Obs.	Position
0·49	0·47	2	0·323	0·325	2	0·38	0·35	2
1·07	1·19	4	0·125	0·08	5	0·035	0·06	3
0·34	0·36	5	0·09	0·08	6	0·54	0·54	4
−0·09	0·11	6						
0·39	0·36	7						
−0·07	0	8						

2,6			2,7			1,8		
Calc.	Obs.	Position	Calc.	Obs.	Position	Calc.	Obs.	Position
0·46	0·41	1	0·75	0·74	1	0·54	0·575	2
0	0	3	0·34	0·32	3	−0·125	0·125	3
0·215	0·24	4	−0·07	0·07	4	0·67	0·70	4

EXPERIMENTAL

E.s.r. Spectra.—The spectra were observed using a Varian E4 spectrometer. The naphthoxyl radicals were obtained using a flow system modified so that the mixing took place virtually in the cavity of the spectrometer. Naphthols were dissolved if possible in a small amount of hot water or, if insoluble, in the minimum amount of ethanol, and the solution diluted with water to a concentration of *ca.* 10^{-3}M. These solutions were run against ceric sulphate (BDH reagent grade) at a concentration of 2×10^{-3}M in 0·5M-sulphuric acid.

Materials.—All naphthols and substituted naphthols used were purified by the usual methods. Their physical constituents agreed well with those of the literature.

[3/1542 *Received, 23rd July,* 1973]

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[9] H. T. Bucherer and K. Seyde, *J. prakt. Chem.*, 1907, **75**, 249.

[10] J. Boeseken, *Rec. Trav. chim.*, 1939, **58**, 3.

[11] L. H. Piette, M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore, and P. J. Scheuer, *J. Phys. Chem.*, 1967, **71**, 29.

[12] I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1967, **12**, 439.

The Identification by Electron Spin Resonance Spectroscopy of Dimeric Species formed in the Autoxidation of Hydroquinone and Quinone

By **Paul Ashworth** and **William T. Dixon,*** Chemistry Department, Bedford College, Regents Park, London N.W.1

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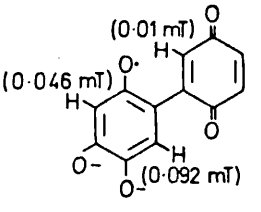
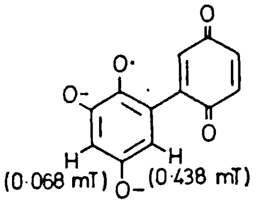
By **Paul Ashworth** and **William T. Dixon**,* Chemistry Department, Bedford College, Regents Park, London N.W.1

Some of the e.s.r. spectra observed during the autoxidation of hydroquinone and quinone appear to arise from the formation of dimeric products in the reaction since these spectra can be obtained from diquinone under similar conditions. The hyperfine splittings in these types of radicals can be explained in terms of the oxidation states of the two quinonoid rings.

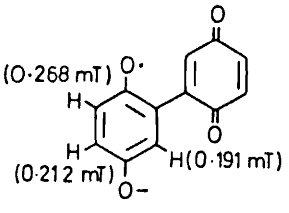
DURING our e.s.r. investigations of the autoxidation of hydroquinone and quinone,[1] we observed what we called ' tertiary radicals,' which, from their e.s.r. spectra, were identified as the dimeric species (IA) and (IB). Radical (IA) had apparently been observed before[2] during the reduction of diquinone by glucose in 10% NaOH, but had been identified as radical (II). We have previously advanced reasons[1] why such an assignment must be incorrect, for under the strongly alkaline conditions employed hydroxylation of the quinone ring invariably occurs giving rise to radicals of type (I). The three doublet splittings observed (0·092, 0·046, and 0·01 mT) are also consistent with (IA) rather than (II).



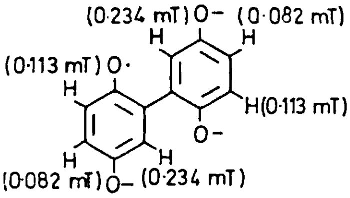
(IA)



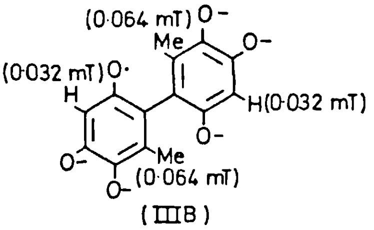
(IB)



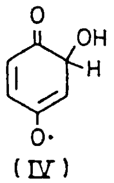
(II)



(IIIA)



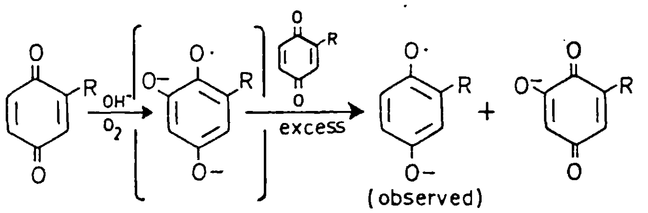
(IIIB)



(IV)

Radicals of type (IIIA) and (IIIB), containing a fully reduced second ring, have been observed[3,4] during the electro-reduction of certain quinones. It is found that the odd electron is shared equally between the two rings (fast spin exchange) even in radical (IIIB), where a high dihedral angle might be expected, and splitting from pairs of equivalent protons is observed in the spectra.

We have now obtained an authentic spectrum of radical (II), in which the e.s.r. coupling constants (0·268, 0·212, and 0·191 mT) are typical of a substituted semiquinone. This spectrum is identical to that obtained by Pedersen[5] during the autoxidation of *p*-benzoquinone, but which was ascribed by him to radical (IV), postulated as the chief intermediate in the hydroxylation process of quinones. However since our spectrum was obtained from diquinone in very dilute alkali, conditions under which only primary radicals are observed,[1] we can be certain that we are correct in our assignment.



Further, from the quinone under the usual conditions for obtaining secondary radicals (10% NaOH), we observed the spectra of (IA) and (IB), previously obtained by us from hydroquinone or quinone under the same conditions. The small doublet splitting of 0·01 mT in the spectrum of radical (IA) is apparently due to coupling with one proton in the quinone ring substituent, and from our knowledge of the relationship between the splittings in primary and secondary radicals we can estimate a small splitting of *ca.* 0·005 mT in radical (II). In fact a splitting of this order was observed in the spectrum obtained by Pedersen, but which we were unable to see due to the limitations of resolution.

We now feel that we have found the correct identity of the radicals associated with the various e.s.r. spectra obtained by us and by other workers during the autoxidations of hydroquinones and quinones. It is interesting that the quinone ring substituent leads to very little delocalisation of the odd electron, whereas the radicals of type (III), containing a fully reduced second ring, exhibit fast spin exchange between the two rings.

[3/1613 *Received*, 31*st July*, 1973]

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[1] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[2] D. C. Reitz, J. R. Hollahan, F. Dravnieks, and J. E. Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

[3] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1964, **41**, 284.

[4] J. Pilar, I. Buben, and J. Pospisil, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3599.

[5] J. A. Pedersen, *J.C.S. Perkin II*, 1973, 424.

MOLECULAR PHYSICS, 1974, VOL. 27, NO. 6, 1709–1710

The E.S.R. spectrum of the tropolonyl radical

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(*Received* 24 *September* 1973)

The E.S.R. spectra of the tropylium radical and of the radical anion of tropone [1], have been studied carefully over the last few years but that of the tropolonyl radical has hitherto eluded detection.

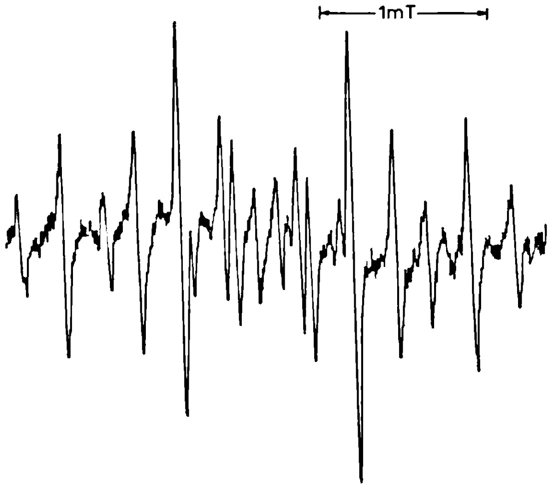
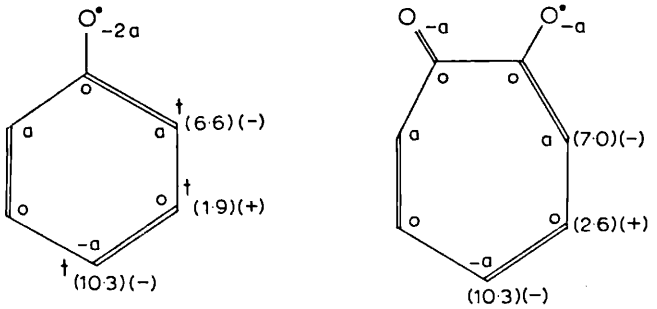


Figure 1. E.S.R. spectrum of the tropolonyl radical.



† Measured in this laboratory.

Figure 2. Skeletons of phenoxyl and of tropolonyl with simplified Hückel m.o. coefficients of the orbital containing the odd electron and the experimental coupling constants in $G = 10^{-4}$ T (in brackets). $\alpha_O = \alpha_C$, and signs are inferred.

Some close chemical resemblances between phenol and tropolone suggest that the latter may undergo oxidation by cerium(IV) ion and that the first intermediate radical might be detectable by means of E.S.R. spectroscopy. We have indeed succeeded in obtaining a relatively intense spectrum of the tropolonyl radical (see figure 1) in a flow system under analogous conditions to those in which phenoxyl could be generated in observable concentrations from phenol [2]. The remarkable similarity between the two sets of coupling constants (see figure 2) suggests that in both cases the radicals resemble pentadienyl and that in simplified m.o. terms, the odd electron occupies an approximately non-bonding orbital symmetrical with respect to the corresponding planes of symmetry perpendicular to the π electron systems.

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[1] PIETRA, F., 1973, *Chemical Reviews*, **73**, 293.
[2] STONE, T. J., and WATERS, W. A., 1964, *J. chem. Soc.*, p. 213.

An Electron Spin Resonance Study of the Autoxidation of Naphthols in the Presence of Hydrogen Peroxide

By **Paul Ashworth** and **William T. Dixon,*** Chemistry Department, Bedford College, Regents Park, London NW1

Reprinted from

JOURNAL
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PERKIN TRANSACTIONS II

1974

An Electron Spin Resonance Study of the Autoxidation of Naphthols in the Presence of Hydrogen Peroxide

By **Paul Ashworth** and **William T. Dixon,*** Chemistry Department, Bedford College, Regents Park, London NW1

A number of radicals have been obtained from polyhydroxylated naphthalenes in alkaline solution by means of autoxidation, and their e.s.r. coupling constants have been measured. A new way of generating radicals derived from naphthalene-1,2-diol is reported in which alkaline hydrogen peroxide is used, and a mechanism for the observed transformation is proposed. Radicals can be obtained from resorcinols in an analogous way.

MANY hydroxylated naphthalene derivatives occur in nature,[1] *e.g.* Vitamins K_1 and K_3, and their formation and behaviour are of great potential interest. It has already been shown that the characterisation of many such compounds can be facilitated by use of the e.s.r. spectra of the corresponding semiquinones,[2] which are formed

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[1] R. H. Thompson, 'Naturally Occurring Quinones,' Academic Press, London, 1971.

[2] L. H. Piette, M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore, and P. J. Scheuer, *J. Phys. Chem.*, 1967, **71**, 29.

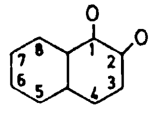
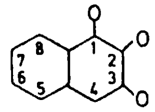
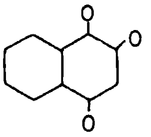
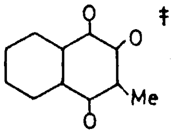
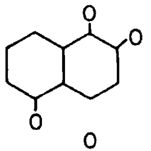
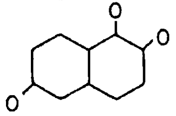
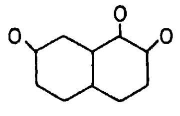
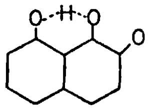
from the parent compounds by autoxidation or reduction, whichever is appropriate. We have prepared solutions of a number of radicals derived from hydroxylated naphthalenes by autoxidation, and have shown that their e.s.r. parameters can be used analytically to identify many of the species thus observed. Of particular interest to us were the radicals formed when hydrogen peroxide was present in the alkaline solutions, because the pattern of hydroxylation was then very different from that observed when oxygen groups are added to the naphthalene nucleus by other means (*e.g.* by using Fremy's salt [3]).

Autoxidation of Naphthalenediols.—In some cases radicals could be generated in alkaline solution by simply shaking in air, but in others no reaction could be detected either from the appearance of the solutions or by means of e.s.r.

Primary radicals are defined as those containing the same skeleton of carbon and oxygen atoms as the starting material. In the cases of the 1,2- and the 1,4-diol, the primary radicals were observed in weak alkali but in the other cases, *i.e.* the 1,7-, 2,3-, 2,6-, and 1,5-isomers, though it was evident that some autoxidation was taking place, only secondary radicals or unresolvable complex spectra were observed. The remaining isomeric diols, in which the oxygen atoms were not 'conjugated' with respect to each other, did not apparently undergo autoxidation, except the 1,3-diol which did give a resolvable spectrum of a secondary radical (*i.e.* containing one more oxygen atom than the primary).

The structures of the various radicals observed were deduced mainly on the basis of production of the same species *via* different chemical pathways, *e.g.* from

TABLE 1

Radical skeleton	Method of generation	Position of oxygen in starting material	Coupling constants (μT)						
			a_3	a_4	a_5	a_6	a_7	a_8	a_H
 †	A B	1,2 1	42	446	28	142	14	130	
	A	2,3		39	0	200	39	184	
 ‡	A	1,2 1,3 1,4 1,2,4	25		13	197	11	154	
 ‡	A	1,4 1,2,4	38 (Me)		26	208	13	151	
	A B	1,2,5 1,5 1,6	98	494		250	16	235	
	A B	2,6 1,6	58	502	140		36	140	
	A B	1,2,7 1,7 2,7	48	497	48	243		102	
	B	1,8	75	460	100	150	100		52

* A, simple autoxidation; B, H_2O_2 + autoxidation. † See M. Adams, M. S. Blois, and R. H. Sands, *J. Phys. Chem.*, 1958, **28**, 774. ‡ See M. R. Das, H. D. Connor, D. S. Leniart, and J. H. Freed, *J. Amer. Chem. Soc.*, 1970, **92**, 2258.

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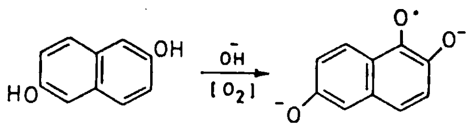
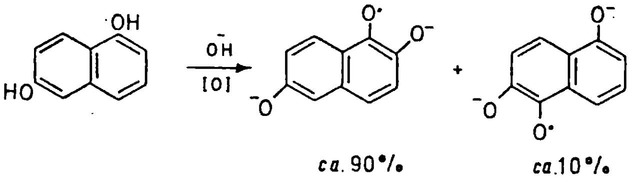
[3] H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, 1971, 249.

different starting materials (see Table 1). In cases where this was not possible we rationalised the spectra on the basis of rules and trends inferred from the better established cases, *e.g.* Scheme 1.



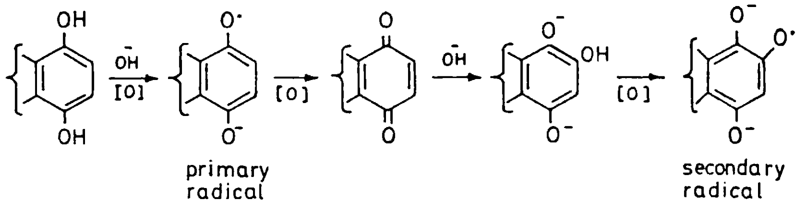
Scheme 1

Radicals obtained in the Presence of Hydrogen Peroxide.—The introduction of hydrogen peroxide into alkaline solutions of hydroquinones or of catechols makes no appreciable difference to the observed e.s.r. spectra of



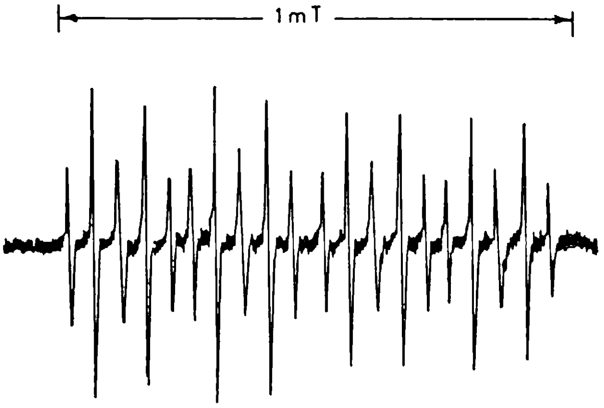
Scheme 2

the semiquinones resulting from autoxidation. However, when hydrogen peroxide was introduced into alkaline solutions of naphthalenediols clear spectra were obtained in every case (*e.g.* see Figure) which correspond to oxygen being added to give eventually a 1,2-naphthosemiquinone derivative (see Table 1). The interesting aspects of these results are that (*a*) the third oxygen atom was never introduced into a 4-position with respect to an α-oxygen atom, and (*b*) the spectra indicate that oxidation occurs preferentially at a β-position. This pattern of substitution calls for an explanation since it is not typical of naphthalene chemistry in general, and we shall offer one after discussing the spectra of further radicals produced in the reactions, usually under more strongly alkaline conditions.



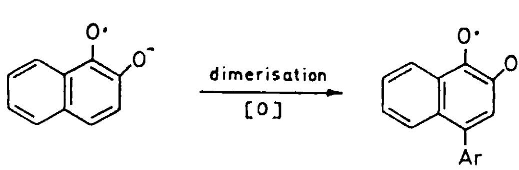
Scheme 3

Further Secondary Radicals and Dimers.—From our previous work on semiquinones[4] we expect secondary radicals to be formed in strong alkali *via* the sequence shown in Scheme 3. This development during the autoxidation applies as much to 1,2- as to 1,4-quinones. However, it seems from our present results that there is an appreciable possibility of dimerisation in the sense of two naphthalene units becoming joined together. Exactly what emerges in the e.s.r. spectrum depends on the balance between this dimerisation[5] and further oxidation. The rule which seems to apply is that radicals dimerise through the positions of highest spin density but the rate of dimerisation depends also on the degree of steric hindrance at that position. For example an intense spectrum of the dimer from naphthalene-1,2-diol (Scheme 4) was observed. In this case there was minimal steric hindrance at the 4-position.

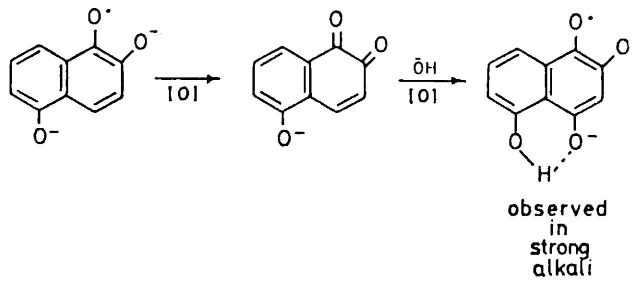


The e.s.r. spectrum of the species obtained from the action of alkaline hydrogen peroxide on naphthalene-2,7-diol

In other cases we can rationalise the results by postulating that steric effects are important in slowing down the dimerisation so that further oxidation of the semiquinone can take place. Thus sometimes steric effects appear to prohibit dimerisation altogether, *e.g.* with naphthalene-1,2,5-triol only the secondary radical was observed in strong alkali (Scheme 5).



Scheme 4



Scheme 5

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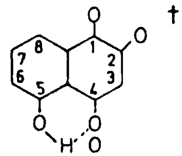
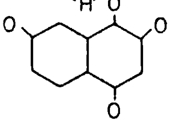
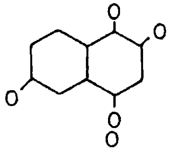
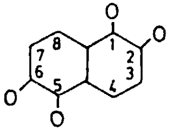
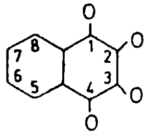
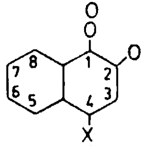
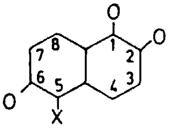
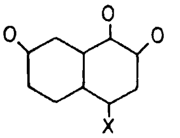
[4] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.
[5] A. I. Scott, *Quart. Rev.*, 1965, 1.

In 1,4-naphthoquinone derivatives, the primary radicals have no positions of high spin density (*i.e.* all the proton coupling constant are less than *ca.* 0·4 mT) and so no dimerisation occurs.

DISCUSSION

The patterns of the sets of coupling constants were much as expected and it is clear that the overall spin distribution is much more affected by a further oxygen atom attached to the skeleton than by an additional aryl or alkyl group. Thus we were able to characterise the dimers without much difficulty, since their coupling constants are similar to those of the monomeric radicals except that one hydrogen atom is missing. As is the case with monocyclic semiquinones, hydroxy-substituents appear to increase spin density on positions *para* to themselves.[4]

TABLE 2

Radical skeleton	Method of generation	Position of oxygen in starting material	Coupling constants (μT)						
			a_3	a_4	a_5	a_6	a_7	a_8	a_H
 †	A	1,2,5	28			260	10	214	39
	A	1,7	60		10	200		164	
	A	1,4,6	40		40		84	150	
	A	1,2,5	33	150			33	150	
	B	2,3			103	73	73	103	
	A	1,2	30		17	120	13	107	
	A	2,6	70	520			40	150	
	B	1,7	62		20	216		80	

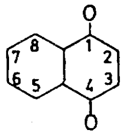
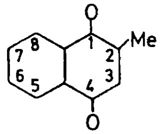
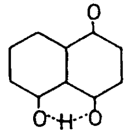
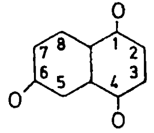
* A, simple autoxidation; B, H_2O_2 + autoxidation. † See ref. 2.

The ease of formation of secondary radicals is similar to that in the autoxidation of catechol or of hydroquinone. The activating effect of the second ring is however illustrated by the formation of a secondary radical from naphthalene-1,3-diol, whereas its monocyclic analogue, resorcinol, is inert under similar conditions.

The autoxidations in the presence of hydrogen peroxide were the most interesting for us, both from the point of view of the mechanism, and because they afforded a way of obtaining a series of 1,2-semiquinones which would otherwise have been difficult to prepare in detectable quantities.

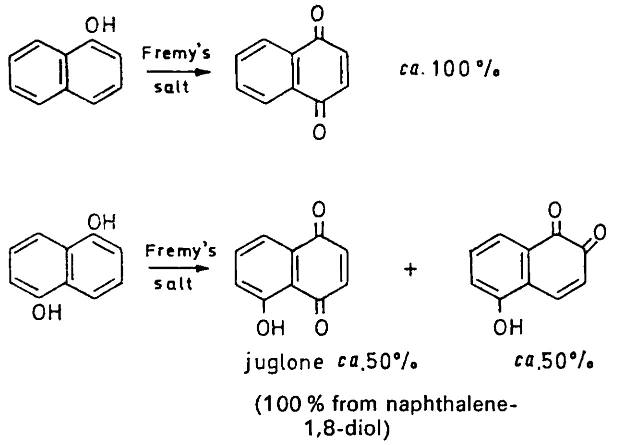
A general observation in these experiments was that, even in the cases when no autoxidation took place in alkaline aqueous solution (as far as one could tell from the absence of colour change or of an e.s.r. signal),

TABLE 3

Radical skeleton	Method of generation *	Position of oxygen in starting material	Coupling constants (μT)						
			a_2	a_3	a_5	a_6	a_7	a_8	a_{Π}
	A †	1,4	324	324	65	58	58	65	
	A ‡	1,4	300 (Me)	235	62	68	68	76	
 §	A	1,4,5	390	270		80	30	112	80
	A	1,4,6	442	278	60		164	0	

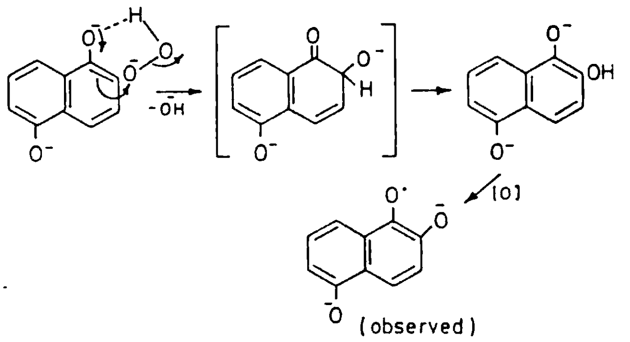
* A, simple autoxidation. † See footnote ‡, Table 1. ‡ Vitamin K_3. § See ref. 2.

resolved e.s.r. spectra were immediately detectable on addition of hydrogen peroxide. This showed that hydrogen peroxide was active at some early stage in the reactions leading to the observed radicals. A second point is that only 1,2-semiquinones were observed, although under the conditions of our experiments 1,4-semiquinones would be long-lived and would also have been observed had they been formed to any appreciable extent. This pattern of reaction products (or rather intermediates in the overall oxidation) is completely different from that observed in the usual radical reactions of naphthols, *e.g.* with Fremy's salt, chromic acid, peracetic acid, *etc.*, in which oxidation occurs preferentially at the 4-position [6] (Scheme 6).



SCHEME 6

In view of the two foregoing points, together with the necessary alkaline conditions, we feel that hydrogen peroxide cannot be involved in a free-radical step and therefore propose a simple reaction between hydrogen peroxide, or its anion HO_2^-, with the ionised naphthol (Scheme 7). The functions of the second ring and a second hydroxy-group seem to be to activate the site of attack. We deduced this point from further experiments, for β-naphthol and various phenols did not react whereas resorcinols and α-naphthol, though they were not autoxidised in alkali, after addition of hydrogen peroxide gave the corresponding semiquinones (Scheme 8).



SCHEME 7

If the mechanism is correct then the lack of attack on the 4-position can be attributed partly to the fixation of the double bonds in the naphthalene skeleton, for the 1,2- and 3,4-bonds are similar in length to the C=C bond in ethylene.[7] The resulting bond alternation

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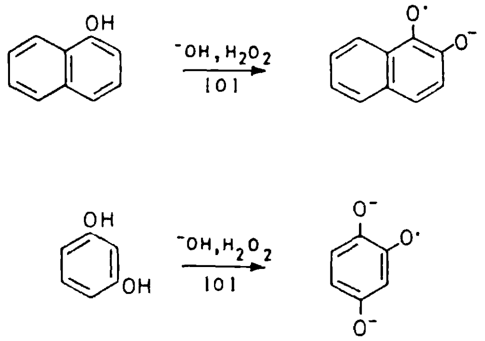
[6] L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 550.

[7] *E.g.* see *Chem. Soc. Special Publ.* No. 18, 'Interatomic Distances,' 1958.

could damp out mesomeric effects markedly in comparison with the situation in benzenoid compounds in which the C–C bonds do not usually vary much in length. Another factor favouring *ortho* attack is the possibility of hydrogen bonding between the hydroperoxy-group and the neighbouring oxygen atoms.



SCHEME 8

If we regard the 1,2-linkage as a double bond, the addition of H_2O_2 or ^-O_2H is similar to an analogous step in the oxidation of purpurogalloquinone by hydrogen peroxide,[8] which involves attack by H_2O_2 on a quinonoid structure; it also resembles the attack on a tertiary carbon atom by peroxide in the oxidation of phthaleins.[9] The main difference here is that the reaction involves the 'reduced' form of the naphthols and not the quinones.

An alternative mechanism involving catalysis by transition metal ions seems unlikely since it does not explain why even activated phenols did not react nor why the presence of an excess of ethylenediamine tetra-acetate in the solutions made no observable difference to the intensities of the spectra obtained with alkaline hydrogen peroxide solutions.

EXPERIMENTAL

Autoxidations were normally carried out in 50% aqueous methanol containing sodium hydroxide (2% w/v), but for the observation of secondary radicals at least 10% sodium hydroxide was required.

Quinones were reduced in 90% dimethylformamide with alkaline dithionite.

In the hydrogen peroxide experiments the solutions contained aqueous 2% alkali and 5% hydrogen peroxide.

The solutions studied were about 10^{-3}M with respect to the naphthalene derivatives.

[3/2305 *Received, 9th November*, 1973]

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[8] P. D. Collier, *J. Chem. Soc.* (*B*), 1968, 1494.

[9] E. McKeown and W. A. Waters, *J. Chem. Soc.* (*B*), 1966, 6679.

Long-range Electron Spin Resonance Coupling Constants in Radical Adducts of Maleic Acid

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London NW1 4NS

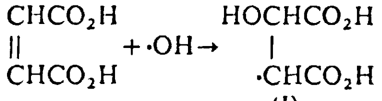
Received 11*th March*, 1974

The e.s.r. spectra of a number of radical adducts of maleic acid have been observed and hyperfine structure arising from γ-, from δ- and from ε-coupling has been revealed. This provides a positive identification of the radicals involved. The origin of the long-range coupling constants is discussed in terms of simple molecular orbital theory and direct magnetic interaction. The difference between spectra observed in acidic and in alkaline conditions, is interpreted in terms of structural changes.

Alkyl or aryl radicals may be trapped by maleic acid,[1, 2] and the short-lived adducts so-formed detected by means of e.s.r. spectroscopy. The sequence of reactions leading to the observed radicals have generally been as follows:

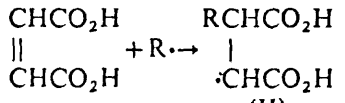
$$\mathrm{Ti^{III}+H_2O_2 \rightarrow Ti^{IV}+\overline{O}H+{\cdot}OH} \qquad (1)$$

$$\mathrm{RH+{\cdot}OH \rightarrow R{\cdot}+H_2O} \qquad (2)$$



$$\begin{matrix}\mathrm{CHCO_2H} & & \mathrm{HOCHCO_2H}\\ \| & +{\cdot}\mathrm{OH}\rightarrow & |\\ \mathrm{CHCO_2H} & & {\cdot}\mathrm{CHCO_2H}\end{matrix} \qquad (3)$$

(I)



$$\begin{matrix}\mathrm{CHCO_2H} & & \mathrm{RCHCO_2H}\\ \| & +\mathrm{R}{\cdot}\rightarrow & |\\ \mathrm{CHCO_2H} & & {\cdot}\mathrm{CHCO_2H}\end{matrix} \qquad (4)$$

(II)

Phenyl adducts have been generated from the corresponding diazonium salts by reduction.[2] In alkaline or neutral solution the reducing species has been $\mathrm{Ti^{III}}$ and in acidic solution the reduction has been achieved by radicals R· formed in reaction (2) where RH is a primary or secondary alcohol or formic acid.

$$\mathrm{PhN_2^+ + [Ti^{III}(edta)] \rightarrow [Ti^{IV}(edta)] + N_2 + Ph{\cdot}}. \qquad (5)$$

It is easy to arrange the conditions so that the consecutive reactions (2) and (4) dominate, and the e.s.r. spectra of the resulting radicals of type (II) consist of four lines. The two coupling constants obtained from each spectrum characterise the adducts but do not positively identify them. These splittings do not, for example, tell us whether or not the species, which has added to the double bond, is the same as that which would have been observed in the absence of maleic acid from the solutions. We now report successful attempts to improve the resolution of the four line spectra, so that in most cases further small splittings appear, which confirm the assumed nature of the adduct radicals.

In the most straightforward cases each of the four lines was split further into a multiplet as appropriate for the number of γ-protons in the adduct. Thus the e.s.r. spectrum of the methyl radical adduct had a small quartet (1 : 3 : 3 : 1) splitting whereas there were small doublet (1 : 1) splittings when either dioxan or ethylenediaminetetra-acetic acid were the " primary " substrates in the $\mathrm{Ti^{III}/H_2O_2}$ system (see table 1). In neutral or in alkaline solution the spectrum of the hydroxyl radical adduct itself has a small doublet splitting.

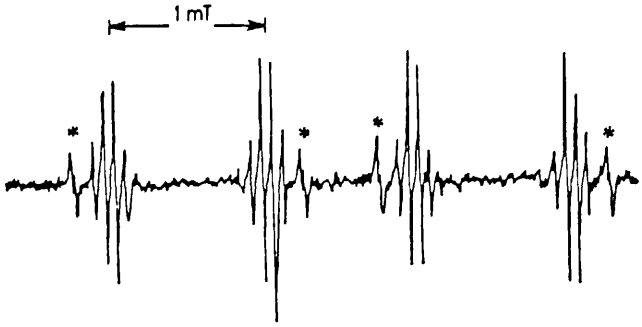
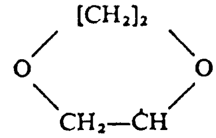


FIG. 1.—E.s.r. spectrum of maleic acid adducts with methyl and hydroxyl (asterisked) radicals.

The spectra obtained from the adducts of radicals of type $RR'\dot{C}OH$ were not so straightforward, since they were less well resolved in neutral or in alkaline solution, but appeared to have small couplings corresponding to the appropriate number of γ- and δ-protons in acid. These " extra " splittings confirm the nature of these radicals. No additional splitting of the four lines was observed in the spectrum ascribed to the phenyl radical adduct, so 2-fluorophenyl was used in the hope that the fluorine splitting might be large enough to observe. In fact a fluorine splitting was observed and it was larger even than that expected from previous studies on aryl semiquinones.[3] All of the results are summarised in table 1.

TABLE 1.—COUPLING CONSTANTS OF RADICALS $RCH(CO_2H)\dot{C}HCO_2H$. NUMBERS OF PROTONS IN BRACKETS

	acid			alkali		
R	$a_\alpha(1)$	$a_\beta(1)$	further splittings	$a_\alpha(1)$	$a_\beta(1)$	further splittings
$\cdot OH$	12.7	20.7	—	15.3	20.2	0.2(1)
$\cdot$(edta—H)†	—	—	—	7.5	19.8	0.9(1) 0.2(N)
$\cdot CH_2OH$	13.7	20.8	0.6(1) 0.3(1)	9.8	20.2	—
$CH_3\dot{C}HOH$	9.5	20.6	0.4(4)	7.5	20.0	0.3(3)
$(CH_3)_2\dot{C}OH$	10.5	20.5	0.3(6)	5.1	20.0	0.3*
$(CH_3)_2COH\cdot CH_2\cdot$	9.0	20.3	*	7.1	19.9	0.6(1) 0.3(7)
$CH_3\dot{C}HOEt$	11.5	20.4	0.3*	6.7	20.0	0.3(3)
	11.2	21.0	0.4(1)	8.0	20.3	0.3*
$\cdot CO_2H$	15.2	20.9	—	8.4	20.0	—
$\cdot CH_3$	13.5	20.8	0.6(3)	10.3	20.3	0.7(3)
$C_6H_5\cdot$	14.6	20.9	—	10.7	20.4	—
o-$C_6H_4F\cdot$	10.9	20.3	1.6(F)			

* Denotes incomplete resolution.

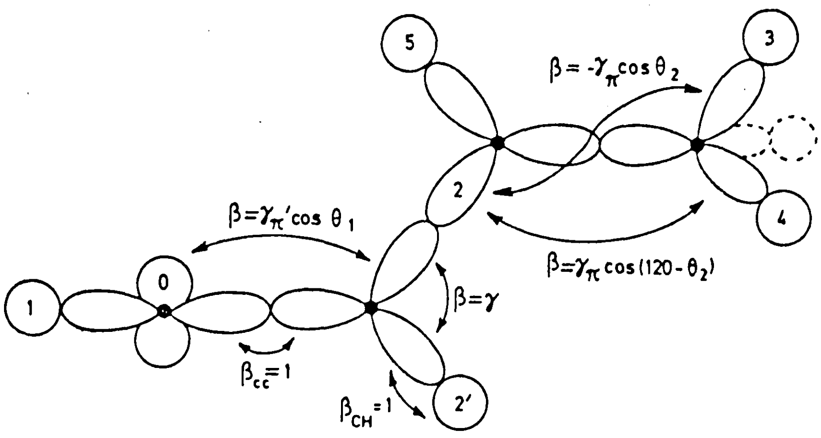
† Most probably a proton α- with respect to one of the carboxyl groups is abstracted.

RESULTS AND DISCUSSION

THE ORIGIN OF THE LONG-RANGE COUPLING CONSTANTS

(i) δ-SPLITTINGS

The patterns of the small coupling constants establish convincingly the structures of the adduct radicals. Relatively large γ-coupling constants have been observed many times, e.g. in radicals from t-butyl alcohol, ether, dioxan etc., [1, 4] and it seems likely that they arise from a combination of hyperconjugation and spin polarisation.[5] The observation of δ-splittings is less common, however, and such splitting generally occurs only in rigid systems such as the adamantyl radicals.[6, 7] It is not difficult to see how coupling through so many σ-bonds arises, since the situation is essentially the same as that leading to large *meta*-coupling constants when aryl rings are twisted out of the nodal plane of a single occupied molecular orbital,[3] e.g. as in the rubrene radical ions.[8] The transmission of spin density through σ-bonded systems has already been explained in simple MO terms,[4, 9, 10] but in view of the complexity of the present problems it is rewarding to examine them in some detail.



$$c_1 = 0;\ c_2 = c_{2'} = -\gamma_\pi' \cos \theta_1 c_0;\ c_5 = -\gamma c_2;\ c_3 = (\gamma_\pi \cos \theta_2 + \gamma^2) c_2$$

FIG. 2.—Diagram showing orbitals and interactions mainly responsible for the σ-spin delocalisation with coefficients of non-bonding orbital. Values of the non-zero parameters are

$$\alpha_C = \alpha_H,\ \gamma_\pi \approx \gamma_\pi' \approx \tfrac{1}{4},\ \gamma \approx \tfrac{1}{4}\sqrt{3}$$

θ_1 = dihedral angle of orbital 2 about C_α—C_β bond with respect to axis of orbital 0. θ_2 = dihedral angle about C_γ—C_δ bond.

Using the MO parameters given in fig. 2, the average coupling constant of the δ-protons, assuming free rotation about the C_γ—C_δ bond is given approximately by:

$$a_\delta = \tfrac{1}{2}\gamma_\pi^2(\gamma' \cos \theta_1)^2\ 508 Z_{\text{eff}}^3 \times 10^{-4} \text{ tesla} \qquad (a)$$

where we take the hyperfine splitting due to the nucleus in a free hydrogen atom to be 50.8 mT and Z_{eff} is the effective atomic number for the hydrogen 1*s* orbital in a molecule. There are several ways of obtaining an order of magnitude for a_δ from this. However, we shall take values of γ_π and γ_π' which have been shown to account for the coupling constants in the vinyl radical and also for the n.m.r. coupling constants in butadiene,[11] i.e. $\gamma_\pi \approx \gamma_\pi' \approx \frac{1}{4}$ so that eqn (*a*) becomes:

$$a_\delta \approx \cos^2 \theta_1\ Z_{\text{eff}}^2. \qquad (a')$$

If $\cos^2 \theta_1$ is about 0.5 then for $Z_{\text{eff}} = 1.0$, $a_\delta \approx 0.5 \times 10^{-4}$ T.

This is of the correct order of magnitude and is close to the limits of resolution of our spectrometer under conditions of flow. If necessary, a_δ can be quickly estimated for any dihedral angle using formula (a^1). We can even go so far as to deduce the conformation about the C_α—C_β bond. The δ coupling constants observed are of the order of 0.03 mT which corresponds to a dihedral angle of about 60°. Similarly the β coupling of about 1 mT (averaged over the different adducts) corresponds to a dihedral angle of about 60°. The resulting conformation is given in fig. 3.

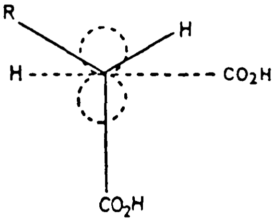


FIG. 3.—One of the two conformations predicted for the $(CH_3)_2\dot{C}OH$ adduct.

(ii) ε-COUPLING CONSTANTS

The splittings from protons attached to α-, to β-, to γ- and to δ-carbon atoms can be explained in terms of transmission of spin density through bonds. The mechanisms involved may be separated approximately into two, i.e., (*a*) hyperconjugation and (*b*) spin polarisation. Appreciable splittings from ε-protons have already been observed [12] and they have been ascribed to " throughspace " interactions. This term has not yet been clearly defined and in many cases where it has been invoked, an extended theory of hyperconjugation of the type given above for δ-splittings can account for the observations. Also, because of the way spin densities tend to be transmitted to alternate orbitals, direct through-space interaction of a hydrogen orbital with the orbital containing the odd electron would result in spin density appearing not in the hydrogen orbital itself, in the first instance, but on the adjacent carbon atom.

In view of these thoughts we have investigated the possibility that ε-splittings arise not from spin density associated with the ε-hydrogen orbitals, but from a direct *magnetic* interaction between those protons and the cloud of spin density on the α-carbon atom. The hypothetical situation which would give the maximum effect of this kind is shown in fig. 4.

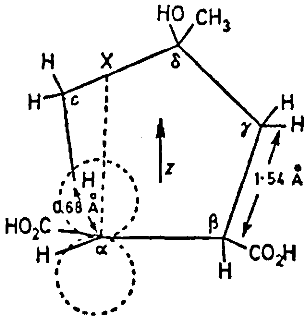


FIG. 4.—Diagram showing nearest approach of an ε proton to the α-carbon atom in adduct $\dot{C}HCO_2H\ CH(CO_2H)CH_2C(OH)(CH_3)_2$.
Point X is nearest approach of a δ proton. Adjacent C—C bonds are all taken to be 1.54 Å.

The Slater-type orbital most commonly used for carbon $2p$ orbitals is:

$$\psi(2p_z) = (\tfrac{1}{4}\sqrt{2\pi})(Z/a_0)^5/^2 z \exp(-Zr/2a_0)$$

where the effective atomic number $Z = 3.25$ and a_0 is the Bohr radius of the hydrogen atom.

The magnetic interaction of a proton with an electron in this carbon $2p_z$ orbital is

$$(508/\pi a_0^3)[\psi(2p_z)]^2 = 2.06 \times 10^3\ z^2\ e^{-6.13r}\ mT$$

where distances are measured in Ångstroms.

For the proton in fig. 5 this becomes 10.2 mT. Now we would not expect that the proton could possibly get nearer to the α-carbon atom than a distpnce somewhat greater than the C—H bond distance, so if we doubled the distance of closest approach the maximum direct coupling is reduced fifty times to 0.2 mT.

Allowing further free rotation of the methyl group and for other possibilities of bending or flapping in the molecule, the estimated ε-splittings are rather less than 0.05 mT. The main point here is that this direct magnetic interaction could be large enough to account for the observed splittings. The effect could be enhanced by steric repulsions of the β-carboxyl group.

The corresponding direct interaction with one of the δ-protons has a maximum value of 0.05 mT. Allowing again for free rotation of methyl groups and for bending within the molecule, this is negligible compared with the coupling due to extended hyperconjugation, and is moreover extremely sensitive to the exact position of the δ carbon atom.

ADDUCTS OF RADICALS DERIVED FROM ALCOHOLS

The pattern of lines in the spectra from the adducts of maleic acid with radicals formed by α-hydrogen abstraction from alcohols, were dependent on the pH of the solutions. The maximum fine structure was observed in strongly acidic solutions and and in the case of the adduct formed from $\cdot CH_2OH$, this fine structure unexpectedly showed two non-equivalent protons. A reasonable way of accounting for this, and for the apparent disappearance of some of the couplings when the solutions are made alkaline, is that there is some rigidity in the molecule, preventing free rotation and the corresponding equivalence of the two methylene protons of the CH_2OH group. This rigidity could arise from hydrogen bonding between the hydroxyl group of CH_2OH and the neighbouring carboxyl group (see fig. 5).

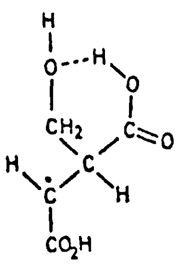


FIG. 5.

One might expect these structures to break down under alkaline conditions.

The results for simple addition of hydroxyl radicals indicate that the rate of exchange of the hydroxyl proton in the CH_2OH is much faster in acidic solution than when conditions are more alkaline.

In conclusion it can be stated that the observed hyperfine splittings in the e.s.r. spectra of these adducts of maleic acid confirm their identities more completely than has previously been possible. The long-range δ-coupling constants arise from extended hyperconjugation through the σ-bonds and ε-splittings from direct magnetic interactions. Both are observed because of favourable conformations.

EXPERIMENTAL

The conditions in our experiments were similar to those of Beckwith and Norman[2] except that the flow system was driven by a peristaltic pump which gave a fine control of the flow rate (*ca.* 10 $cm^3\ s^{-1}$). The concentrations used were approximately 0.05 $mol\ dm^{-3}$ for Ti^{III} and peroxide, 0.25 $mol\ dm^{-3}$ for the diazonium salts and for the substrates about 0.5-1.0 $mol\ dm^{-3}$. The acidic solutions contained 0.5 $mol\ dm^{-3}$ sulphuric acid and the " alkaline " solutions were at pH 7-9.

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[8] R. Biehl, K. P. Dinse, K. Mobius, M. Plato and H. Kurreck, *Tetrahedron*, 1973, **29**, 363.
[9] J. A. Pople and D. B. Santry, *Mol. Phys.*, 1964, **7**, 269.
[10] W. T. Dixon, *Mol. Phys.*, 1965, **9**, 201.
[11] W. T. Dixon, *J. Chem. Soc. A*, 1967, 1879.
[12] P. Smith, R. A. Kaba and P. B. Wood, *J. Phys. Chem.*, 1974, **78**, 117.

5555 LONG-RANGE E.S.R. COUPLING
6666 LONG-RANGE E.S.R. COUPLING
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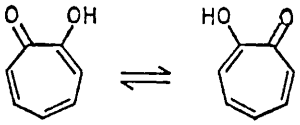
E.s.r. Spectra of Radicals Derived from Tropolones and Benztropolones

By **W. T. Dixon** * and **D. Murphy**, Bedford College, London NW1 4NS

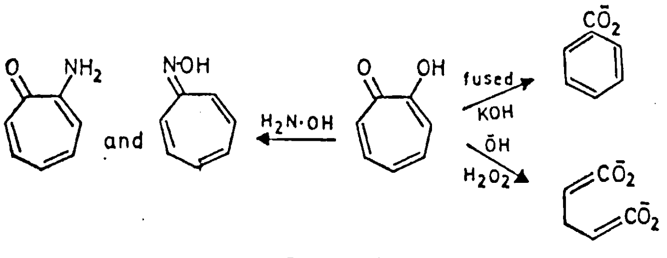
The oxidation of tropolones and benztropolones such as purpurogallin by cerium(IV) in a flow system yields radicals which can be characterised by means of e.s.r. spectroscopy. The spin distribution can be related to non-bonding orbital coefficients in model compounds. In alkaline solutions 1′,2′-dihydroxy-3,4-benztropolone and its derivatives can be autoxidised to corresponding semiquinones from which intense e.s.r. spectra can be obtained. Secondary radicals may also be formed when the 4′-position is vacant. The tropolone analogue of *p*-benzosemiquinone can be observed in hexamethylphosphoramide, but ring contraction takes place too quickly for this to be detected in aqueous solution.

THE existence of the tropolone structure was first realised[1] in 1945, and since then it has been found that derivatives of 2-hydroxycycloheptatrienone (I) occur quite widely in nature,[2] *e.g.* in the Thuja conifers, some penicillin moulds, and the autumn crocus.



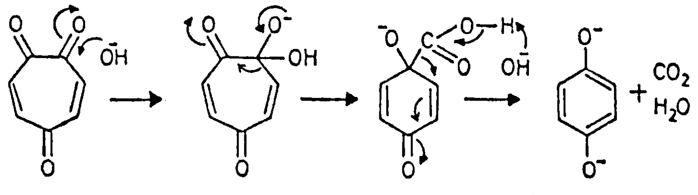
(I)

Dewar[1] rationalised the properties of tropolone and predicted that it should undergo ready electrophilic substitution and generally resemble phenol. In fact electrophilic attack is more or less confined to the 5-position and tropolones have additional possibilities of nucleophilic substitution as well as ring-opening reactions[2] (Scheme 1).



SCHEME 1

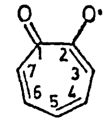
Previous work on radicals containing the tropolone skeleton has largely been confined to the di- and tri-



SCHEME 3

TABLE 1

E.s.r. parameters (a/mT) of radicals from Ce^{IV} oxidation of tropolones (splittings for the corresponding phenoxyl radicals in parentheses)



Substituents	a_3	a_4	a_5	a_6	a_7
	0·7 (0·66)	0·25 (0·18)	1·03 (1·02)	0·25 (0·18)	0·7 (0·66)
4-Pr^i (β-Thujaplicin) *	0·625 (0·59)	a_H 0·10 (0·08)	1·05 (1·02)	0·25 (0·18)	0·725 (0·70)
6-CH_2·CO_2H,7-CO_2H	0·725	0·275	1·05	a_{CH_2} 0·113	
4,7-$(CO_2H)_2$,6-CH_2·CO_2H	0·77		1·00	a_{CH_2} 0·117	
4,6,7-$(CO_2H)_3$	0·75		1·00		

* Assignments made by comparison with the corresponding phenoxyl radical, which we have studied together with its isomers.

TABLE 2

E.s.r. spectra from autoxidation of 5-hydroxytropolones; assignments made by comparison with the benzenoid cases (effects of the isopropyl group assumed to be similar to those of methyl)

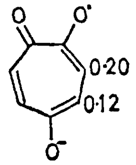
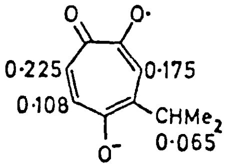
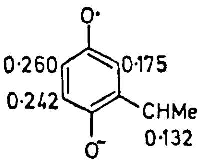
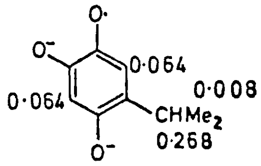
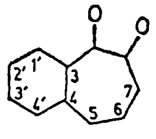
Starting material	Solvent	Radical(s)
5-Hydroxytropolone	HMPA	
	H_2O	*p*-Benzosemiquinone (0·235 × 4) Hydroxysemiquinone (0·06, 0·48, 0·135)
5-Hydroxy-4-isopropyl tropolone	HMPA	
	H_2O	 
5-Hydroxy-3,4-benztropolone	HMPA	Naphthosemiquinone (0·33, 0·025, 0·065)
	H_2O	Naphthosemiquinone (0·33, 0·058, 0·066)

TABLE 3

E.s.r. spectra (a/mT) from 3,4-benztropolones

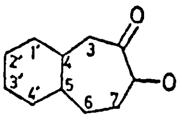


(a) Oxidation by Ce^{IV} in acid solution; corresponding naphthoxyl splittings in parentheses
(b) Autoxidation in aqueous alkaline solution

Substituents		a_7	a_6	a_5	$a_{4'}$	$a_{3'}$	$a_{2'}$	$a_{1'}$
	(a)	0·85 (0·825)	0·25 (0·175)	1·05 (1·075)	0·25 (0·25)	0·10 (0·065)	0·25 (0·25)	0·0 (0·0)
1',2'-$(OH)_2$,6-CO_2H	(a)	0·75		1·00	0·065	0·065		
	(b)	0·013		0·05	0·358	0·045		
1',2'-$(OH)_2$,6-CO_2Et	(a)	0·70		1·025	0·081	0·081		
	(b)	as with 6-CO_2H						
1',2'-$(OH)_2$, 3'-Me,6-CO_2H	(a)	0·775		1·025	0·07	a_{Me} 0·07		
	(b)	0·013		0·013	0·46	a_{Me} 0·013		
1',2'-$(OH)_2$, 4'-Me,6-CO_2H	(a)	0·75		1·025	a_{Me} 0·086	0·086		
	(b)	0·03		0·085	a_{Me} 0·049	0·0		
1',2',3'-$(OH)_3$ (purpurogallin)	(a)	0·70	0·25	0·90	0·85			
	(b)	0·055	0·28	0·075	0·11			
1',2',3'-$(OH)_3$,6·CO_2H	(a)	0·75		0·925	0·85			
	(b)	0·05		0·05	0·145			

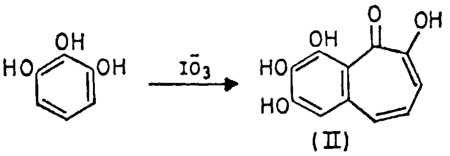
? a.k.

Spectrum from 4,5-benztropolone:



(a) a_3 1·04 (1·075), a_7 0·15 (0·145), a_6 0·0 (0·0), a_4 0·11 (0·145), $a_{3'}$ 0·56 (0·54), $a_{2'}$ 0·06 (0·12), $a_{1'}$ 0·48 (0·43).

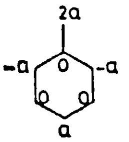
hydroxybenztropolones[3,4]. the most well-known of which is purpurogallin (II) (easily formed from pyrogallol). Until recently[5] no e.s.r. spectra of directly



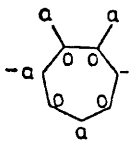
(II)

related radicals had been reported, though radicals containing the tropone skeleton[6,7] have been observed. A spectrum ascribed to the semiquinone of purpurogallin[3] has subsequently proved to be due to that of pyrogallol (see later).

With the phenol-like properties of tropolone in mind, we oxidised it in a flow system with cerium(IV) and were able to observe tropolone analogues of phenoxyl and some accessible derivatives, showing that the balance between production and destruction is similar for the two types of radical. The e.s.r. parameters of the tropolonyl radicals are, surprisingly, nearly the same as those of the corresponding phenoxyl radicals,[8] the main difference being a larger value of what we assume is negative spin density at the '*meta*'-position of the seven-membered ring radical. It seems that the two carbon–oxygen groups of tropolonyl behave as if they were only one, and this can be partly rationalised by comparison with simple MO models consisting of corresponding frameworks of carbon $2p_\pi$ orbitals: both in the model system for phenoxy (i) and in that for tropolonyl (ii) the odd electron occupies a non-bonding orbital.[9]

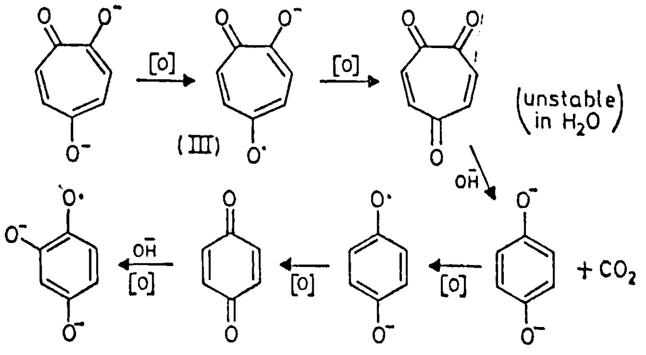


(i) Alternant model for phenoxyl (*i.e.* benzyl) with NBO coefficients (a = $1/\sqrt{7}$)



(ii) Corresponding model for tropolonyl (a = $1/\sqrt{5}$)

Analogues of p-*Semiquinones*.—Pressing the analogy between phenol and tropolone still further, we prepared 5-hydroxytropolone in the hope of obtaining a relatively stable radical, in alkaline solution, which could resemble *p*-semiquinone. In faintly alkaline solution an e.s.r. spectrum identical with that of *p*-benzosemiquinone was obtained, which in more alkaline solution was quickly replaced by the familiar spectrum of hydroxysemiquinone.[10] Evidently the seven-membered ring must have contracted. The most likely explanation for this is that since tropolone or its simple derivatives are stable at ordinary temperatures, and require drastic conditions for ring contraction, oxidation to the unstable quinone may have occurred (Scheme 2). The mechanism for the



SCHEME 2

loss of CO_2 could be as shown in Scheme 3. This is similar to other mechanisms proposed for the production of six-membered rings from tropone and tropolone derivatives.[2]

The ring contraction step could result in the formation of the anion of 2,5-dihydroxybenzoic acid. However, experiments carried out with this acid under similar conditions did not lead to the above pattern of radical products, and only the spectrum of the primary radical (IV) was observed. When the solutions were made strongly alkaline some decarboxylation did occur, however. This evidence is consistent with the decarboxylation of the tropoquinone being concerted with the formation of the six-membered ring as indicated in the suggested mechanism.

The foregoing results by no means prove that the radical (III) is in fact formed, though it does seem likely that it exists for a short time. In order to detect this intermediate we resorted to an aprotic solvent,[11] hexamethylphosphoramide (HMPA), in which it seems that many free radicals are much longer-lived than in aqueous solutions.* It appears that by using the sparingly soluble sodium methoxide in conjunction with this solvent, the base concentration can be kept low enough to slow down the overall oxidation rate without preventing the first step. We obtained spectra from hydroxytropolone and hydroxythujaplicin, which correspond to tropolone analogues of the *p*-semiquinones and which decayed in the former case to give *p*-benzosemiquinone. The results are summarised in Table 2. The primary radical from 5-hydroxy-3,4-

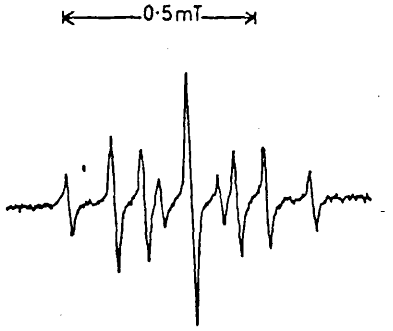


FIGURE 1 E.s.r. spectrum of the tropolone analogue of *p*-benzosemiquinone

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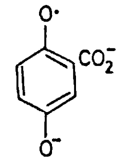
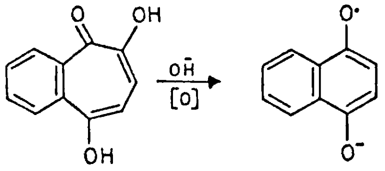
* We have, for example, observed the semiquinone of 2,6-dihydroxynaphthalene [coupling constants 0·42, 0·13, and 0·07 mT (all twice)] in this solvent, whereas only degradation products could be detected in aqueous solutions.

benztropolone (V) was not observed even in HMPA; only the corresponding naphthosemiquinone (VI) was obtained.



(IV)



(V) (VI)

Radicals from Di- and Tri-hydroxybenztropolones.—These hydroxylated benztropolones are formed by the interaction of *ortho*-quinones with pyrogallol or an appropriate derivative. They behave in two distinct ways, depending on the conditions, and therefore form a class of their own.

(a) *Autoxidation in alkaline solutions.* As one might expect by analogy with hydroxylated naphthoquinones, in alkaline solution semiquinones are formed in which spin densities generally differ little from those observed (or expected) for the corresponding naphthosemiquinones[12] (see Table 3).

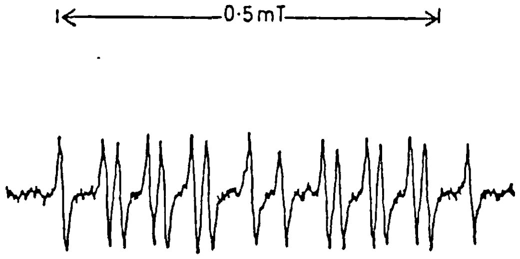
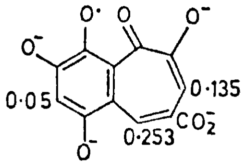
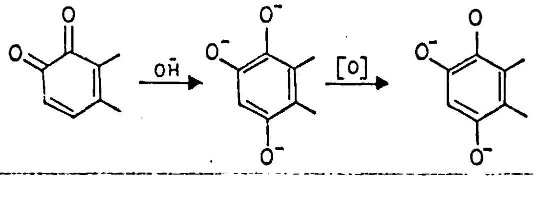


FIGURE 2 E.s.r. spectrum of purpurogallosemiquinone

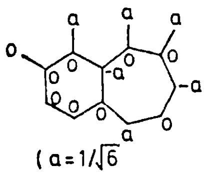
The authentic e.s.r. spectrum of the semiquinone from purpurogallin is clear and long-lived and we would expect to see it if purpurogallin were a major intermediate in the autoxidation of 1′,2′-dihydroxy-3,4-benztropolone as suggested previously.[4] Secondary radicals are formed in the autoxidations of derivatives of this last compound, and in one case we obtained a pure spectrum which we ascribe tentatively to the species (VII). No secondary radicals were observed when the 4′-position was blocked by a methyl group. These results suggest that the secondary radicals are derived from the quinone in the usual way rather than by oxygenation at the 3′-position.[4]



(VII)

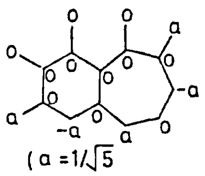


(b) *Spectra in acidic solution.* Oxidation by cerium(IV) in the flow system took place under acidic conditions, and completely different patterns of coupling constants were observed (see Table 3). The spectra can be rationalised by looking upon these radicals as being derived from the tropolone unit, which in protonated molecules seems to be the most easily oxidised part. The patterns of coupling constants can be explained as before with the help of simple hydrocarbon models: thus for 1′,2′-dihydroxy-3,4-benztropolone, the NBO coefficients are as shown in (iii), and for the purpurogallin model as shown in (iv). It appears that the presence of the 3′-oxygen atom in purpurogallin makes a different pattern of delocalisation possible.



(a = $1/\sqrt{6}$)

(iii)



(a = $1/\sqrt{5}$)

(iv)

EXPERIMENTAL

Commercial samples were purified by vacuum sublimation. 3,4-Benztropolone,[13] 4,5-benztropolone,[14] 1′,2′-dihydroxy-3,4-benztropolones,[15] 4-hydroxytropolones,[16] the tropolone carboxylic acids,[3] and purpurogallin carboxylic acid [17] were prepared by literature methods. The conditions and flow system for the cerium(IV) oxidations were as previously reported,[18] and the autoxidations were conducted in the usual way for generating semiquinones.[10]

[4/861 *Received, 30th April,* 1974]

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Substituent Effects in the E.s.r. Spectra of Phenoxyl Radicals

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Received 17*th April*, 1974

Regularities observed in the e.s.r. spectra of many *o*-, *m*- and *p*-substituted phenoxyl radicals allow unambiguous assignments of the coupling constants as well as the determination of their relative signs. It is shown that semiquinone anions can be classed as phenoxyl radicals and similarly for radicals from the oxidation of trihydroxybenzene derivatives.

With suitable parameters, the patterns of splittings in these radicals can be rationalised by means of McLachlan's SCF theory; a heteroatom model and an inductive model both explain most of the observed trends. INDO calculations gave a rather poor account of the splittings in phenoxyl.

The e.s.r. of para-benzosemiquinones [1] and of phenoxyl [2] have long since been available, yet although systematic investigations of substituent effects in semiquinones have been undertaken at various times, little has been added to the original work of Stone and Waters on short-lived phenoxyl radicals.[3] These authors made the important observation that the algebraic sum of the ortho and meta coupling constants in a para-substituted aryloxyl radical is approximately independent of the substituent. (See table 1). This simple rule enabled them to deduce empirically that these two coupling constants must generally have opposite signs. In fact, the relationship also holds good for *p*-benzo semiquinone where the two splittings are equal and of the same sign. We have investigated the origin and limitations of this intriguing rule and have also discovered analogous relationships among the ortho- and meta-substituted isomers.

The first necessity was to obtain more experimental data, for there were many gaps to be filled in the list of e.s.r. spectra of mono-substituted phenoxyl radicals and it was also necessary to find substituents which had relatively large effects on the spin distribution. We have remeasured spectra previously reported because our equipment seems to give improved spectra for this class of transient radical [4] (see fig. 1).

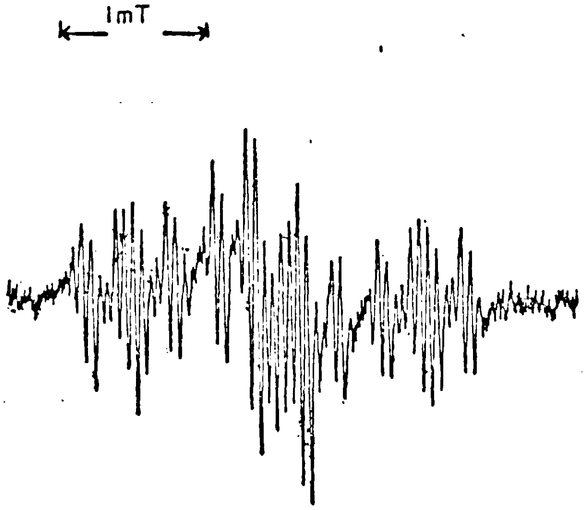


FIG. 1.—Spectrum from oxidation of *m*-methoxyphenol.

The relatively complete spectra of which we have now obtained has enabled us to assign the splittings, from more or less obvious trends, and also to deduce their relative signs.

EXPERIMENTAL

Most of the radicals were produced by flowing 10^{-4} M solutions in 0.5 M sulphuric acid against 10^{-4} M CeIV solutions. The alkaline solution spectra were at pH = 7-9. Spectra from *o*- and *p*-semiquinone anions were obtained in a static system which gave much better line widths. Coupling constants were measured to within ±0.01 mT.

PARA-SUBSTITUTED PHENOXYL RADICALS

The results for this class of radicals are given in table 1. In order to obtain a " smooth " change in relative splittings in going from X ≡ NO_2, through X ≡ OMe to X ≡ $\bar{O}$ (semiquinone) the ortho and meta splittings have to have opposite signs in the majority of cases since then $|a_o + a_m| = 4.7 \pm 0.2$ G. Presumably the large coupling constants correspond to positive spin densities so that the small splittings usually correspond to negative spin densities. From the results for meta substituted phenoxyl radicals, it is clear that the smaller proton splitting must be ascribed to the meta position and, therefore, that is the site of the negative spin densities observed. The coupling constant in semiquinone must be negative to maintain continuity.

TABLE 1.—COUPLING CONSTANTS (IN -10^{-4} T) OF PROTONS IN PARA-SUBSTITUTED PHENOXYL RADICALS

substituents	a_2	a_3	a_4	a_5	a_6
NO_2	7.0	−2.4	$\|a_N\| = 2.4$	−2.4	7.0
COOH	6.75(7.1)	−2.2(−2.3)	—	−2.2	6.75
CHO	6.8	−2.2	$\|a_H\| = 0.3$	−2.2	6.8
$COCH_3$	6.75	−2.1	—	−2.1	6.75
H	6.6[6.6]	−1.8[−1.8]	10.2[10.2]	−1.8	6.6
CH_3	6.1[6.2]	−1.4[−1.6]	$\|a_{CH_3}\| = 12.5$	−1.4	6.1
$CHMe_2$	6.0	−1.2	$\|a_{CH_3}\| = 0.4$ $\|a_H\| = 4.5$	−1.2	6.0
Cl	6.4	−1.9	$\|a_{Cl}\| = 1.9$	−1.9	6.4
F	6.25	−1.45	$\|a_F\| = 27.5$	−1.45	6.25
OCH_3	4.9[5.2]	0.0[−0.7	$\|a_{OMe}\| = 2.1$	0.0	4.9
NH_2	4.0	0.5	$\|a_N\| = 6.6$ $\|a_{NH}\| = 8.0$	0.5	4.0
$\bar{O}$ (alkali)	2.37[2.5]	2.37	—	2.37	2.37
OH (acid)	2.4{2.45}	2.4		2.4	2.4

[ ] value calculated using heteroatom model, ( ) value calculated using inductive model, { } mean value of results from OMe derivative.

ORTHO SUBSTITUTED PHENOXYL RADICALS

Two important conclusions arise from inspection of table 1. First, it is clear that substituents lead to a change in the spin distribution in these radicals but that these changes can be arranged in a regular series and depend roughly on the electron-donating power of the substituent. Secondly, using this regularity, semiquinone anions can be regarded not as totally different species but rather as a phenoxyl radical with a particular substituent, i.e., X ≡ $\bar{O}$. From the results given in table 2 it is clear that there are also trends in the splitting patterns when the substituents are in the ortho

TABLE 2.—COUPLING CONSTANTS (-10^{-4} T) IN ORTHO-SUBSTITUTED PHENOXYL RADICALS

substituents	a_2	a_3	a_4	a_5	a_6
NO_2	$\|a_N\| = 2.1$	−1.2	10.25	−2.4	7.25
COOH	—	−1.25(−0.6)	10.2(10.3)	−2.1(−2.4)	7.15(7.8)
CHO	—	−1.7	10.0	−2.0	7.1
$COCH_3$	—	−1.5	10.25	−2.0	7.0
H	6.6	−1.8	10.2	−1.8	6.6
CH_3	$\|a_{CH_3}\| = 7.5$	−2.0[−2.3]	9.7[9.6]	−1.5[−1.6]	6.0[5.9]
$CHMe_2$	—	−2.0	9.6	−1.5	6.0
Cl	$\|a_{Cl}\| = 1.05$	−2.0	9.8	−1.6	6.0
F	$\|a_F\| = 16.8$	−2.1	10.0	−1.4	5.5
OCH_3	$\|a_{OCH_3}\| = 1.8$	−1.9[−2.6]	8.5[8.1]	0.0[−0.3]	4.3[4.0]
NH_2	$\|a_N\| = 6.62$ $\|a_{NH}\| = 8.13$	−0.9	6.62	1.5	2.6
$\bar{O}$ (alkali)	—	0.75[0.6]	3.75[3.5]	3.75	0.75
OH (acid)		1.0{1.2}	4.1{4.25}	4.1	1.0

for figures in brackets refer to table 1 position. However, there is the initial problem of assignment and we have had to arrive at those given in the table by finding consistent regularities. The ambiguities could not be resolved convincingly by any simple arithmetic relationship and we had to resort to a graphical procedure (see fig. 2). What we have done is to plot the algebraic sum (or the difference) of pairs of splitting constants against each of the remaining two. This gives rise to graphs containing series of points and those which fall on the same smooth curve must correspond to each other, remembering that only one point on each curve can arise from one particular substituent. Since the parent radical phenoxyl, and *o*-benzo semiquinone both give points lying on the curves we can assign all four splittings for each radical. We also deduce that the two splittings in ortho-semiquinone have the same sign and that in the radical with X = NH_2, the two small coupling constants have opposite signs. For clarity in fig. 2 we have used the final assignments which were the outcome of the investigation of all the obvious possibilities.

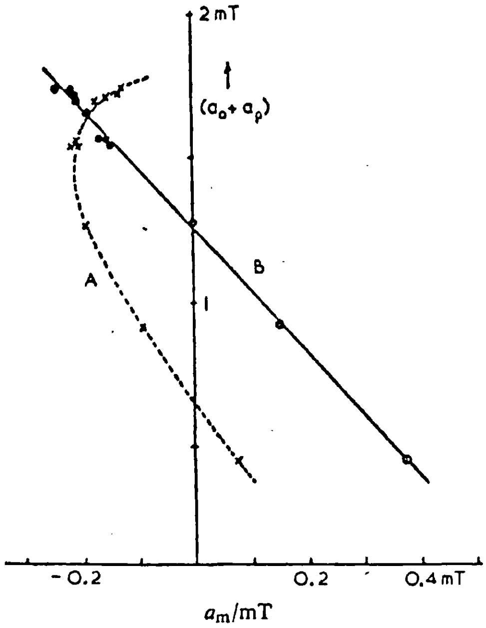


FIG. 2.—Graph for coupling constants for ortho-substituted phenoxyl radicals. A, $a_m = a_3$; B, $a_m = a_5$.

META-SUBSTITUTED PHENOXYL RADICALS

The results for these are given in table 3 and the assignments were made by an analogous method to those considered above, one of the resulting graphs being given

TABLE 3.—COUPLING CONSTANTS (IN -10^{-4} T) IN META-SUBSTITUTED PHENOXYL RADICALS

substituents	a_2	a_3	a_4	a_5	a_6
NO_2	7.35	$\lvert a_N \rvert = 0.5$	9.8	−2.1	6.75
COOH	7.25(7.4)	—	9.9(9.8)	−1.9(−1.6)	6.5(5.9)
CHO	7.1	—	9.8	−2.0	6.75
$COCH_3$	7.1	—	9.9	−1.9	6.5
H	6.6	−1.8	10.2	−1.8	6.6
CH_3	5.9[6.2]	$\lvert a_{CH_3} \rvert = 1.5$	10.5[10.2]	−1.9[−2.0]	7.1[6.7]
$CHMe_2$	5.9	$\lvert a_H \rvert = 0.8$	10.3	−1.9	7.0
Cl	6.2	$\lvert a_{Cl} \rvert = 0.25$	10.5	−2.1	7.5
F	5	$\lvert a_F \rvert = 5.8$	10.75	−2.25	8
OCH_3	3.5[4.6]	$\lvert a_{OCH_3} \rvert = 0.6$	11.4[10.8]	−2.3[−2.4]	9.0[8.0]
NH_2	3.1	$\lvert a_N \rvert = 6.8$ $\lvert a_{NH} \rvert = 8.1$	10.9	−2.0	8.6
$\bar{O}$ (alkali)	−0.7[−0.8]	—	11.2[12.8]	−2.8[−3.4]	11.2
OH (acid)	3.75{3.5}		10.0{10.2}	−2.3{−2.3}	11.0

for figures in brackets refer to table 1 in fig. 3. As expected, the radical from resorcinol can be treated as a meta-substituted phenoxyl radical and the smallest splitting observed in its spectrum would appear to be due to negative spin density on the 2 position, which differs from previous conclusions.[5] In simple m.o. terms it is clear that the odd electron goes into an antisymmetrical orbital when X = $\bar{O}$ so that a_6, a_5, and a_4 all maintain the same sign along the series whereas a_2 has to change rather drastically.

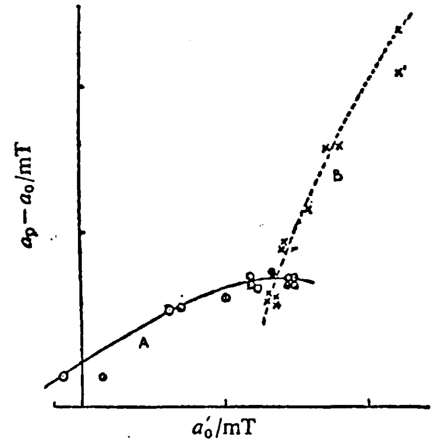


FIG. 3.—Graph for coupling constants for *meta*-substituted phenoxyl radicals. ○, × points if $a_2 = +0.07$ mT in " semiquinone " from resorcinol. A, $a_0' = a_2$; B, $a_0' = a_6$.

Once again the effects of substituents are in a similar order to their electron donating power and we can arrange them in the following series:

$$NO_2;\ CO_2H;\ H;\ Me, Cl;\ F;\ OMe;\ NH_2;\ \bar{O}$$

A worthwhile point to remember here is that, as implied by Stone and Waters,[3] these results and inferences are self-contained and do not depend on any parallels drawn between these radicals and those of other types.

RADICALS FROM DI- AND TRI-HYDROXY BENZENE DIRIVATIVES

Attempts to make assignments in *p*-semiquinones have centred around " addition " rules [6-8] which state that the effects of substituents are additive. These rules have been developed extensively only for substituents which have relatively little effect on the overall spin distribution, such as alkyl groups and halogen. We now prefer to follow graphical procedures analogous to those used above.

TABLE 4.—COUPLING CONSTANTS (IN 10^{-4} T) IN RADICALS FROM DI-SUBSTITUTED PHENOXYL RADICALS

	a_2	a_3	a_4	a_5	a_6
2$\bar{O}$, 3Me	—	$a_{Me} = 0.65$	2.9[3.0]	4.15[3.6]	0.3[0.3]
2$\bar{O}$, 4Me	—	0.15[0.24]	$a_{Me} = 4.85$	3.8[3.6]	0.95[0.7]
2$\bar{O}$, 3OMe	—	$a_{OMe} = 0.65$	1.3[1.8]	4.75[4.0]	0.55[0.4]
2$\bar{O}$, 4OMe	—	0.0[−0.6]	$a_{OMe} = 1.1$	3.7[4.1]	0.75[0.8]
2$\bar{O}$, 3CO_2H	—	—	5.15(5.2)	2.9(3.5)	1.7(2.4)
2$\bar{O}$, 4CO_2H	—	1.25(2.8)	—	3.25(3.6)	0.75(1.3)
2$\bar{O}$, 3$\bar{O}$	—	—	−0.95[−1.6]	5.5[4.3]	0.95
2$\bar{O}$, 4$\bar{O}$	—	−0.6[−1.4]	—	4.98[6.1]	1.35[1.0]
4*N*, 2Me	—	1.75[2.1]	—	2.6[2.8]	2.4[2.4]
4$\bar{O}$, 2OMe	—	0.57[0.9]	—	3.66[3.5]	2.01[2.2]
4$\bar{O}$, 2CO_2H	—	2.6(4.8)	—	2.0(2.5)	2.25(3.3)
2OH 6OH*	$a_{OH} = 0.75$	−1.5[−2.0]	7.6[7.6]	−2.0	$a_{OH} = 0.75$

* In flow system using ceric ammonium nitrate as oxidant under near-neutral conditions; for figures in brackets refer to table 1.

Once again, regularities can be found by plotting for example the sum of two splittings against the third and there are smooth transitions to the semiquinones of 1,2,4-trihydroxybenzene and of pyrogallol [9] from those of quinol or catechol (e.g., see fig. 4). The smallest splitting in the semiquinone of 1,2,4-trihydroxybenzene turns out to be negative. In the radical from phloroglucinol the expected Jahn–Teller distortions are evidently being rapidly averaged out and the sum of the three coupling constants (23.4 G) is much the same as it is in all meta-substituted phenoxyl radicals.

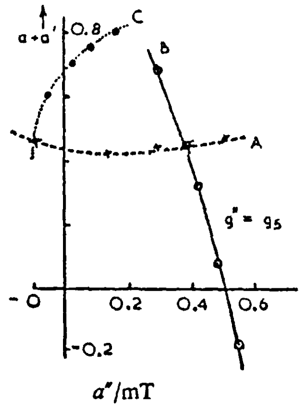
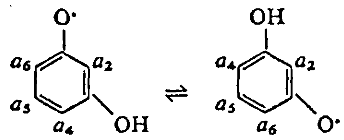


FIG. 4.—Graph for coupling constants in 3-substituted *o*-semiquinones. A, $a'' = a_4$; B, $a'' = a_5$; C, $a'' = a_6$.

E.S.R. SPECTRA OF SEMIQUINONES IN ACID SOLUTION

In acid solution the semiquinones from quinol catechol [9] and resorcinol [5] are protonated and, provided the rate of proton exchange is fast enough, an averaged spectrum is observed.[10, 11]



The results we have obtained in acid solution are shown in the tables. From the coupling constant of the proton on position 2 in resorcinol, it is clear that OH has approximately the same effect as OMe, as suggested by Carrington and Smith.[10] In the table the empirical predictions are made using the results for corresponding methoxy-substituted derivatives. The agreement between the empirical estimate and experiment is very good.

THEORY OF SPIN DENSITIES IN PHENOXYL-TYPE RADICALS

The results of INDO calculations[12] were disappointing for, as in similar radicals,[13] calculated negative spin densities are much too high and the coupling constants are highly sensitive to bond lengths, e.g.,

$$\text{C—O} = 1.3\,\text{Å},\ \text{C—C} = 1.40\,\text{Å},\ \text{C—H} = 1.08\,\text{Å}$$

$$a_o = -0.50,\ a_m = +0.28,\ \text{and}\ a_p = -0.44\ (\text{in mT})$$

with carbon–carbon bond lengths of 1.46, 1.34A (alternating) the predictions become

$$a_o = -0.58;\ a_m = 0.38;\ a_p = -0.73.$$

EMPIRICAL SCF THEORY

Because of the occurrence of appreciable negative spin densities in many of the radicals observed, simple m.o. theory [14] could not be applied satisfactorily, so McLachlan's approach [15] was used to include such a possibility. The familar problem of parameterisation appears here for it was discovered that none of the existing sets of parameters given for oxygen [14, 16] gave good predictions for phenoxyl. Taking the only variable parameters for atom X as being the coulomb integral $\alpha_X = \alpha + h_X\beta$, and the resonance integral to a neighbouring carbon atoms $\beta_{CX} = k_X\beta$, we found a family of values of h_X, k_X which gave exact predictions for phenoxyl and good predictions for oxygenated derivatives such as *o*- and *p*-benzosemiquinone and the semiquinones from 1,2,4- and 1,2,3-trihydroxybenzenes. One such pair was $h_X = 1.6$, $k_X = 1.3$ with a Q value [17] of -3.0 mT. Treating the substituents as heteroatoms, each can be assigned two parameters as above for oxygen. With $h_X = 1.5$, values for methyl, $k_{CH_3} = 0.3$ and methoxyl $k_{OMe} = 0.6$ lead to good predictions confirming the signs and relative magnitudes of the observed coupling constants. These results imply that the McLachlan approach using this parameterisation can be used with a fair degree of confidence to assist in the assignment of coupling constants and to confirm the nature of radicals. No satisfactory parameters could be found for electron-attracting substituents. An even more simple theoretical model for phenoxyl is to regard it as a benzene positive ion on which is attached an O^- substituent.[18, 19] We consider only a change in Coulomb integral of the adjacent carbon atom so there is one "inductive" parameter for each substituent, i.e., the coulomb integral $\alpha' = \alpha + \delta_X\beta$.

The best agreement over the range of radicals studied was with a Q value of -2.4 mT and $\delta_{\breve{O}} = -1.5$, $\delta_{Me} = -0.2$, $\delta_{CO_2H} = +0.2$, $\delta_{OMe} = -0.6$. Though the results with this simple model were not so good when there were two electron-donating groups para with respect to each other, the calculations for $X = CO_2H$ did confirm the assignments given in the tables.

CONCLUSIONS

The inference which can be drawn from this investigation is that the splitting patterns observed in a given class of radicals can be expected to change in a smooth way with substitution. This variation with substituents, however, is not necessarily as simple as implied by attempts to impose addition [6] or superposition rules [20] which could lead, perhaps, to false conclusions if pushed too far.

The trends deduced from the spectra have been confirmed by simple m.o. theory in conjunction with McLachlan's refinement. These trends do not themselves depend critically on the parameterisation and so add to our confidence that the theoretical models proposed will be useful as aids in the assignment of coupling constants in related radicals.

It is interesting that recent work on the radiolysis of alkaline solutions of phenols has led to the production of aminophenoxyl radicals [21] which have different e.s.r. parameters to those given above. We tentatively suggest that these differences arise from rapid proton exchange on the oxygen in our acidic solutions. However, the reported assignments must be wrong according to our work, for the data fit our curves. The splittings in ortho-aminophenoxyl have to be assigned as follows:

$$a_3 = 0.0,\ a_4 = 0.431,\ a_5 = 0.294,\ a_6 = 0.101 \text{ mT}.$$

In ref. (21) a_5 and a_6 were assigned the other way around. This illustrates how useful this approach can be. In the absence of a sufficiently complete seties of results on related compounds we would have to resort to the empirical theories.

[1] B. Venkataraman and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.
[2] J. K. Becconstall, S. Clough and G. Scott, *Trans. Faraday Soc.*, 1960, **56**, 459.
[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.
[4] W. T. Dixon, W. E. J. Foster and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.
[5] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302.
[6] B. Venkataraman, B. G. Segal and G. K. Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.
[7] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.
[8] J. A. Pedersen, *J.C.S. Perkin II*, 1973, 424.
[9] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.
[10] I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1967, **12**, 439.
[11] I. C. P. Smith and A. Carrington, *Mol. Phys.*, 1964, **8**, 101.
[12] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, N.Y., 1970).
[13] C. Thomson, *Electron Spin Resonance* (Chem. Soc. Spec. Period Report, 1973), p. 1.
[14] G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333.
[15] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[16] K. A. Lott, E. L. Short and D. N. Waters, *J. Chem. Soc. B*, 1969, 1232.
[17] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764.
[18] A. Carrington, *Quart. Rev.*, 1963, **17**, 67.
[19] M. R. C. Symons, *Adv. Phys. Org. Chem.* (Academic Press, New York, 1963), vol. 1, p. 283.
[20] J. C. Schug, T. H. Brown and M. Karplus, *J. Chem. Phys.*, 1962, **37**, 330.
[21] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1974, **78**, 523.

1111 E.S.R. SPECTRA OF PHENOXYL RADICALS
2222 E.S.R. SPECTRA OF PHENOXYL RADICALS
3333 E.S.R. SPECTRA OF PHENOXYL RADICALS
4444 E.S.R. SPECTRA OF PHENOXYL RADICALS
5555 E.S.R. SPECTRA OF PHENOXYL RADICALS
W. T. DIXON, M. MOGHIMI AND D. MURPHY 6666
W. T. DIXON, M. MOGHIMI AND D. MURPHY 7777
W. T. DIXON, M. MOGHIMI AND D. MURPHY 8888
W. T. DIXON, M. MOGHIMI AND D. MURPHY 9999
W. T. DIXON, M. MOGHIMI AND D. MURPHY 0000

FREE-RADICAL REACTIONS AND ELECTRON SPIN RESONANCE SPECTROSCOPY

BY

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Reprinted from Annual Reports B
1972

London
The Chemical Society

4 Free-radical Reactions and Electron Spin Resonance Spectroscopy

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1 Introduction

The main difficulty confronting a Reporter in the field of free radicals is that of classifying the work which has been done. In a way the first obvious choice is to divide the material into work involving (i) direct observation of free radicals, which mainly involves the use of e.s.r. spectroscopy, although visible and u.v. spectra are also employed for this purpose, and (ii) other work which affords indirect evidence of free-radical reactions. In this second approach the analysis of the products or, in kinetic runs, the analysis of starting material at different times plays a major role.

Since the Reporter has been concerned with e.s.r., this article is naturally biased in that direction, but even a casual glance at the papers which have appeared over the past twelve months shows that investigators in the free-radical field are turning more and more towards e.s.r. spectroscopy for inspiration or for proving a point.

The introduction of this convenient technique into the subject has necessarily brought with it a different experimental approach and has polarized interest towards radicals which can be observed. Previously, in what one might broadly call the 'kinetic' approach, experimental conditions were arranged so that reactions were relatively controlled and as 'clean', *i.e.* as simple, as possible. One aimed at obtaining analysable solutions. In contrast, to some extent at least, the principle aim in the e.s.r. field is that of obtaining high concentrations of a single type of radical, so that by analysis of its spectrum various things about it, including what it is, can be deduced.

Generally speaking, although the radical observed does give rise to products which depend on its environment, it is not usually the most important radical or species in the reaction, in the sense that in the majority of interesting radical reactions a highly reactive species is produced and actually starts the reaction which then gives rise to secondary, tertiary, *etc.* stages. Somewhere along the line the balance of production and destruction of a radical leads to its having a high concentration and hence that species is the one observed in the e.s.r. spectrometer. Since e.s.r. spectrometers have been widely available the emphasis in free-radical chemistry has swung more and more over to these 'accessible' radicals and possibly their reactions. The means of generating them are still comparatively few, stretching chemical and mechanical ingenuity to the full. Most radicals are reactive and have to be generated continuously by one or other well-tried techniques, *e.g.* by means of irradiation (radioactive, electron, or u.v.), flow systems, electrolysis, auto-oxidation, and so on. Alternatively, one might artificially prolong the lifetime of a radical by trapping it in an unreactive solid.

Although one could use the types of experiment as a basis for classification, the Reporter prefers instead to use the types of radicals themselves to classify the rather heterogeneous material which appeared during 1972.

2 Simple Alkyl and Aryl Radicals

There has been little evidence, this year, of a great deal of work on the reactions of simple alkyl or aryl radicals, although it seems that reactivity patterns of the methyl radical[1] and the phenylation of heterocyclic systems such as thiophen[2] or the pyridiumm cation[3] still evince some interest.

The way towards some further possibilities in this direction has been pointed out in the study of the decay of methyl radicals formed in γ-irradiated methyl isocyanide between 77 and 125 K.[4] As the well-known 1 : 3 : 3 : 1 quartet ascribed to methyl diminishes, a 1 : 1 : 1 triplet increases in amplitude. This new signal is attributed to the radical $\dot{C}H_2NC$ and strongly suggests that a hydrogen abstraction has taken place:

$$\dot{C}H_3 + CH_3NC \rightarrow \dot{C}H_2NC + CH_4$$

The absence of any splitting from the methylene protons is attributed to the large anisotropic coupling constants of the α-protons in a polar molecule of this sort, so that the outer lines of the 1 : 2 : 1 triplet (due to the rotating CH_2 group) are broadened, but the centre line ($m_I = 0$) remains sharp. A remarkable thing about this experiment is that if the deuteriated isocyanide is used, $\dot{C}D_3$ decays much more slowly than $\dot{C}H_3$ and does not give the expected $\dot{C}D_2NC$. One cannot help feeling that this system needs further investigation.

Other 'simple' aliphatic radicals have been investigated. For example, the e.s.r. spectrum of an 'old' radical, vinyl, has been reported[5,6] and some 'new' ones, propargyl and butatrienyl,[6] have been made in an argon matrix by photolysis of HI in the presence of the appropriate poly-yne, *e.g.* (1). Unlike vinyl, these radicals appear to be axially symmetric. Some new phenyl-type radicals have also been observed,[7] *i.e.* 2-, 3-, and 4-pyridyl, using the technique[8] of condensing the vapours of sodium metal mixed with a chloropyridine diluted with argon on

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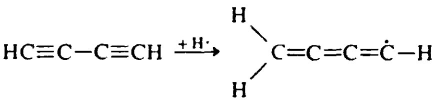
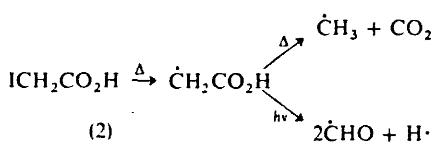
[1] W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, 1972, **94**, 1632.
[2] C. M. Carmaggi, G. De Luca, and A. Tundo, *J.C.S. Perkin II*, 1972, 412.
[3] J. M. Bonnier and J. Court, *Bull. Soc. chim. France*, 1972, 1834.
[4] J. T. Wang and F. Williams, *J. Amer. Chem. Soc.*, 1972, **94**, 2930.
[5] S. Nagai, S. Ohnishi, and I. Nitta, *J.C.S. Perkin II*, 1972, 379.
[6] P. H. Kasai, *J. Amer. Chem. Soc.*, 1972, **94**, 5950.
[7] P. H. Kasai and D. McLeod, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 720.
[8] J. E. Bennett and A. Thomas, *Nature*, 1962, **195**, 995.

to a cold finger, thus trapping these reactive radicals in an inert matrix. Like phenyl the pyridyls appear to be σ-radicals.



(1)

The usefulness of freezing-out radicals in an inert matrix was again demonstrated in the pyrolysis[9] of iodoacetic acid. According to the conditions, one might see methyl and/or formyl, which are secondary radicals, the primary radical (2) being seen only after initial pyrolysis at a relatively low temperature.



(2)

The 'universal chlorine or bromine abstractor', triethylsilyl, formed by the action of t-butyl radicals on triethylsilane, has been used with good effect to obtain many halogenated alkyl radicals.[10] As regards the α-halogenated methyl radicals, almost every combination from $\dot{C}H_3$ to $\dot{C}F_3$, to $\dot{C}Cl_3$, and to $\dot{C}Me_3$ has been achieved.[10a] Of particular interest are the ^{13}C coupling constants in the fluorinated methyl radicals, which vary from 272 G in $\dot{C}F_3$ to 38 G in $\dot{C}H_3$, indicating a much higher *s* character in the odd-electron orbital in the former case, and suggesting that the geometry of these radicals changes from pyramidal in the case of $\dot{C}F_3$ to planar in the case of $\dot{C}H_3$.

In an analogous investigation of radicals of the type $(SiMe_3)_x\dot{S}iMe_{3-x}$, the ^{29}Si splitting changed from 183 G for $x = 0$ to 65 G for $x = 3$, presumably showing that the steric hindrance of the larger groups pushes the molecule closer to a planar configuration.

In a somewhat similar investigation of β-fluorinated ethyl radicals,[10b] the ^{19}F coupling constant was much smaller in the case of $\dot{C}H_2CF_3$ (29.8 G) than with $\dot{C}H_2CHF_2$ (49.5 G) or with $\dot{C}H_2CH_2F$ (45.4 G), and the spectra all showed temperature dependence and the broadening of lines arising most probably from restricted rotation about the carbon–carbon bond. Similar effects are observed when larger groups (*e.g.* trialkyl-silyl or -germanyl) are attached to the β-carbon atom.[11]

3 Neutral Radicals of Group IV Elements

We have already seen that hydrogen is easily abstracted by t-butoxyl radicals from the trialkylsilanes, and the resulting radical whose spin density is localized

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[9] P. H. Kasai and D. McLeod, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 7975.

[10] (*a*) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1972, **23**, 209; (*b*) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6485.

[11] T. Kawamura, P. Meakin, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 8065.

mainly on a relatively electropositive atom is attracted, in a sense, to electronegative atoms such as Cl or Br rather than to hydrogen, for example. Thus in contrast to methyl, which tends if anything to abstract hydrogen, the metalloid nature of silicon makes attack on halogen or oxygen more likely. In fact, under favourable conditions, chain reactions with di-t-butyl peroxide may take place,[12] as is the case with a variety of diarylsilanes (3). A rather similar type of chain

$$\underset{(3)}{Ph_2SiH_2} + BuO\cdot \longrightarrow Ph_2\dot{S}iH \xrightarrow{Bu_2O_2} BuO\cdot$$

process may also occur with the analogous tin compound and certain alkyl halides, *e.g.* (4), once the reaction has been started.[13] Since the main organic product of this reaction is 1,1,1-triphenylethane, it seems that the chain involves

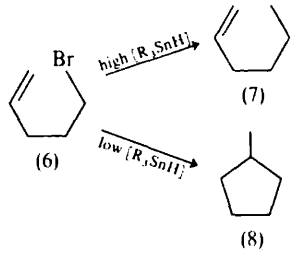
$$\underset{(4)}{Ph_3CCH_2Cl} \xrightarrow[\text{initiator}]{Bu_3SnH} \underset{0.23}{Ph_2CHCH_2Ph} \; \underset{:}{+} \; \underset{19}{Ph_3CCH_3}$$

halogen abstraction by the stannyl radical and hydrogen abstraction by the alkyl radical (5). This is one example of homolytic substitution and it seems that the process is accelerated by electronegative ligands on the tin, according to results

$$\begin{tikzcd} Ph_3CCH_2Cl \arrow[r, "Bu_3\dot{S}n"] & \underset{(5)}{Ph_3C\dot{C}H_2} + Bu_3SnCl \arrow[d, "Bu_3SnH"] \\ & Ph_3CCH_3 + Bu_3\dot{S}n \end{tikzcd}$$

of photolysis of di-t-butyl peroxide and chlorinated stannane derivatives[14] (which is in fact an S_H2 process).

These substitution reactions on tin have been used to investigate the interconversions between isomeric radicals,[15,16] *e.g.* the conversion of (6) into (7) and



(6)

(7) hex-1-ene

(8) methylcyclopentane

---

[12] S. L. Sosin, V. P. Alekseeva, and V. V. Korshak, *Doklady Akad. Nauk S.S.S.R.*, 1972, 203, 129.

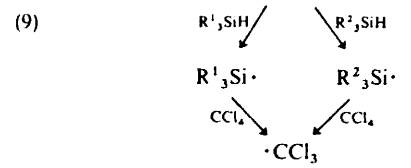
[13] M. L. Poutsma and P. A. Ibarbia, *Tetrahedron Letters*, 1972, 3309.

[14] A. G. Davies, B. P. Roberts, and J. C. Sciano, *J. Organometallic Chem.*, 1972, **39**, C55.

[15] C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6059.

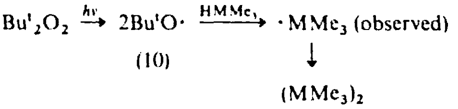
[16] C. Walling and A. Cioffari, *J. Amer. Chem. Soc.*, 1972, **94**, 6064.

(8). Evidently when the competition between cyclization and further hydrogen abstraction favours the latter process (because the concentration of the hydrogen source R_3SnH is large) there is not enough time to form the cyclopentylmethyl radical which eventually would give rise to the cyclic product. Cyclization to the six-membered ring is apparently unfavourable here. More general studies of radicals of the type $\dot{M}R_3$ have been accomplished[17,18] and various kinetic experiments have been attempted using these systems.[18,19] For example, relative rates of hydrogen abstraction from alkylated silanes (9) by $\dot{C}Cl_3$ have been found


(9)

by analysis of the products obtained, say in carbon tetrachloride. Since all of the silicon radicals attack the solvent, there is a continuous supply of $\dot{C}Cl_3$ and so there is always a straight competition taking place.

The rates of dimerization (or self-reaction) of the radicals of the type $\dot{M}Me_3$ (M = C, Si, Ge, or Sn) and more complicated types in a system in which a chain reaction does not take place[18] have been measured using e.s.r. The chemical system is the familiar $Bu^t_2O_2 + HMMe_3$ and the radical (10) production is kept


$$Bu^t_2O_2 \xrightarrow{h\nu} 2Bu^tO\cdot \xrightarrow{HMMe_3} \cdot MMe_3\ (\text{observed}) \longrightarrow (MMe_3)_2$$
(10)

going by u.v. irradiation. The irradiation is continually 'chopped' and the light-chopping is synchronized with the corresponding signal amplitude and 'collected' by a computer, which makes it possible to measure the absolute decay rate. This is the technique developed by Weiner and Hammond.[20] The results are that the larger the radicals are, the slower they decay, suggesting that the reaction involved is largely diffusion-controlled. The kinetics are, as expected, second order.

Another example of the tendency of the radicals of type $\dot{M}R_3$ to attack electronegative sites is their reaction with oxygen leading to the formation of peroxyl radicals (11).[21] The order of stability of these peroxyl radicals as observed by e.s.r. is Pb > Sn > Si, with Ge somewhere in between.

$$Bu^t_2O_2 \xrightarrow[Me_3MH]{h\nu} Me_3\dot{M} \xrightarrow{O_2} Me_3MOO\cdot$$

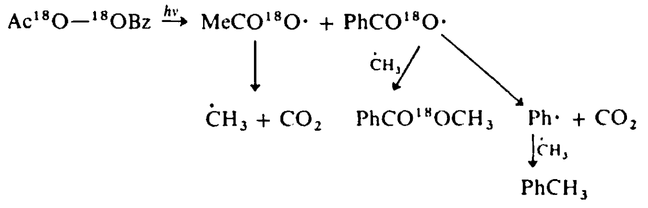
(11) M = Pb, Sn, Si, or Ge

---

[17] J. E. Bennett and J. A. Howard, *J.C.S. Perkin II*, 1972, 322.
[18] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.
[19] L. H. Sommer and L. A. Ulland, *J. Amer. Chem. Soc.*, 1972, **94**, 3803.
[20] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 968.
[21] J. E. Bennett and J. A. Howard, *J. Amer. Chem. Soc.*, 1972, **94**, 8244.

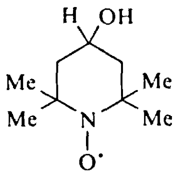
4 Decomposition of Organic Peroxides

Some interesting work on cage effects has appeared, showing that the course of the radical decomposition of acyl peroxides depends on the viscosity of the solution and hence on whether the radical pair initially formed can diffuse easily out of the solvent cage. This has been investigated in solution[22] by comparing the products when the solution contains a mixture of benzoyl peroxide and acetyl peroxide with those obtained when it contains only the mixed peroxide MeCO·O_2·OCPh. In a parallel type of experiment in the solid phase,[23] the mixed peroxide gave toluene and methyl benzoate but none of the products found in the liquid phase at 60 °C. Labelling with ^{18}O showed that the peroxy oxygen was favoured in coupling with methyl. Presumably the radicals, once formed, are kept together in a cage, so we would expect Scheme 1 to apply to the main course



Scheme 1

of the reaction. However, it cannot be taken for granted that decompositions of this class of compound are always radical processes, for the decompositions of cumyl peracetate[24] and of cumyl peroxide, or its potassium salt,[25] are mixed radical–ionic reactions depending on the solvent. So too is the reaction between benzoyl peroxide and triethylamine[26] in the absence of oxygen, which has been shown to involve radicals in part by the use of the nitroxide radical (12). An



(12)

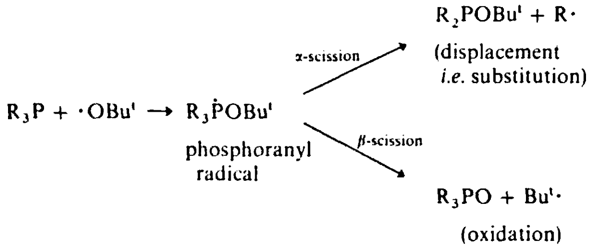
analogous reaction with dimethyl sulphide,[27] which is first order with respect to both the sulphide and benzoyl peroxide and which can become explosive, is apparently a purely ionic process.

---

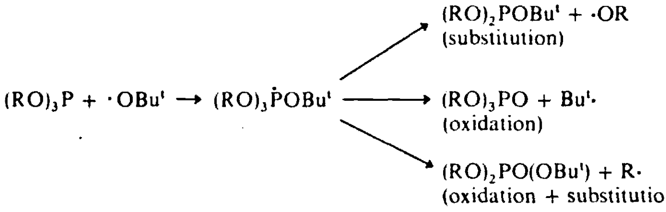
[22] W. A. Pryor, E. H. Morkved, and H. T. Bickley, *J. Org. Chem.*, 1972, **37**, 1999.
[23] N. J. Karch and J. M. McBride, *J. Amer. Chem. Soc.*, 1972, **94**, 5092.
[24] J. E. Leffler and F. E. Schrivener, jun., *J. Org. Chem.*, 1972, **37**, 1794.
[25] N. A. Sokolov, L. G. Usova, and V. A. Shushunov, *Zhur. org. Khim.*, 1972, **8**, 751.
[26] B. M. Sogomonya and N. M. Beileryan, *Uch. Zap. Erevan. Univ. Estestv. Nauki*, 1970, 3, 148.
[27] W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, 1972, **37**, 2885.

5 Radicals Containing Quadrivalent Phosphorus

The chemistry of alkylated phosphorus compounds parallels that of the organic chemistry of the silicon group of elements rather closely. Developments in techniques have now made it possible to observe the intermediate radicals in the reactions of the t-butoxyl radical with alkylated phosphines[28] or phosphites.[28-30] The products and radicals formed can be explained by Schemes 2 or 3. In a number of cases both the intermediate phosphoranyl radicals and the alkyl radicals formed from their decomposition have been observed by e.s.r. and, as one might expect, bulky groups like t-butyl make the best leaving groups.[29]



Scheme 2



Scheme 3

It is interesting that it is not apparently necessary to postulate phosphoranyl radical intermediates to explain the kinetics of the autoxidation of trimethyl phosphite, triphenylphosphine, or methyl diphenyl phosphinite,[31] although steps where they could be formed are written as in Scheme 4. In fact one would have thought that phosphoranyl radicals would be important in autoxidations

$$RO_2\cdot + R_3P \longrightarrow R_3PO + RO\cdot$$
$$RO\cdot + R_3P \longrightarrow R_3PO + R\cdot$$

Scheme 4

---

[28] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, 94, 6033.

[29] A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

[30] W. G. Bentrude, E. R. Hansen, W. A. Khan, and P. A. Rogers, *J. Amer. Chem. Soc.*, 1972, 94, 2867.

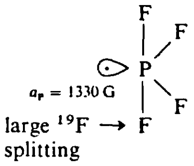
[31] Y. Ogata and M. Yamashita, *J.C.S. Perkin II*, 1972, 730.

when they are formed, because they react easily with molecular oxygen to give peroxyl radicals (13) which can be observed by means of their e.s.r. spectra.[29,32]

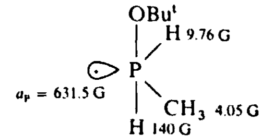
$$\mathrm{X_4P\cdot + O_2 \longrightarrow X_4POO\cdot}$$

(13)

The structure of these phosphoranyl radicals is itself of great interest.[28] According to theory[33] the ligands are at four corners of a trigonal bipyramid and in the case of $\dot{\mathrm{P}}\mathrm{F_4}$ (14) the large ^{19}F coupling comes from the two fluorines in the axial positions. This helps the assignments in the alkylated radicals, *e.g.* (15).



(14)



(15)

The other striking thing about these radicals is the very large phosphorus hyperfine splitting.

The corresponding radicals of arsenic[34] also have large splittings from the 'central' nucleus (1900 G), showing that 20% of the odd-electron density is associated with the arsenic 4*s* atomic orbital. The chemical behaviour of these compounds is also similar to that of phosphoranyl radicals, except that from the nature of the products it seems that the displacement is favoured, *e.g.* Scheme 5.

$$\mathrm{Ph_3As + Bu^tO\cdot \longrightarrow Ph_3\dot{A}sOBu^t \longrightarrow Ph_2AsOBu^t + Ph\cdot}$$

Scheme 5

Similar results have been found with other simple phosphorus radicals ($\mathrm{PO_3}^{2-}$, $\mathrm{PO_2OH}^{\bar{\cdot}}$, $\mathrm{HPO_2}^{\bar{\cdot}}$, and $\mathrm{PhPO_2}^{\bar{\cdot}}$) in aqueous solution.[35] These radicals are formed from the corresponding anions by hydrogen abstraction by hydroxyl in the titanium(III)–$\mathrm{H_2O_2}$ system. They cannot really decompose in the manner of the phosphoranyl radicals just discussed but can add to double bonds and nitroalkane *aci*-anions to give appropriate radicals. The large ^{31}P splittings in these phosphorus(IV) radicals (~500 G) show that the general structure must be similar to the trigonal bipyramid with the odd electron confined mainly to the equatorial plane. The absence of splitting from the phenyl protons in $\mathrm{PhPO_2}^{\bar{\cdot}}$ indicates that the phenyl group is also probably joined to the phosphorus by a bond in the equatorial plane (in view of the other results just discussed) though

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[32] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, 94, 2528.

[33] J. Higuchi, *J. Chem. Phys.*, 1969, 50, 1001.

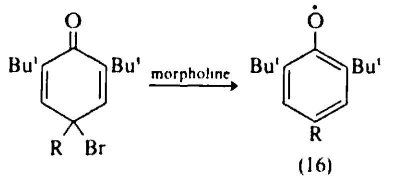
[34] E. Furimimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1972, 94, 5932.

[35] B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, *J.C.S. Perkin II*, 1972, 1508.

this is not exactly the view put forward.[35] There are evidently some interesting stereochemical problems to be solved in these phosphorus radicals.

6 Phenoxyl and Semiquinone Radicals

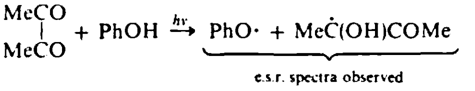
Various new ways of generating phenoxyl radicals have been found. In the first place, since hindered phenols give stable radicals very easily, they may be used as spin traps in any reactions in which there are more active radicals.[36] As one might expect, phenoxyl or related radicals may be obtained from derivatives of the keto-forms of phenol by appropriate choice of reagent,[37,38] *e.g.* (16).



(or *ortho*-isomer)

(16)

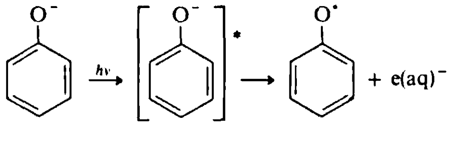
The excited states of diketones have also been used not only to produce the phenoxyl radical from phenol itself but in such concentrations that the rate of dimerization can be found.[39] In these experiments, solutions of the diketone and phenol were photolysed and steady concentrations of radicals were observed by e.s.r. (Scheme 6). Again the rotating-sector method, already mentioned, was used to look at the relative rates of decay of these radicals so that termination constants could be measured.



$$\begin{matrix}\mathrm{MeCO}\\ |\\ \mathrm{MeCO}\end{matrix} + \mathrm{PhOH} \xrightarrow{h\nu} \underbrace{\mathrm{PhO\cdot} + \mathrm{Me\dot{C}(OH)COMe}}_{\text{e.s.r. spectra observed}}$$

Scheme 6

Irradiation of phenol in alkaline solution can give appreciable concentrations of phenoxyl directly.[40] This involves excitation of the phenoxy-anion, most probably, so that the first part of the reaction appears to be as shown in Scheme 7.



Scheme 7

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[36] C. M. Camaggi and M. J. Perkins, *J.C.S. Perkin II*, 1972, 507.

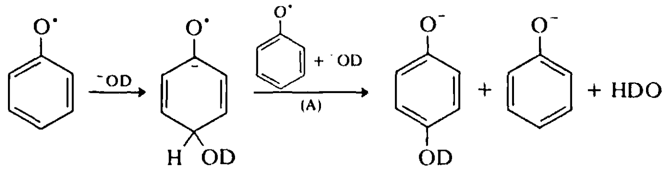
[37] D. K. Rasuleva, A. A. Volod'kin, V. V. Ershov, N. N. Bubov, S. P. Solodovnikov, A. P. Prokof'ev, and S. G. Kukes, *Izvest. Akad. Nauk S.S.S.R., Ser khim.*, 1972, 1446.

[38] A. P. Prokof'ev, S. P. Solodnikov, A. A. Volod'kin, and V. V. Ershov, *Doklady Akad. Nauk S.S.S.R.*, 1972, 204, 1114.

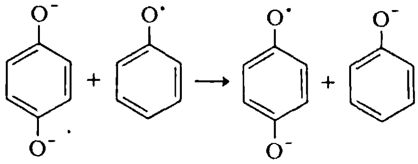
[39] L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, 1972, 94, 585.

[40] M. Coccivera, M. Tomkiewicz, and A. Green, *J. Amer. Chem. Soc.*, 1972, 94, 6598.

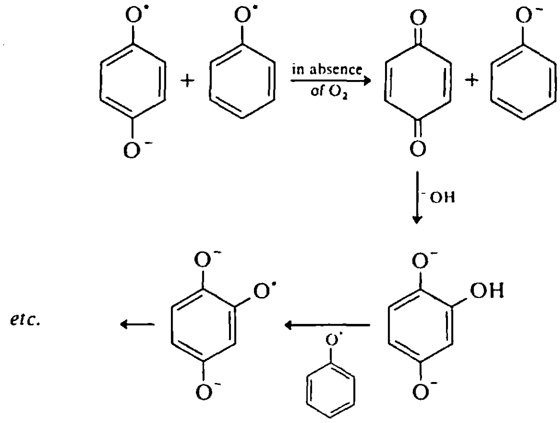
Now the e.s.r. spectra of semiquinone and even hydroxylated semiquinones are also observed in this system (depending on the pH), so their formation is rationalized in Scheme 8 (in D_2O for clarity). Once the polyhydroxylated benzenes are formed they would quickly react with the relatively reactive phenoxyl radicals to give corresponding semiquinones (Scheme 9). Presumably, by the same token, quinones could easily arise in a similar way, since the steps leading to the other radicals have been confirmed by e.s.r. work on the autoxidation of substituted hydroquinones (Scheme 10).[41] in the presence of oxygen these last steps take place with O_2 as the oxidizing agent. Similar reactions take place in alcoholic



Scheme 8



Scheme 9



Scheme 10

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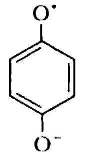
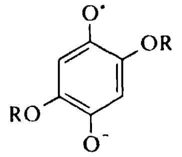
[41] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

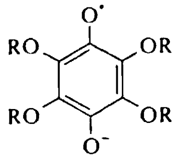
solutions,[42,43] the main difference being that (*a*) alkyl groups cause greater complexity of spectra which can increase the difficulty in analysing overlapping spectra, though the ENDOR technique can be of help,[43] and (*b*) the alkoxy-groups seem to add on in pairs so that the radicals observed, starting with hydroquinone, are (17), (18), and (19).



(17)



(18)

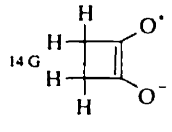


(19)

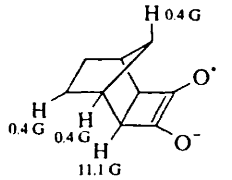
In these various reactions it is only the step (A) of Scheme 8 which is not immediately obvious as a possibility. It was introduced tentatively to account for the fact that, during irradiation of phenolic solutions at pH 11 in D_2O, both the aryl protons and those of the HDO formed gave emission n.m.r. spectra.[40] The formation of a radical pair, of admittedly short lifetime, of the type implied by step (A) could account for the spin polarization of both types of proton. This work shows how potentially powerful a combination of CIDNP and e.s.r. could be in probing the details of radical reactions.

7 Semidiones and Related Radicals

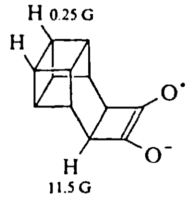
More development has been taking place in the study or semidiones, especially those in which the two oxygen atoms are attached to a ring system.[44] For example, it has been shown that the cyclobutene ring is a favourable system for delocalization of the spin density to remote nuclei: starting from the parent compound (20), further rings have been built on so that in (21) the remote couplings even four carbon atoms away from the oxygen are still 0.4 G. The assignments have been confirmed by deuterium substitution. In the remarkable radical (22), couplings with protons five carbon atoms away from the oxygen are



(20)



(21)



(22)

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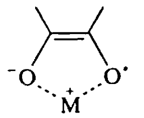
[42] D. C. Reitz, J. R. Holkihar, F. Dravnieks, and J. E. Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

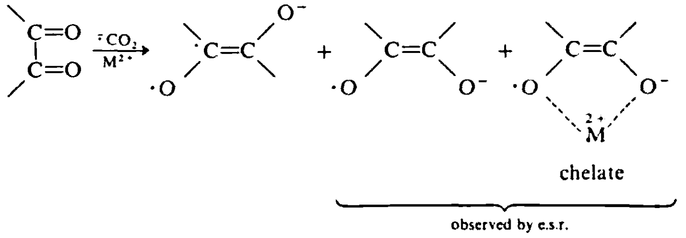
[43] N. M. Atherton and A. J. Blackhurst, *J.C.S. Faraday II*, 1972, **68**, 470.

[44] G. A. Russell, P. A. Whittle, R. G. Keske, G. Holland, and C. Aubrichon, *J. Amer. Chem. Soc.*, 1972, **94**, 1693.

still observable (0.25 G). These radicals were made by the autoxidation of the bis(trimethylsiloxy)alkene in strong alkali. Another feature of semidiones which has been investigated as the formation of gegenions with metal cations.[45,46] When acetol, for example, is treated with base (MOBu^t; M = alkali metal), the semidiones generated, half life ~0.5 min, are in the *cis*- and *trans*-forms.[45] The larger the metal ion, the greater is the proportion of the *cis*-form, owing to chelate formation, *e.g.* (23). This is favoured by bulky substituents. In the case of the Group II metals these chelates can be quite stable and have been observed as a third type of radical when diketones are reduced by $\dot{C}H_2OH$ or $\dot{C}O_2$ after these have been generated by the Ti^{III}–H_2O_2–substrate system in the first mixing chamber of a multi-flow system (Scheme 11).[46]



(23)



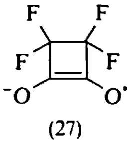
Scheme 11

A number of perfluorinated semidiones and related radicals have been produced by electrolytic reduction,[47] *e.g.* (24)—(29). For some reason these radicals are much more stable than their hydrogen analogues.

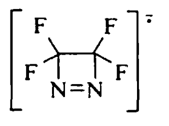
$(CF_3)_2CO^{\cdot-}$ (24)

$(CF_3CO)_2^{\cdot-}$ (25)

$(CF_3)_2CS^{\cdot-}$ (26)



(27)



(28)

$[FC_3N{=}NCF_3]^{\cdot-}$ (29)

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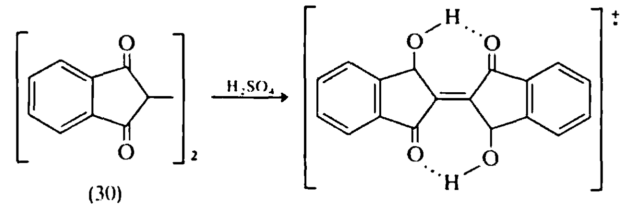
[45] G. A. Russell and D. F. Lawson, *J. Amer. Chem. Soc.*, 1972, 94, 1699.

[46] A. J. Dodds, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 2053.

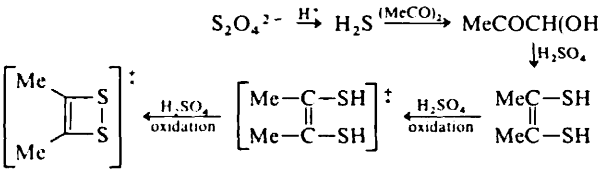
[47] G. A. Russell, G. L. Gerlock, and G. R. Underwood, *J. Amer. Chem. Soc.*, 1972, 94, 5209.

8 Sulphur Radicals

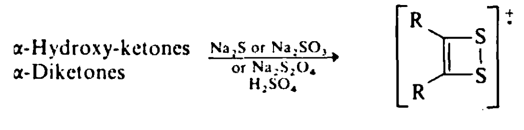
Not every one-electron reducing agent gives rise to semidione-type radicals with diketones. Thus whereas the tetraketone (30), derived from ninhydrin reduced by dithionite, with sulphuric acid gives the radical (31), biacetyl instead gives a sulphur radical *via* the route[48] shown in Scheme 12. The big difference between the chemistry of sulphur and that of oxygen becomes apparent here, for rather than form multiple bonds, sulphur atoms tend to combine with each other. Thus whereas simple reduction of diketones gives semidiones (negative ions) under the above conditions, 1,2-dithiole radicals (32), which are positive ions, are produced.



(30) (31)

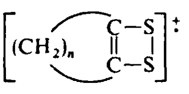


Scheme 12

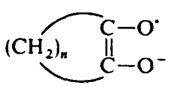


(32) (overall oxidation)

The coupling constants of the nearest (β-) methylene protons in the bicyclic radicals (33) are only about a third of those in the semidiones (34), suggesting that the spin density is more on the sulphur in the former than it is on the oxygen in the latter.



(33)



(34)

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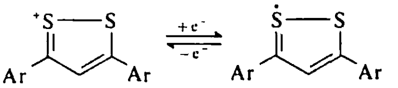
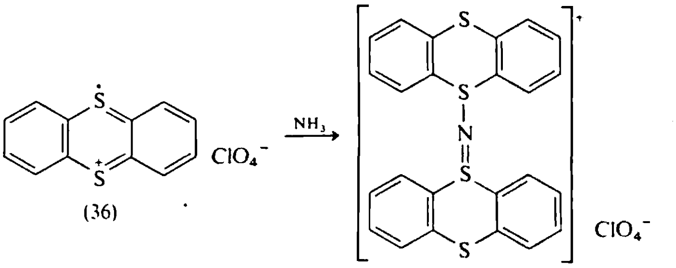
[48] G. A. Russell, R. Tanikega, and E. R. Jalaty, *J. Amer. Chem. Soc.*, 1972, **94**, 6125.

Rather similar types of radical (35) may be obtained by electrolytic reduction of dithiolylium[49] ions in acetonitrile. When the temperature is lowered in this system the e.s.r. signal diminishes, but presumably without appreciable broadening. On reheating it reappears and this effect is ascribed to a dimerization–dissociation equilibrium.



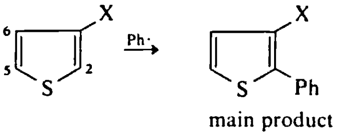
(35)

The thianthrene molecule ion (36) reacts with ammonia to give a cation[50] in which two thianthrene moieties are connected *via* sulphur to a nitrogen atom.



(36)

When there is a substituent in the 3-position in thiophen, the 2-position is activated towards attack by phenyl radicals (relative to the 4-position) (Scheme 13).[51] This tendency appears to hold whatever the nature of substituent X. It would appear from this that polar effects are not the most important ones.



Scheme 13

Another rather unexpected result is that thiazol-2-yl radicals,[52] formed by pyrolysis or photolysis of 2-iodothiazole, attack aromatic compounds to yield *ortho* : *meta* : *para* ratios of products in the opposite sense to those accustomed in electrophilic substitution, *i.e.* anisole, 70 : 15 : 13; nitrobenzene, 60 : 12 : 27. Thus *para*-substitution is relatively favoured by what are usually called 'deactivating' groups.

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[49] C. T. Pedersen, K. Bechgaard, and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 430.

[50] H. J. Shine and J. J. Shine, *J. Amer. Chem. Soc.*, 1972, 94, 1026.

[51] C. M. Camaggi, G. DeLuca, and A. Tundo, *J.C.S. Perkin II*, 1972, 1594.

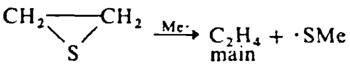
[52] G. Vernin, R. Jauffred, C. Ricard, H. M. J. Dou, and J. Metzger, *J.C.S. Perkin II*, 1972, 1145.

Diphenyl thioketone reacts with Grignard reagents[53] to give a thioether *via* a long-lived free radical (37) whose e.s.r. spectrum shows that it is of the benzhydryl type. This implies attack by R· (alkyl) on the sulphur atom, and other

$$Ph_2C{=}S \xrightarrow{RMgX} RS\dot{C}Ph_2 \longrightarrow RSCHPh_2$$

(37)

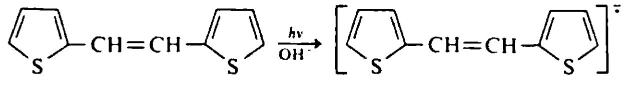
studies have further confirmed that sulphur is in general open to attack by radicals. For example, the high yields of alkene which are found when episulphides (38) react with methyl radicals[54] indicate that the main process is abstraction of sulphur by the alkyl radical.



(38)

The products of photolysis of methyl ethyl sulphide[55] in order of their yields include: $MeH > MeSSEt > EtSSEt > EtH$, together with all the other combinations, showing the presence of methyl, ethyl, and the two sulphide radicals.

Some interesting effects are observed when the various isomeric dithienylethylenes (39) are reduced in alkali.[56] Mixtures of the e.s.r. spectra of rotational isomers can be resolved with the aid of a computer.



(39)

When anions of thiophen in which there are one or two CHO groups in the 2- or 5-positions are generated by photolysis of the parent molecule in alkaline solution,[57] the aldehyde group does not rotate freely, according to the e.s.r. evidence, but is effectively locked.

9 Aromatic Radical Ions

As with other well-worn fields, it becomes increasingly difficult to say anything new or unexpected about aromatic radical ions. There still remain, however, many radicals which have incompletely explored structures and which are intrinsically interesting. Some of these are the annulene radical ions, for they give information about the structure of the parent molecule. One example is

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[53] M. Dagonneau, J. F. Hemidy, D. Cornet, and J. Vialle, *Tetrahedron Letters*, 1972, 3003.

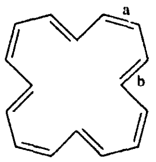
[54] E. Jakubowski, M. G. Ahmed, E. M. Lown, H. S. Sandhu, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1972, 94, 4094.

[55] D. R. Tycholitz and A. R. Knight, *Canad. J. Chem.*, 1972, 50, 1734.

[56] L. Lunazzi, A. Mangini, G. Placucci, P. Spagnolo, and M. Tiecco, *J.C.S. Perkin II*, 1972, 172.

[57] L. Lunazzi, G. F. Peduli, M. Tiecco, C. Vincenzi, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 751.

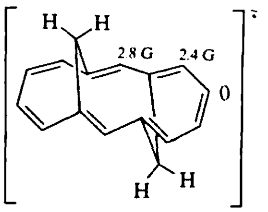
[16]annulene,[58] which has several possible structures having different combinations of *cis*- and *trans*-bonds. The anion can be generated electrolytically and in the e.s.r. spectrum the proton hyperfine splittings are approximately 4.0 G (8 protons), 1.0 G (4 protons), and 0.75 G (4 protons). This is consistent with an '85' structure (40). The convention is to designate alternate bonds as either



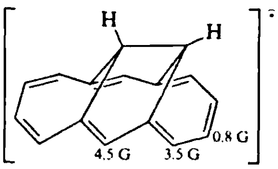
(40) [16]-85-Annulene

cis (0), *e.g.* bond 'a', or as *trans* (1), *e.g.* bond 'b'. Starting with *cis*, the collection of zeros and units are then taken as a binary number and this is converted into decimals. In this case the binary number starting at 'a' is 01010101 = $2^6 + 2^4 + 2^2 + 1 = 85$.

The smaller coupling constants are assumed to be negative if we are to take the molecule as being planar and the Q-value is not to be too different from those usually applied to aromatic radical ions. The effect of bridging forces the annulenes out of the planar configuration and this is reflected in the coupling constants, for example in the two bridged [14]annulenes (41) and (42).[59] The



(41) *trans* bridges



(42) *cis* bridges

different patterns of coupling constant can be ascribed to different degrees of puckering in the rings. Similarly, in 7,12-dihydropleiadene anion (43) the coupling constants of the methylene protons give a clue about the conformation of the seven-membered ring.[60] Here ENDOR has been used to help in the analysis of the e.s.r. spectrum.

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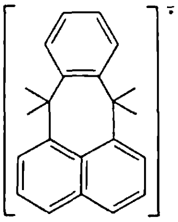
[58] J. F. M. Oth, H. Baumann, J. M. Giller, and G. Schröder, *J. Amer. Chem. Soc.*, 1972, **94**, 3498.

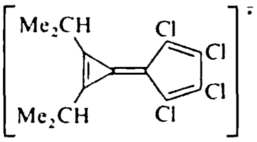
[59] F. Gerson, K. Mullen, and E. Vogel, *J. Amer. Chem. Soc.*, 1972, **94**, 2924.

[60] R. D. Allandoerfer, P. E. Gallagher, and P. T. Lansbury, *J. Amer. Chem. Soc.*, 1972, **94**, 7702.



(43)

Kinetic studies of reactions of radical ions can be made using the linewidths in e.s.r. spectra, as in the electrochemical oxidation/reduction of aromatic species, where the broadening of lines arises from exchange between the radical ion and the parent molecule.[61] For fast reactions the stopped-flow technique in conjunction with the electronic spectra can be applied, *e.g.* as in protonation of perylene radical ions.[62] Slower reactions such as the reaction between the anthracene negative ion and water[63] can be followed in a more leisurely fashion.



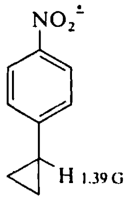
(44)

Linewidth alternation in the e.s.r. spectrum of a calicene derivative (44) has been used to arrive at a value of the barrier against rotation of the isopropyl groups of about 1.5 kcal mol^{-1}.[64] In this and related radicals the rings are *not* coplanar.

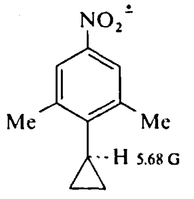
10 Nitro Radical Anions

The main interest in nitro radical ions is now as an aid in exploring different types of chemical structure. In fact the existence of the easily reduced nitro-group in a molecule enables a 'spin probe' to be introduced. Good examples of this are investigations of the cyclopropyl groups:[65,66] when it is attached to the 4-position of the nitrobenzene negative ion (45) the β- and γ-coupling constants are 1.39 G and 0.27 G, respectively.[65] On introduction of two methyl groups into the 3- and 5-positions (46), the β-splitting rises to 5.68 G, showing that steric hindrance has pushed the cyclopropyl group as a whole into a more favourable position. Insertion of an acetylenic linkage between the aromatic ring and the cyclopropyl

[61] B. A. Kowert, L. Marcoux, and A. J. Bard, *J. Amer. Chem. Soc.*, 1972, **94**, 5538.
[62] G. Levin, C. Satphen, and M. Swarc, *J. Amer. Chem. Soc.*, 1972, **94**, 2652.
[63] S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, 1972, **94**, 6076.
[64] S. Niizuma, S. Konishi, H. Kokubun, and M. Konizumi, *Chem. Letters*, 1972, 643.
[65] L. M. Stock and P. E. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 7686.
[66] C. E. Hudson and N. L. Bauld, *J. Amer. Chem. Soc.*, 1972, **94**, 1158.

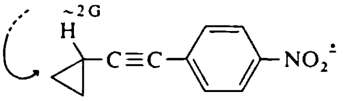


(45)



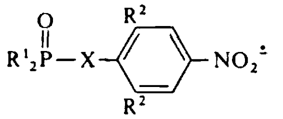
(46)

group (47) effectively removes strong steric interactions and the whole group rotates freely down to quite low temperatures.[66]



(47)

An attempted study of the effects of conformation on ^{31}P coupling constants[67] in radical ions of the type (48) where X = O or S was not completely convincing



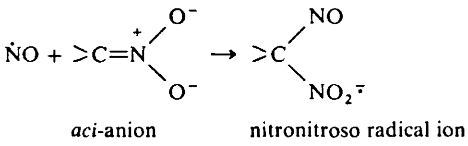
(48)

in view of the large number of factors involved. A good way of producing aliphatic nitro-anions is to employ the *aci*-anion of nitromethane (49) as a spin trap.[68,69] The resulting radicals have been examined by e.s.r. for a very wide selection of radicals X·, produced by Ti^{3+}–H_2O_2 and other systems, and again

$$X\cdot + CH_2NO_2^- \longrightarrow XCH_2NO_2^{\dot{-}}$$

(49)

the nitro-group can be regarded as a useful spin probe. Other *aci*-anions of nitroalkanes or oximes have been allowed to react with NO or NO_2 to give radical anions (Scheme 14).[69]



Scheme 14

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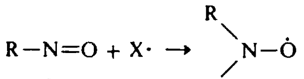
[67] W. M. Gulick, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 29.

[68] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

[69] G. A. Russell, R. K. Norris, and A. R. Metcalf, *J. Amer. Chem. Soc.*, 1972, **94**, 4959.

11 Nitroxide Radicals

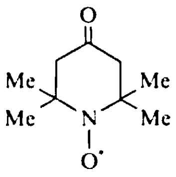
One might almost say that these have become the most popular class of radicals. This is largely because many of them are easily formed, are quite stable, and are not charged, and so can be used in neutral solutions or in non-aqueous solvents. Thus nitroso-compounds (50) can be used as spin traps.[70] The resulting nitroxide



$$R{-}N{=}O + X\cdot \longrightarrow \underset{X}{\overset{R}{}}\!\!\!\!\!\searrow\!\!N{-}\dot{O}$$

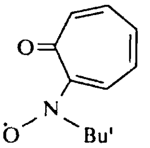
(50)

radicals may well have structures of interest and this is another useful role of the nitroxide grouping as a spin probe. Thus di-t-butyl nitroxide has been used to study micelles in detergent solutions[71] and various nitroxides have been used to study the pulse radiolysis of cytosine, thymine, guanine, and adenine.[72] In this case the fact that the nitroxide (51) does *not* react with the radical formed by adenine shows that the site of the odd electron must be relatively hindered.



(51)

Being stable magnetic species, nitroxides may be used to quench excited states, *e.g.* of stilbene or naphthalene.[73] They have also been used to produce ^{13}C contact chemical shifts in the n.m.r. spectra of aromatic molecules.[74] As with the nitro-group, the main interest in nitroxides will probably be that they will introduce unpaired spin into structures of interest, *e.g.* attached to a seven-membered ring as in (52).[75] Similarly, in azabicycloheptyl *N*-oxyl derivatives (53)



(52) 2-t-butylaminotropone *N*-oxyl radical; $a_N = 12.7$ G, $a_4 = a_6 = 0.93$ G, and $a_3 = a_5 = a_7 = 1.86$ G

---

[70] C. M. Camaggi, R. J. Holman, and M. J. Perkins, *J.C.S. Perkin II*, 1972, 501; A. L. Bluhen and J. Winstein, *J. Org. Chem.*, 1972, **37**, 1748.

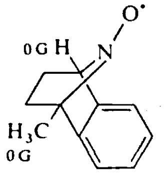
[71] N. M. Atherton and S. J. Strach, *J.C.S. Faraday II*, 1972, **68**, 374.

[72] T. Brusted, H. Bugge, W. B. G. Jones, and E. Wold, *Internat. J. Radiat. Biol.*, 1972, **22**, 115.

[73] R. A. Caldwell and R. E. Schwerzel, *J. Amer. Chem. Soc.*, 1972, **94**, 1035.

[74] I. Morishima, K. Kawakami, T. Yonezawa, K. Goto, and M. Imanari, *J. Amer. Chem. Soc.*, 1972, **94**, 6555.

[75] T. Toda, E. Mori, and K. Murayama, *Bull. Chem. Soc. Japan*, 1972, **45**, 1852.



(53)

the coupling constants have yet to be explained satisfactorily.[76] In this case zero coupling with bridging hydrogens shows that they are in the nodal plane.

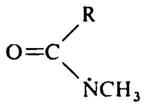
12 Radicals related to Amines

Photolysis of halogenoamines gives rise to the corresponding amino-radicals. For example, if conducted in sulphuric acid solution, dialkylaminium cations (54), which are isoelectronic with the corresponding simple alkyls, are obtained and can be detected by means of their e.s.r. spectra.[77] The interesting thing about the e.s.r. parameters of these radicals is that they are nearly the same as in their carbon analogues, *i.e.* $a_\alpha = 23$ G, $a_\beta = 34$ G, and $a_N = 19$ G.

$$R_2\overset{+}{N}HCl \xrightarrow{h\nu} R_2\overset{+\bullet}{N}H + Cl\cdot$$

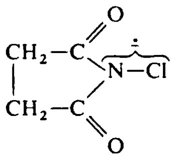
(54)

The simple amido-radicals (55) can also be made from the photolysis of the chloramide.[78] The coupling constants indicate that these radicals are of a π-type, as are the simple amino-radicals.



(55) $a_N = 15$ G, $a_{CH_3} = 29$ G

It is interesting to compare these results with those from the γ-irradiation of *N*-halogenosuccinimide single crystals.[79] The trapped radicals have the odd electron in the σ^* orbital of the N–halogen bond (56). It may be that in the solid dissociation is prevented and that some similar type of radical is a precursor to



(56)

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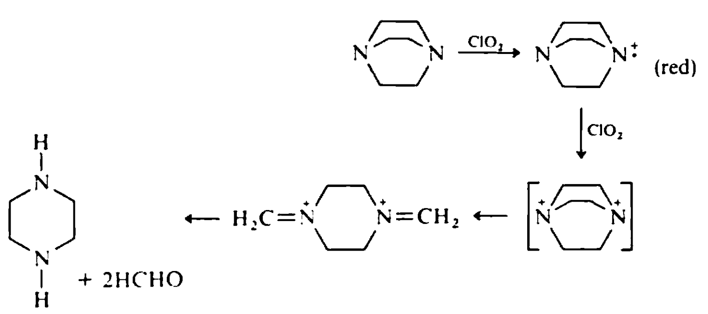
[76] D. J. Kosman, *Tetrahedron Letters*, 1972, 3317.
[77] W. C. Danen and R. C. Rickard, *J. Amer. Chem. Soc.*, 1972, **94**, 3254.
[78] W. C. Danen and R. W. Gillert, *J. Amer. Chem. Soc.*, 1972, **94**, 6853.
[79] G. W. Nielson and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1582.

amino- or amido-radicals in solution. The interaction of solvated electrons (sodium in a large excess of liquid ammonia) with amides or thioamides leads also to mono- and di-negative ions, (57) and (58), observable in a flow system by e.s.r.[80] In the dianions the e.s.r. spectra show that there is restricted rotation about the C—Ar bond, perhaps owing to repulsion of the two negative charges (one of which is associated with the ring, approximately).

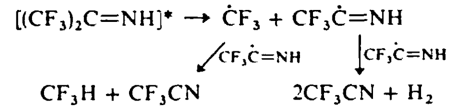
$$ArCONH_2 \xrightarrow{e^-} \underset{(57)}{[ArCONH_2]^-} \text{ or } \underset{(58)}{[ArCONH]^{2-}}$$

A kinetic study of the reaction between chlorine dioxide and triethylenediamine[81] by means of the stopped-flow method shows that the red intermediate must be an aminium cation radical. The mechanism is as shown in Scheme 15.



Scheme 15

In the photolysis of hexafluoroacetone imine[82] the products, analysed by mass spectrometry, are, in order of abundance, $CF_3CH > CF_3H > H_2$, and this is explained by the sequence shown in Scheme 16. A somewhat related reaction,



$$\begin{array}{ccc} [(CF_3)_2C{=}NH]^* \longrightarrow \dot{C}F_3 + CF_3\dot{C}{=}NH & & \\ \swarrow^{CF_3\dot{C}=NH} & & \downarrow^{CF_3\dot{C}=NH} \\ CF_3H + CF_3CN & & 2CF_3CN + H_2 \end{array}$$

Scheme 16

the isomerization of oximethionocarbamate,[83] yields a high enough concentration of the iminyl radical intermediate (59) for it to be detected by e.s.r. Where there is an *ortho*-fluorine substituent the ^{19}F splitting is relatively large (2.3 G) and this is rationalized by a through-space interaction (60).

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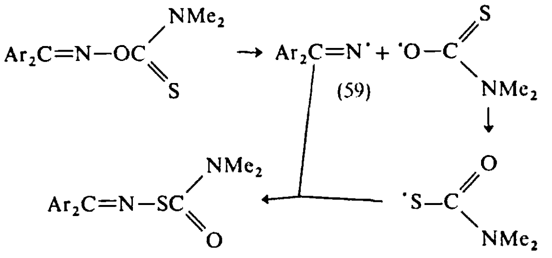
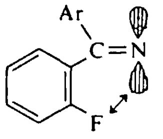
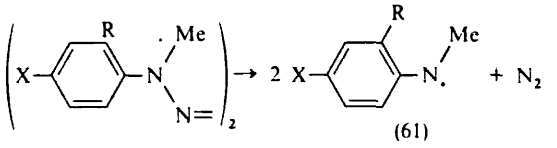
[80] I. H. Elson, T. J. Kemp, and T. J. Stone, *J.C.S. Faraday II*, 1972, **68**, 1452.
[81] G. T. Davis, M. M. Demet, and D. H. Rosenblatt, *J. Amer. Chem. Soc.*, 1972, **94**, 3321.
[82] F. S. Toby, S. Toby, and G. O. Pritchard, *J. Amer. Chem. Soc.*, 1972, **94**, 4441.
[83] R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *J.C.S. Chem. Comm.*, 1972, 721.





(60)

In the e.s.r. spectra of *N*-t-butylanilino-radicals,[84] the ring-proton splittings are relatively insensitive to substituents. In the case of the corresponding *N*-methylanilino-radicals (61) it is found that loss of nitrogen from the starting



azo-compound is much greater when there is an *ortho*-methyl group on the aromatic ring. Also with the *ortho*-methyl compound, the reaction is virtually independent of the *para*-substituent X, implying that efficient overlap between the half-filled orbital on the nitrogen and the aromatic π-system is important in determining the rate of decomposition.

13 Delocalization of Odd Electrons through σ-Bond Frameworks

Although already implied and accepted as the explanation of β coupling constants in ethylvinyl *etc.*, σ-spin delocalization, as it has been called,[85] is more important than has previously been thought. Its presence has been deduced in nitro-aromatic radicals,[86] nitroxides,[87] or in α-substituted benzyl radicals,[85] when steric hindrance pushes the plane of the ring away from that of the *p*-orbital of the extra-nuclear atom which has the largest spin density [see (62)]. This is shown,

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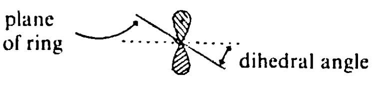
[84] S. F. Nielsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, 1972, **94**, 1610.

[85] W. J. VanderHoek, B. A. C. Rousseluw, J. Schmidt, W. G. B. Huysmans, and W. J. Mijs, *Chem. Phys. Letters*, 1972, **13**, 429.

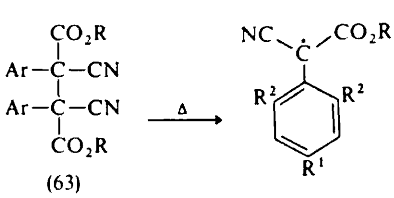
[86] D. R. Geske, J. L. Ragle, M. A. Bambenek, and A. Balch, *J. Amer. Chem. Soc.*, 1964, **86**, 987.

[87] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.



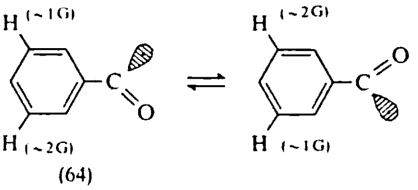
(62)

for example, in the e.s.r. spectra of substituted methoxycarbonylcyanobenzyl radicals, made by the thermolysis of 1 : 2 diarylsuccinonitriles (63). There is an increase in the coupling constants of the *m*-protons relative to the *o,p*-protons



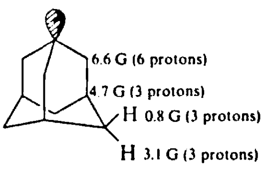
(63)

and an overall decrease in spin density on the ring. Whereas the spin densities on the *o*- and *p*-positions decrease rapidly with the dihedral angle, the *m*-proton splittings do not change much because even in the perpendicular conformation they are of the order of 2 G. This has already been confirmed[88] by the e.s.r. spectrum of the benzoyl radical (64), which shows a major splitting from the *m*-protons (1.16 G), which are equivalent, indicating that this is a σ-radical but that a rapid flip-over is occurring. The assignments here have been made relative to the β-splittings in the vinyl radical.

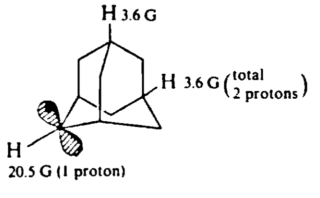


(64)

After a number of vain attempts it seems that the e.s.r. spectra of 1- and 2-adamantyl radicals, (65) and (66), have been observed.[89,90] As expected, the patterns of coupling constants in these radicals are very different from each other,



(65) 1-adamantyl



(66) 2-adamantyl

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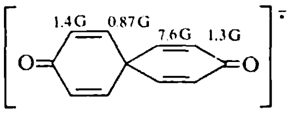
[88] P. J. Krusic and T. A. Rettig, *J. Amer. Chem. Soc.*, 1972, **94**, 722.

[89] P. J. Krusic, T. A. Rettig, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 995.

[90] R. V. Lloyd and M. T. Rogers, *Chem. Phys. Letters*, 1972, **17**, 428.

but both show splittings remote from the site of the odd orbital. In the case of 1-adamantyl[89] the low β-coupling constant (6.6 G) is attributed to the pyramidal conformation at the 1-position. The spectrum of 2-adamantyl[90] was badly resolved, so the smaller coupling constants were obtained using the ENDOR technique. The assignments agreed with appropriate INDO calculations. An interesting point here is that 1-adamantyl is longer lived in an oxidizing atmosphere than its 2-isomer,[91] in spite of its being a σ-radical. This perhaps shows that σ-radicals are not necessarily more reactive than similar π-radicals. In fact there is evidence to show that negative groups attached to the carbon of a methyl radical tend to push it out of planarity.[92] This is shown up by the way α- and β-coupling constants do not run parallel to each other. Many simple radicals will have appreciable σ-character according to this.

As a final example, the anion radical from a spirotetraenedione has been obtained[93] and the coupling constants have been assigned as shown in (67). The splittings were assigned with reference to related radicals and also confirmed by calculation. Evidently the radical is not symmetrical as one might have expected by comparison with the semiquinone type radical from 4,4'-dihydroxybiphenyl, but then in this case the two rings are mutually perpendicular. One consequence of this is that if it were symmetrical there would be two degenerate orbitals into which the odd electron might go; hence, according to the Jahn–Teller theorem, the molecule would distort to remove this degeneracy. The radical therefore resembles a cyclohexadienyl type with the spin localized on one ring [see (68)].



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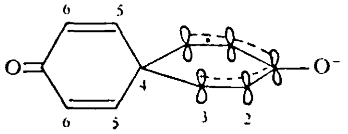

(68)

The 6-position, in the other ring, is effectively in the *m*-position and has a larger spin density than the proton attached to the 5-position. This is thus another case of σ-spin delocalization.

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[91] I. Tabushi, Y. Aoyama, S. Kojo, J. Hamuro, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1972, **94**, 1177.

[92] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.

[93] F. Gerson, R. Gleiter, G. Moshuk, and A. S. Dreiding, *J. Amer. Chem. Soc.*, 1972, **94**, 2919.

(1)

4 Electron Spin Resonance Spectroscopy and Free Radical Reactions

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Dept. of Chemistry, Bedford College, Regent's Park, Inner Circle, London NW1 4NS

1 Introduction

Once again this year has been one of further consolidation rather than of innovation in the field of free radical chemistry. Leaving aside the explosion of interest in CIDNP and related topics, which give information about what happens immediately before there is a change of spin multiplicity and, more particularly, about the species involved in such a step, most studies of free radicals and their reactions have utilized electron spin resonance.

Classical 'kinetic' studies, of the type long-used in electrophilic aromatic substitution, in which different molecules on sites compete for some active radical such as hydroxyl, aryl, alkyl or even hydrogen H·, seem to be dwindling in the absence of any clearly defined aims or interpretation. This might be expected, since the emphasis tends to be on substituent effects in the molecules 'attacked' and not so much on the free radicals themselves. Any branch of chemistry which pertains to a class of compounds will consist mainly of their synthesis, analysis, and their chemical and physical properties.

E.s.r. is an analytical technique *par excellence* for free radicals, and is also useful in following their reactions, *i.e.* by means of their rates of disappearance, appearance of new radicals, *etc.* Not only do e.s.r. spectra provide useful fingerprints for radicals, the exact values of the coupling constants (and also the *g*-factors) depend rather critically on the geometry of the radical in question, and this aspect is one that is being very actively pursued.

The 'synthesis' of free radicals is achieved by relatively few methods. One usually starts with organic molecules in which all the spins are paired. Unpaired spins can only be introduced either by photons, inorganic radicals, or by thermal or mechanical (the same thing really) fission of bonds. A survey of the literature shows relatively few main groups of active workers, each of which has developed expertise in a particular technique of getting free radicals. One might regard these techniques as ways of initiating the synthesis of radicals, and they consist in the main of radiolysis (*i.e.* irradiation with γ-rays), irradiation or reduction of peroxides, nitro-compounds, ketones, *etc.*, auto-oxidation and oxidation by metal ions such as Ce^{IV}. Usually the radicals of interest arise from some secondary

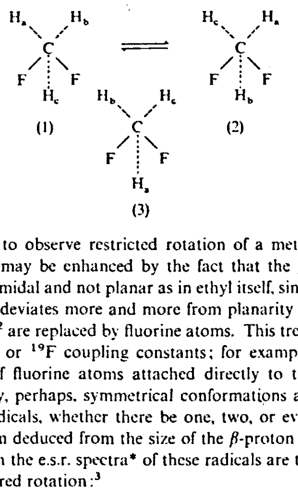
②

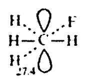
or tertiary process. For example, hydroxyl radicals, formed from the reduction of N_2O by solvated electrons which are, in turn, formed in the γ-radiolysis of water, attack aromatic substrates to give, in general, adduct radicals.

Apart from the predictable investigations of stable radical anions or nitroxides of more and more intriguing shapes, and the filling in of 'gaps' in the array of simple radicals which have been studied, the most interesting developments have been in stereochemistry. The conformations and configurations of radicals have been very much emphasized and some stereospecific radical reactions have been thoroughly investigated. As was the case last year, it seems that the best way of classifying the material is in terms of the types of radicals.

2 Simple Alkyl and Aryl Radicals

Remarkably strong steric interactions of fluorine atoms exist in fluorinated alkyl radicals, so much so that fluorinated ethyl radicals invariably give e.s.r. spectra which are temperature dependent, implying hindered rotation. For example, $\dot{C}F_2CH_3$ has an internal rotation barrier of about 2 kcal mol^{-1} and exists in an equilibrium between the three equivalent forms (1)—(3).[1] It is unusual to actually be able to observe restricted rotation of a methyl group directly, and the effect here may be enhanced by the fact that the geometry at the α-carbon atom is pyramidal and not planar as in ethyl itself, since the arrangement about the α-carbon deviates more and more from planarity as hydrogen, alkyl, or even CF_3 groups[2] are replaced by fluorine atoms. This trend is deduced from the changes in ^{13}C or ^{19}F coupling constants; for example, a(α-F) increases with the number of fluorine atoms attached directly to the α-carbon atom. Rather unexpectedly, perhaps, symmetrical conformations are the most stable for β-fluoroethyl radicals, whether there be one, two, or even three β-fluorine atoms. This has been deduced from the size of the β-proton coupling constants in (4) and (5), though the e.s.r. spectra* of these radicals are temperature dependent, showing hindered rotation:[3]





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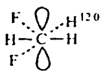
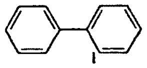
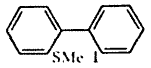


(5)

The e.s.r. spectra of chloro- and bromoalkyls also generally show some temperature dependence, as one might expect, and there is a certain amount of rather flimsy theoretical and empirical evidence that there are unsymmetrical halogen bridges in molecules such as $\dot{C}H_2CH_2Cl$ and $\dot{C}H_2CH_2Br$. This idea of halogen bridging is deduced from low values of β-proton splittings,[4,5] *trans* addition reactions,[6] and also from CIDNP observed in the n.m.r. spectra of the products of addition reactions.[7] Perfluoroalkyl radicals, formed by the u.v. irradiation of perfluorinated fatty-acid salts of Pb^{IV}, abstract protons, but not fluorine atoms, from $-CHF_2$ or $-CH_2F$ groups,[8] and methyl radicals abstract hydrogen from the α-positions of side-chains of alkylbenzenes, in preference to adding to the aromatic skeleton.[9] This contrasts somewhat with the behaviour of phenyl,[10] thiazolyl,[11] or even hydrogen atoms,[12] which tend to add to aromatic rings in a rather unselective way. In such studies the isomer distribution of the products may not be simply related to the relative reactivities of the original positions.[10] A dramatic decrease in attack *ortho* to a t-butyl group[9,11] shows the importance of steric factors in such reactions. Phenyl radicals will not only abstract aliphatic hydrogen atoms, but also iodine, and since the rate of this process with (6) is the same as that with (7), there can be no 'anchimeric assistance' from sulphur in the latter case.[13] This may be attributed to a large dihedral angle, making such assistance *via* S-bridging unfavourable.



(6)



(7)

3 Benzyl-type Radicals

The technique of γ-irradiation of aqueous solutions containing nitrous oxide has proved to be an efficient way of generating organic radicals *via* the hydroxyl

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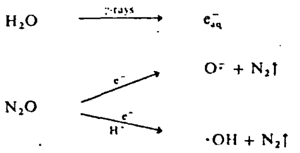
[1] K. Schen and J. K. Kochi, *Chem. Phys. Letters*, 1973, 23, 233.
[2] R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, 95, 1512.
[3] I. Biddles, J. Cooper, A. Hudson, R. A. Jackson, and J. T. Wiffen, *Mol. Phys.*, 1973, 25, 225.

* When not specifically stated splittings are given in unity of G (= 10^{-4} T).

[4] I. H. Elson, K. S. Chen, and J. K. Kochi, *Chem. Phys. Letters*, 1973, 21, 72.
[5] K. S. Chen, I. H. Elson, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, 95, 5341.
[6] P. S. Skell, R. P. Pavlis, D. C. Lewis, and K. J. Shea, *J. Amer. Chem. Soc.*, 1973, 95, 6735.
[7] J. H. Hargis and P. B. Sherkin, *J.C.S. Chem. Comm.*, 1973, 179.
[8] P. B. Ayscough, J. Machora, and K. Mach, *J.C.S. Faraday II*, 1973, 69, 750.
[9] S. J. Hammond and G. H. Williams, *J.C.S. Perkin II*, 1973, 484.
[10] J. T. Hepinstall, jun., and J. A. Kempmeier, *J. Amer. Chem. Soc.*, 1973, 95, 1904.
[11] G. Vernin, H. J. M. Dou, and J. Metzer, *J.C.S. Perkin II*, 1973, 1093.
[12] W. A. Pryor, T. H. Liu, J. P. Stanley, and R. W. Henderson, *J. Amer. Chem. Soc.*, 1973, 95, 6993.
[13] W. C. Danen, D. G. Saunders, and K. A. Rose, *J. Amer. Chem. Soc.*, 1973, 95, 1612.

3

radical or its anion (Scheme 1). The $O^{\cdot-}$ ion abstracts hydrogen readily from alkyl groups and so generates, for example, benzyl radicals from alkylbenzenes. The electronic spectra of these radicals have been observed in pulse radiolysis experiments[14] and it has been shown that the mechanism in strongly alkaline solution is direct hydrogen abstraction, whereas in more acidic solutions (below pH ~ 10) a more complex process occurs (Scheme 2). In both extreme cases the main product is bibenzyl. The reaction in alkaline solution has been utilized to generate many substituted benzyl radicals,[15] which are remarkable in that the coupling constants depend only very slightly on the nature of the substituents, *e.g.* (8) and (9).

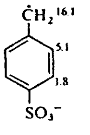


Scheme 1

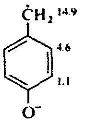
$$C_6H_5CH_3 + O^{\cdot-} \longrightarrow C_6H_5CH_2\cdot + OH^-$$

$$C_6H_5CH_3 + \cdot OH \longrightarrow \underset{\text{observed}}{[C_6H_5CH_3(OH)]} \xrightarrow{H^+} C_6H_5CH_2\cdot \quad etc.$$

Scheme 2

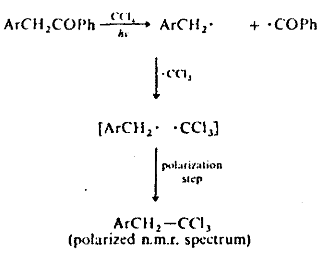


(8)



(9)

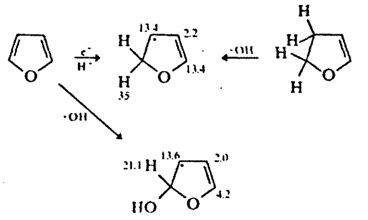
The signs of the fluorine coupling constants in *o*-, *m*-, and *p*-fluorobenzyl have been determined using CIDNP,[16] since the polarizations induced depend on the signs of the coupling constants. The reaction used was the photolysis of the appropriate benzylphenone in carbon tetrachloride (Scheme 3). The *o*- and *p*-fluorine coupling constants were positive but the *m*-F was negative, as expected. Similar empirical conclusions have been deduced from studies of aryl semiquinones.[17] The conformation of α-difluorobenzyl radicals is a planar one in the absence of *ortho* substituents.[18] This has been deduced from the fluorine splittings, which are about 50 G, compared with 56 G in $\dot{C}FHCONH_2$, known to be planar, and with 72 G in $\dot{C}F_2CONH_2$, which is pyramidal.



Scheme 3

4 Cyclic Adduct Radicals

The γ-radiolysis of water gives solvated electrons which can be effectively regarded as hydrogen atoms; these may add on to suitably active species such as furan to give adducts analogous to cyclohexadienyl. As we have already said, the presence of N_2O leads to hydroxyl radicals which can add on similarly, or abstract active hydrogen atoms. Thus the parent radicals of the furan series[19] can be obtained in concentrations sufficiently large for detection by e.s.r. (Scheme 4).



Scheme 4

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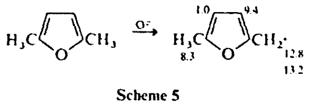
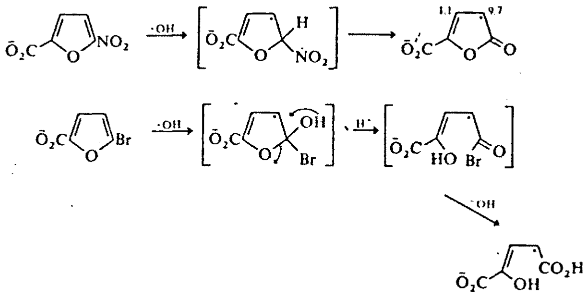
[14] H. C. Christensen, K. Sehested, and E. J. Hart, *J. Phys. Chem.*, 1973, 77, 983.
[15] P. Neta and R. H. Schuler, *J. Phys. Chem.*, 1973, 77, 1368.
[16] (a) J. Bargon and K. G. Seigert, *J. Phys. Chem.*, 1973, 77, 2877; (b) D. Bethell, M. R. Brinkman, and J. Hayes, *J.C.S. Chem. Comm.*, 1972, 1324.
[17] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1973, 1533.
[18] L. D. Kispert, H. Liu, and C. U. Pittman, jun., *J. Amer. Chem. Soc.*, 1973, 95, 1657.
[19] R. H. Schuler, G. P. Laroff, and R. W. Fessemdem, *J. Phys. Chem.*, 1973, 77, 456.

(4)

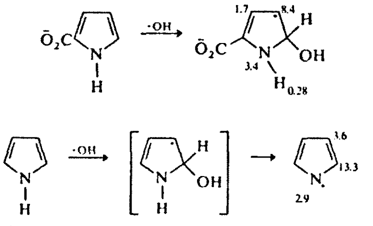
In base, when the active species in the presence of N_2O is $O^{\bar{\cdot}}$, 2,5-dimethylfuran yields an analogue of benzyl (Scheme 5). 2-Nitrofurans lose the nitro-group when subject to attack by ·OH in a similar way,[20] but in the case of 1-bromofuranoic acid the ring opens (Scheme 6). Similar types of adducts are formed with pyrole derivatives,[21] although the parent molecule itself reacts further to eliminate water (Scheme 7).



Scheme 5

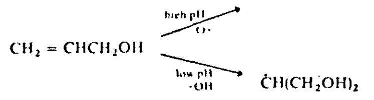


Scheme 6



Scheme 7

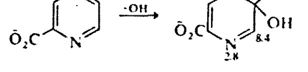
The tendency of ·OH to add to unsaturated systems wherever that is possible is again illustrated by the radiolysis of aqueous allyl alcohol[22] in the presence of N_2O (Scheme 8).



Scheme 8

Renewed interest in Fenton's reagent has led to further exhaustive studies of the isomer distributions of products from the hydroxylation of nitrobenzene, chlorobenzene, toluene *etc.*,[22] and a large number of hydroxycyclohexadienyl-type radicals have been identified by means of e.s.r. spectroscopy in the oxidation of benzene- and pipidine-carboxylic acids[23] by Fenton's reagent (Scheme 9).

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + {}^{-}OH + \cdot OH$$



Scheme 9

5 Further Radicals from Peroxides

Fenton's reagent has also been used to oxidize unsaturated aliphatic compounds[24,25] and some interesting reactions have developed. From alkynes a number of possibilities can occur, depending on whether substrate-reducing or -oxidizing agents are present in excess (Scheme 10). Similar types of situation can occur in Ti^{III}–H_2O_2, and e.s.r. kinetic studies indicate that the acetonyl radical is reduced by Ti^{III} quite effectively in neutral solution.[26] Limitations in the kinetic approach not only to the Ti^{III}–H_2O_2 system, but also to steady-state situations in general, have been pointed out again.[27]

During the photolysis of maleoyl phenyl peroxide,[28] fission of the peroxy bond leads to the formation of two carboxyl radicals in the same molecule and CO_2 is lost stepwise, so that there is appreciable probability of again forming

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[20] C. C. Greenstock, I. Dunlop, and P. Neta, *J. Phys. Chem.*, 1973, 77, 1187.

[21] A. Samuri and P. Neta, *J. Phys. Chem.*, 1973, 77, 1629.

[22] M. K. Eberharat and M. Yoshida, *J. Phys. Chem.*, 1973, 77, 589; M. Simic, P. Neta, and E. Hayon, *ibid.*, p. 2662.

[23] T. Shiga, T. Kishimoto, and E. Tomita, *J. Phys. Chem.*, 1973, 77, 330.

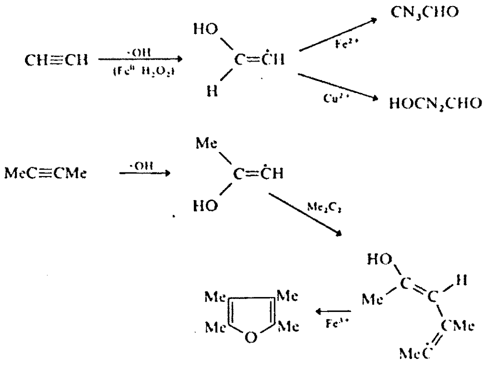
[24] C. Walling and G. M. El Taliawi, *J. Amer. Chem. Soc.*, 1973, 95, 844.

[25] C. Walling and G. M. El Taliawi, *J. Amer. Chem. Soc.*, 1973, 95, 848.

[26] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

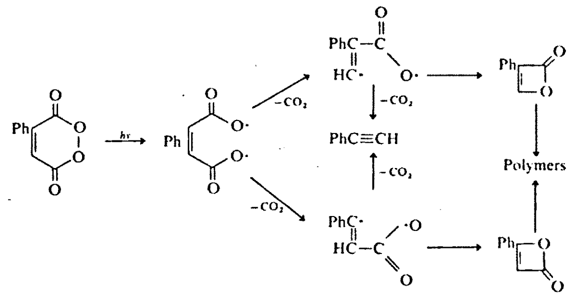
[27] D. Meisel, G. Czapski, and Samuni, *J.C.S. Perkin II*, 1973, 1702.

[28] M. M. Martin and J. M. King, *J. Org. Chem.*, 1973, 38, 1588.

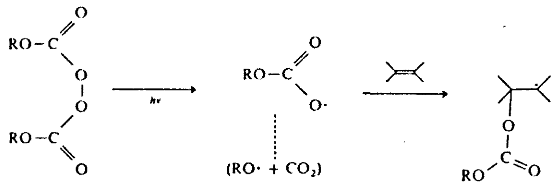


Scheme 10

a bond between the two radical fragments (Scheme 11). In contrast to alkylcarboxyl radicals, alkoxy-adducts with CO_2 are comparatively long-lived and add on to double bonds[29] to form carbonates (Scheme 12). However, in the absence of alkenes the e.s.r. spectra of the alkoxyl radicals only are observed.



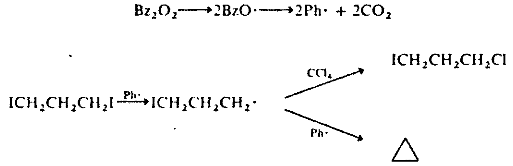
Scheme 11



Scheme 12

6 Radical Reactions of Cyclopropyl Derivatives

It is not difficult, it seems, to form cyclopropane by a free radical path. For example, 1,3-di-iodopropane reacts with benzoyl peroxide in carbon tetrachloride to form, amongst other things, cyclopropane (Scheme 13).[30] However, the three-membered ring is easily opened by radical attack and some interesting stereochemistry results. The radical bromination of *cis,cis*-trimethylcyclopropane[31] gives only three of the possible products which may be formed by the sequence shown in Scheme 14. The observed products show that the initial bromine attack was from an equatorial direction and this has been confirmed in a number of other cases.[32]



Scheme 13

Generally speaking, cyclopropyl itself can only be observed at low temperatures, since it tends to open to form an allyl-type radical (Scheme 15).[33] Thus ring-opening occurs by fission of the bond opposite to the site of the odd electron.

Facile ring-expansion can occur if there is an odd electron on a side chain[34] attached to the cyclopropyl ring (Scheme 16), and this is really the same type of reaction as the ring-opening by a bromine atom. A similar type of reaction takes place in cyclopropoxyl radicals, but there the formation of a ketonic group is preferred to the formation of a four-membered ring (Scheme 17).[35]

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[29] D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, 95, 2635.

[30] A. F. Drury and L. Kaplan, *J. Amer. Chem. Soc.*, 1973, 95, 2217.

[31] G. G. Maynes and D. E. Applequist, *J. Amer. Chem. Soc.*, 1973, 95, 856.

[32] K. J. Shea and P. S. Skell, *J. Amer. Chem. Soc.*, 1973, 95, 6728.

[33] K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, 95, 7036.

[34] M. P. Doyle, R. W. Raynolds, R. A. Barents, T. R. Bade, W. C. Danen, and C. T. West, *J. Amer. Chem. Soc.*, 1973, 95, 5988.

[35] C. H. De Puy, H. L. Jones, and W. M. Moore, *J. Amer. Chem. Soc.*, 1973, 95, 477.

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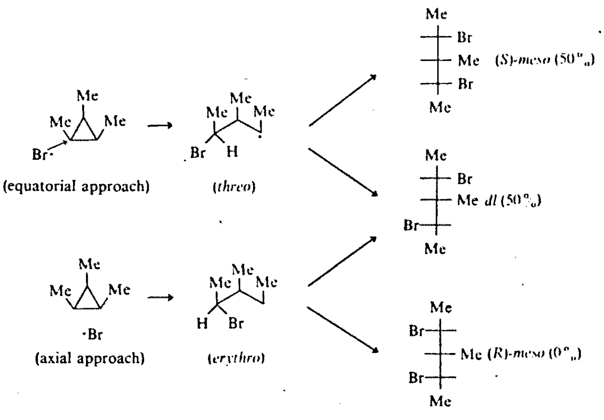
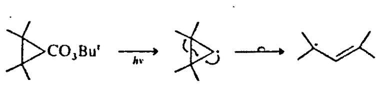
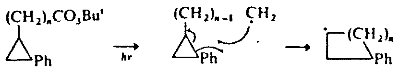


Scheme 14

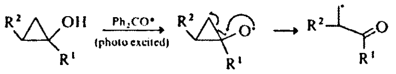


(seen at low temperatures)

Scheme 15



Scheme 16



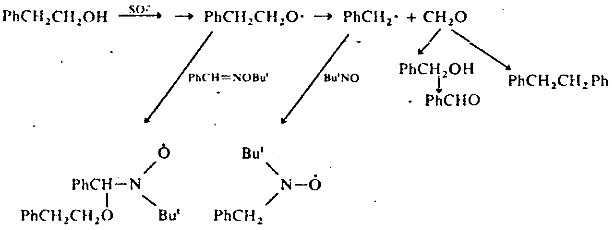
Scheme 17

7 Further Aliphatic Radical Reactions

Alcohols may undergo hydrogen abstraction from the hydroxyl group during the decomposition of persulphate ion[36] catalysed by photons or reducing metal ions such as Ag^I. The reaction is supposed to proceed by simple electron transfer:

$$R^1R^2CHOH \xrightarrow{SO_4^{\bullet-}} [R^1R^2CHOH]^{\bullet+} \xrightarrow{-H^+} R^1R^2CHO\cdot$$

The alkoxyl radical may be trapped by the *N*-oxide $PhCH{=}N\begin{smallmatrix}\nearrow O\\ \searrow Bu^t\end{smallmatrix}$, which adds on alkyl and alkoxyl radicals to give nitroxides; the latter may be identified from their e.s.r. spectra. In a particular case the reaction proceeds as shown in Scheme 18. The mechanism has been elucidated by means of the ingenious device of conducting it first in the presence of the above radical trap, which evidently stops the reaction before the break-up of the alkoxyl radical, and then separately in the presence of t-butyl nitrone, which traps alkyl radicals but not alkoxyl radicals. The adduct of $Ph\dot{C}HCH_2OH$ is a very minor constituent of the nitroxide product of which the major component is benzyl t-butyl nitroxide.



Scheme 18

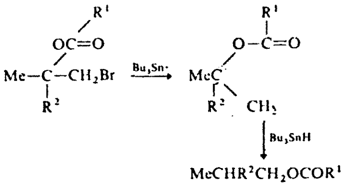
An interesting radical rearrangement occurs[37] when the halogen atom is abstracted from a β-bromoalkyl ester by trialkyltin hydride plus t-butoxyl radicals (Scheme 19). The most plausible mechanism seems to be that the ester group 'walks' to its new position (Scheme 20). It is interesting that in the case when R^2 = phenyl it migrates, perhaps *via* formation of a cyclohexadienyl-type of intermediate (Scheme 21). Intramolecular radical cyclization also takes place in the addition of perfluoroalkyl iodides to hepta-1,6-diene in preference to simple addition to one of the double bonds (Scheme 22).[38]

[36] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 630.

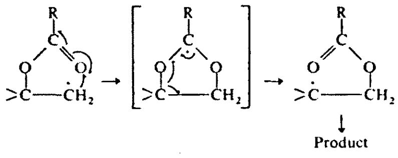
[37] A. L. J. Beckwith and C. B. Thomas, *J.C.S. Perkin II*, 1973, 861.

[38] N. O. Brace, *J. Org. Chem.*, 1973, 38, 3167.

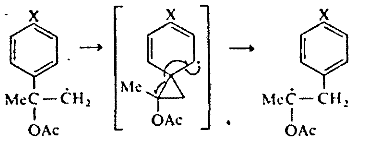
⑦



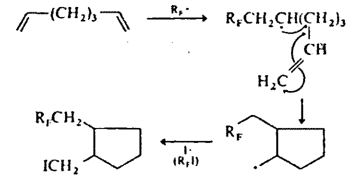
Scheme 19



Scheme 20

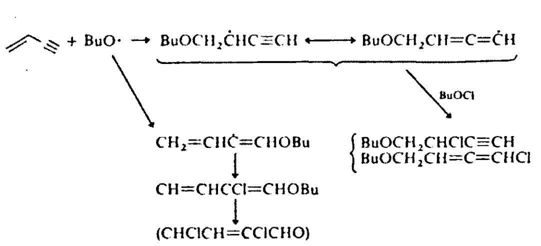


Scheme 21



Scheme 22

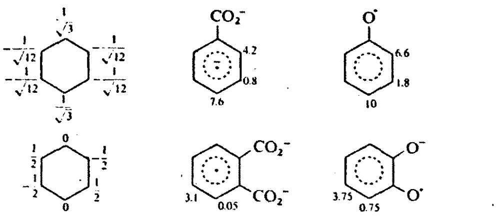
The radical addition of t-butyl hypochlorite to vinylacetylene[39] starts with addition of t-butoxyl to one end of the molecule and thereafter chlorine goes on at one of the others (Scheme 23).



Scheme 23

8 Radical Ions

A particularly interesting anion which has been generated with great difficulty is that of hexafluorobenzene,[40] *i.e.* $C_6F_6^-$, which although it would seem superficially to resemble $C_6H_6^-$ is evidently completely different, since the six fluorine nuclei have splittings of 137 G. The reason for this enormous coupling constant is that the odd electron is in a σ rather than a π molecular orbit. This is itself a result of the large number of electrons in the π molecular orbitals owing to the fact that each fluorine atom contributes two π-electrons. Because of this the odd electron goes into the first empty σ anti-bonding orbital instead of the first π^* orbital as is the case with the benzene negative ion. Dinegative ions of benzenoid carboxylic acids have been produced in basic media by reduction with solvated electrons[41] and the carboxylate group has a similar effect to oxygen in phenoxyl or semiquinone ions so that the coupling constants rather resemble those in those radicals. These splitting patterns can be understood in terms of the symmetry of the benzene MOs as shown in Scheme 24, the substituents having the effect of putting the odd electron into the orbital with the greatest value at the adjacent carbon atoms.



Scheme 24

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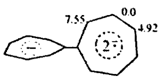
[39] M. L. Poutsma and P. A. Ibarbia, *J. Amer. Chem. Soc.*, 1973, **95**, 6000.

[40] L. F. Williams, M. B. Yin, and D. E. Wood, *J. Amer. Chem. Soc.*, 1973, **95**, 6475.

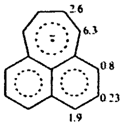
[41] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 620.

The heptafulvalene trinegative ion[42] has been prepared and there is coupling only with the protons of one ring. Since these are large, and in view of the strong repulsions between the two ring systems arising from three negative charges, it seems that the two rings could be perpendicular to each other, as shown in (10).

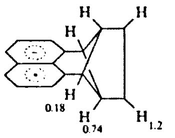


(10)

Some naphthalene negative ions have been generated, usually electrolytically, and it is found that t-butyl or trimethylsilyl groups attached to the naphthalene skeleton do not have very much effect on the spin distribution.[43] However, bridges across the *peri*-positions can have much greater effects,[44] as well as providing rigid frameworks through which spin density can be transmitted relatively efficiently, *e.g.* (11) and (12).[45]



(11)



(12)

The negative ions of halogenoquinolines have been studied polarographically[46] and from the half-wave potential loss of chloride ions could be deduced. Thus both quinoline itself and 6-fluoroquinoline gave simple half-wave potentials corresponding to the formation of their negative ions. 6-Chloroquinoline, on the other hand, gave two half-wave potentials, one corresponding to that of quinoline. This is attributed to the sequence shown in Scheme 25. It is doubtful, however, that the sigma 6-quinolinyl radical would ever actually have a discrete existence. A disproportionation step in the presence of protons seems more likely. Steric strain is apparent from the e.s.r. spectra of 4,4′-polymethylene-biphenyl radical anions (13),[47] but when the methylene chain is longer than 15 CH_2 units the coupling constants indicate that strain is virtually absent.

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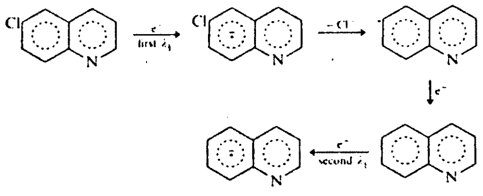
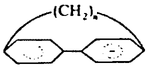
[42] N. L. Bauld, C. S. Chang, and J. H. Eilert, *Tetrahedron Letters*, 1973, 153.
[43] A. G. Evans, B. Jerome, and N. H. Rees, *J.C.S. Perkin II*, 1973, 2091.
[44] S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, 1973, 95, 1874.
[45] S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, 1973, 95, 2940.
[46] K. Alwain and J. Grimshaw, *J.C.S. Perkin II*, 1973, 1811.
[47] K. Ishizu, F. Nimoto, H. Hasegawa, K. Yamunoto, and N. Nakazaki, *Bull. Chem. Soc. Japan*, 1973, 46, 140.



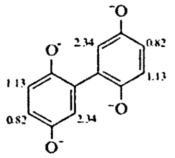
Scheme 25



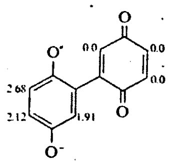
(13)

Incidentally, aromatic radical anions can be produced advantageously by using trimethylsilylsodium[48] rather than sodium metal dispersed in a suitable solvent.

Further e.s.r. work has been done on the auto-oxidation of hydroquinones and quinones[17,49,50] and dimeric intermediates, *e.g.* (14) and (15), positively identified.[49b] It is interesting that whereas spin density is transmitted around the ring of an aryl substituent attached to semiquinone, the carbonyl groups of a quinonoid substituent seem to present a barrier to the odd electron. The e.s.r. spectra of some of these dimeric species were originally attributed to radicals of different structures,[49] and this illustrates the dangers of trying to identify radicals only on the basis of the number and type of coupling constants in an e.s.r. spectrum. A remarkable feature about some 'heterocyclic' semiquinones[50] is that the second rings containing nitrogen atoms, *e.g.* (16) and (17), seem to have but little effect on the spin density, which remains mainly on the semiquinone part.



(14)



(15)

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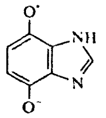
[48] H. Sakumi, A. Okada, H. Umino, and M. Kira, *J. Amer. Chem. Soc.*, 1973, 95, 955.
[49] (*a*) J. A. Pedersen, *J.C.S. Perkin II*, 1973, 424; (*b*) P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1973, 2128.
[50] M. K. V. Nair, K. S. V. Santhanaan, and B. Venkataraman, *J. Magn. Resonance*, 1973, 9, 229.



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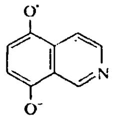
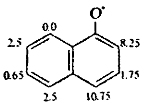
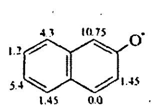


(17)

A number of naphthoxyl radicals, *e.g.* (18) and (19), have been identified by e.s.r.[51] and it seems that substituents have little effect on the spin distribution, which is slightly different in the case of β-naphthoxyl (19) from that expected by comparison with phenoxyl and naïve MO theory.

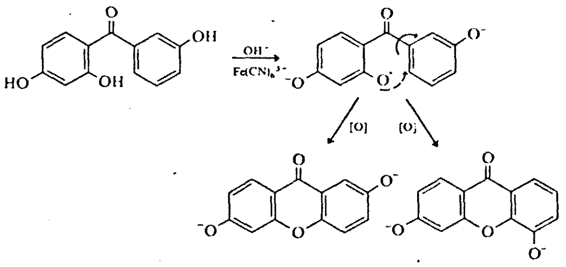


(18)



(19)

A ring-closure reaction has been observed when suitably hydroxylated benzophenones are oxidized by alkaline ferricyanide to xanthones (Scheme 26).[52] It would be interesting to see whether it is the dihydroxylated ring which under-



major product

minor product

Scheme 26

goes the initial attack, because although the radical cyclization *via* the oxygen shown in Scheme 26 looks feasible, the spin density on the oxygen atom must be small, whereas in the *para*-position of phenoxyl it is large.

9 Radicals containing Group IV Elements

Several more examples of S_H2 reactions of tin and lead compounds have been reported and these can be grouped into those which occur at a halogen atom[52,54]:

$$RCl = \dot{S}nMe_3 \rightarrow R\cdot + ClSnMe_3$$

which are of course already well-known and which are used extensively in the case of alkylsilyl radicals for the production of alkyl radicals, and those which take place at the Group IV atom:[55]

$$BuO\cdot + R_nSnX_{4-n} \rightarrow BuOSnR_{n-1}X_{4-n} + R\cdot$$
$$(X = \text{halogen})$$

This last type of reaction is to be contrasted with the reaction with tin tetra-alkyltin, where hydrogen abstraction takes place in preference to substitution:[55]

$$R^1CH_2SnR^2_3 + BuO\cdot \rightarrow BuOH + R^1\dot{C}HSnR^1_3$$

The rates of addition of Group IV radicals to carbonyl compounds[56] are in the order:

$$R_3Si\cdot > R_3Ge\cdot \sim R_3Sn\cdot > R_3Ph\cdot$$

and the rate of this reaction with a given radical $R_3M\cdot$ is in the order:

diketone > oxalate > ketone > trifluoroacetate > acetate

The reactions of the silicon analogue of the t-butoxyl radical have been studied *via* photolysis of the peroxide:[57]

$$Me_3SiOOBu^t \xrightarrow{h\nu} Me_3SiO\cdot + Bu^tO\cdot$$

This radical reacts with the starting material to give a silicone ether by an S_H2 mechanism:

$$Me_3SiO\cdot + Me_3SiO_2Bu \rightarrow Me_3SiOSiMe_3 + \cdot O_2Bu$$

In the presence of alkenes both primary radicals may add:

$$Me_3SiO\cdot + CH_2{=}CH_2 \rightarrow MeSiOCH_2CH_2\cdot$$

and with buta-1,3-diene there are several possibilities, such as straightforward addition or more complex reactions, *e.g.* Scheme 27. In the case of organosilyl

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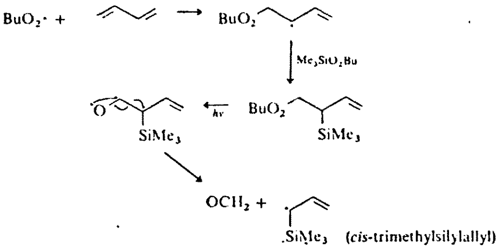
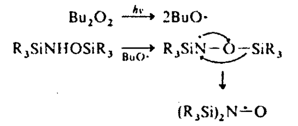
[51] W. T. Dixon, W. E. J. Foster, and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.
[52] P. D. McDonald and G. A. Hamilton, *J. Amer. Chem. Soc.*, 1973, 95, 7752.
[53] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1056.
[54] D. A. Coates and J. M. Tedder, *J.C.S. Perkin II*, 1973, 1570.
[55] A. G. Davies and J. C. Scaiano, *J.C.S. Perkin II*, 1973, 1777.
[56] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.
[57] D. J. Edge and J. K. Kochi, *J.C.S. Perkin II*, 1973, 182.
[58] R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, 1973, 95, 3983.



Scheme 27

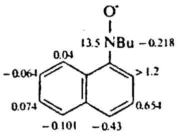
derivatives of hydroxylamine, rearrangement to the nitroxide can occur:[58]



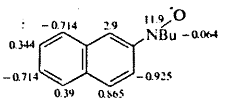
$$Bu_2O_2 \xrightarrow{h\nu} 2BuO\cdot$$
$$R_3SiNHOSiR_3 \xrightarrow[BuO\cdot]{} R_3Si\dot{N}-O-SiR_3 \longrightarrow (R_3Si)_2N\dot{-}O$$

10 Radicals containing Nitrogen

Nitroxides are still probably the most widely studied radicals because of their ease of formation, use of nitroso-compounds as radical traps, and their stability. They are so stable that large enough concentrations can be achieved to enable one to obtain their n.m.r. spectra in some cases. From the n.m.r. spectrum one can obtain the signs of the coupling constants since they determine the direction of the 'contact' chemical shift. This exercise has been completed for α- and for β-naphthyl t-butyl nitroxides, (20) and (21).[59] The spin distributions bear



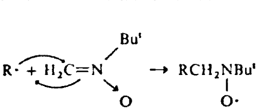
(20)



(21)

almost no relationship to those in α- and β-naphthoxyl, and in the case of the α-naphthyl derivative the coupling constants suggest that there is some degree of twisting about the carbon–nitrogen bond. A variety of cyclic nitroxides have been prepared and the spin label allows investigation of the flapping of rings[60] as well as their conformations[61] to be determined from the e.s.r. parameters.

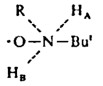
An interesting class of nitroxide radicals has been studied using the spin trap (22). Addition occurs at the carbon atom and the radical formed may be strongly



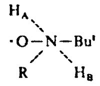
(22)

Scheme 28

asymmetric, *i.e.* Scheme 28.[62] Looking along the methylene-carbon–nitrogen bond there will be two stable conformations, (23) and (24). If R is an asymmetric



(23)



(24)

group such as $CH_3\overset{|}{C}HOH$, then even when there is fast interconversion between these two conformations the two protons will have different average splittings. The disparity increases with the size of R·.

If there is sufficient steric hindrance alkyl groups may be forced to add to the oxygen of a nitroso group rather than to the nitrogen atom (Scheme 29).[63a] From the coupling constant of the nitrogen atom (*ca.* 10 G) the *N*-alkoxyanilino-radical is probably a π-type and so are the aliphatic analogues, *e.g.* Scheme 30.[63b] On the other hand, iminoxyl radicals are of σ-type,[64] as are iminyl radicals (Scheme 31).

An interesting rearrangement takes place after radical attack on aryl hydrazonates.[65]

To finish this section on nitrogen radicals it seems appropriate to mention the reduction of nitroxides to the corresponding secondary amines with iron carbonyls (Scheme 33).[66]

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[59] J. L. Duncan, A. R. Forrester, G. McConnachie, and P. D. Mallinson, *J.C.S. Perkin II*, 1973, 718.

[60] R. E. Rolfe, K. D. Sales, and J. H. P. Utley, *J.C.S. Perkin II*, 1973, 1171.

[61] V. Malatesta and K. V. Ingold, *J. Amer. Chem. Soc.*, 1973, 95, 6390, 6395; *J.C.S. Perkin II*, 1973, 2134; S. F. Nelsen and R. T. Landis, sec., *J. Amer. Chem. Soc.*, 1973, 95, 6454.

[62] B. C. Gilbert and M. Trenwith, *J.C.S. Perkin II*, 1973, 1834.

[63] (a) S. Terabe and R. Konaka, *J.C.S. Perkin II*, 1973, 369; (b) W. C. Danen, C. T. West, and T. T. Kensler, *J. Amer. Chem. Soc.*, 1973, 95, 5716.

[64] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, 95, 2963, 3422.

[65] A. F. Hegarty, J. A. Kearney, and F. L. Scott, *J.C.S. Perkin II*, 1973, 1422.

[66] H. Alper, *J. Org. Chem.*, 1973, 38, 1417.

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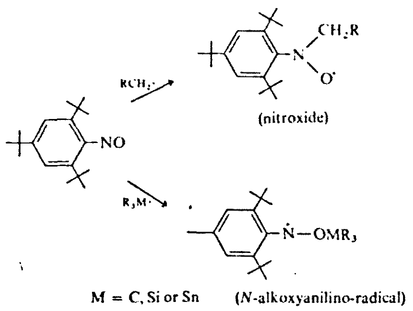
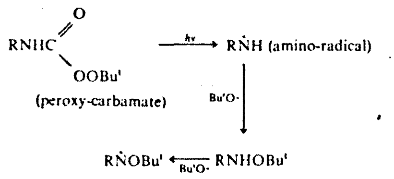
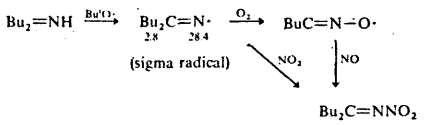


Scheme 29



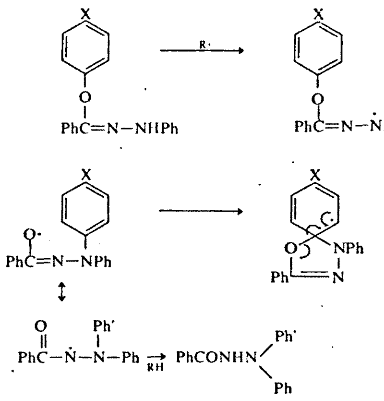
Scheme 30



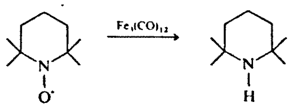
Scheme 31

11 Radicals containing Group V Elements

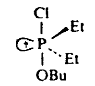
The work on phosphoranyl radicals[67,68] and the corresponding arsenic compounds has continued along the same lines as last year. The structure of these radicals is one of a trigonal bipyramid with alkoxyl or halogen ligands filling the axial positions preferentially, *e.g.* (25) and (26). The phosphorus and arsenic compounds undergo similar types of reaction (Scheme 34).



Scheme 32



Scheme 33



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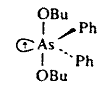

(26)

Some chelating ligands have been attached to phosphorus, yielding 'spirophosphoranyl' radicals,[68] and exchange of halogen between equatorial and axial positions has been observed by e.s.r. (Scheme 35).

12 Radicals containing Group VI Elements

The pulse radiolysis of thiols or 'sulfhydryl' compounds leads to sulphur radicals, which readily form links with further sulphur to give a negative ion in which

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[67] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.
[68] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1416.

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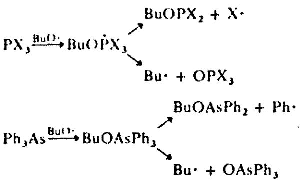
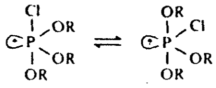
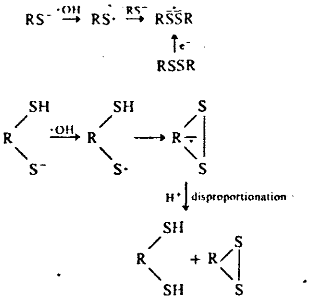


Scheme 34



Scheme 35

there are two sulphur atoms (Scheme 36).[70,71] This well-known oxidative coupling of sulphur is so strong a tendency that it appears that it can even happen with dialkyl sulphides (Scheme 37).[72] A great variety of radicals may be generated from such aliphatic sulphur cation radical, for example when there is a β-hydroxyl group (Scheme 38).[73]



Scheme 36

Some interesting thiophen derivatives (27)—(29) have been prepared in which different isomers can be distinguished in the e.s.r. spectra.[74]

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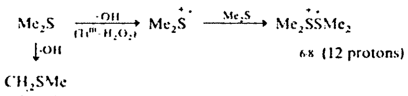
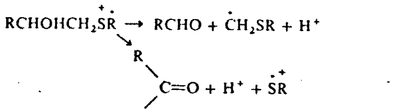
[69] E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1973, 95, 6574.
[70] M. Z. Hoffman and E. Hayon, *J. Phys. Chem.*, 1973, 77, 990.
[71] P. C. Chan and B. H. J. Bielski, *J. Amer. Chem. Soc.*, 1973, 95, 5504.
[72] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748.
[73] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 272.
[74] C. M. Camaggi, L. Lunazzi, and G. Placucci, *J.C.S. Perkin II*, 1973, 1491.

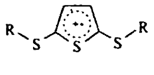


Scheme 37

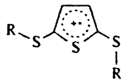


(trapped but no observed directly)

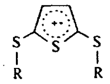
Scheme 38



(27) *cis,cis*

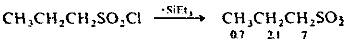


(28) *cis,trans*

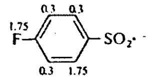


(29) *trans,trans*

Sulphonyl radicals (30) and (31) have been prepared by abstraction of chlorine from sulphonyl chlorides[75] with the triethylsilyl radical. The assignments were made on the assumption of twisting of the $-SO_2\cdot$ and that the configuration at the sulphur is pyramidal, the preferred conformation leading to asymmetry. This is rather different from the case of the primary alkyl sulphonyls, (32)—(34), where rotation is relatively unrestricted, it seems..



$$CH_3CH_2CH_2SO_2Cl \xrightarrow{\cdot SiEt_3} \underset{0.7}{CH_3}\underset{2.1}{CH_2}\underset{7}{CH_2}SO_2\cdot$$



(31)

13 Spin Delocalization through σ-Bonds

The existence of substantial β-proton coupling constants in alkyl radicals and in alkyl-substituted aromatic radicals proves in itself that spin density

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[75] A. G. Davies, B. P. Roberts, and B. R. Sanderson, *J.C.S. Perkin II*, 1973, 626.
[76] J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, 1973, 95, 1516.

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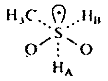
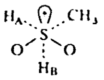
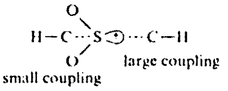


(32)

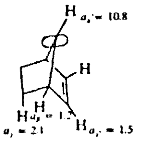


(33)

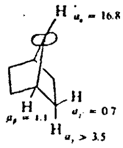


(34)

can be transmitted through σ-bonds. This process, which arises from the interaction of a π-type atomic orbital and the orbitals of a neighbouring σ-bond, is called hyperconjugation and the idea can be extended to account for some very long-range coupling constants, *e.g.* those in (35) and (36).



(35)



(36)

In the bridged naphthalene anion already mentioned there is even an observable δ-coupling constant. These long-range splittings generally are observed in systems in which a rigid conformation exists which is favourable for each hyperconjugative interaction. There are some empirical rules, which have some foundation in simple MO theory, which amount to saying that transmission through a σ-system only occurs when the bonds are lined up with each other. More sophisticated theories[77] are able to account for negative spin densities on γ-protons as well as positive densities on β- and δ-protons when the conformation is favourable (see the Figure).

Particular cases of σ-delocalization occur when the steric forces cause twisting in aromatic systems.[17,78,79] The coupling constants of protons attached to aryl substituents generally arise from a mixture of two components, one from transmissions of spin density through the π-system and the other through the σ-system. Twisting becomes apparent when the *ortho* and *para* proton splittings decrease in relation to the *meta* proton coupling constants. When the twisting becomes much more pronounced a situation is found in which the *meta* splitting is much larger than the others, *e.g.* in the rubrene positive or negative radical ions (37).[79] A particularly clear example of this effect appears in the series of aryl semiquinones (38)—(40).[17] The large *meta* coupling, which is apparent when the aryl ring is approximately perpendicular to the nodal plane of the odd electron,[17] is simply a case of δ-coupling described before.

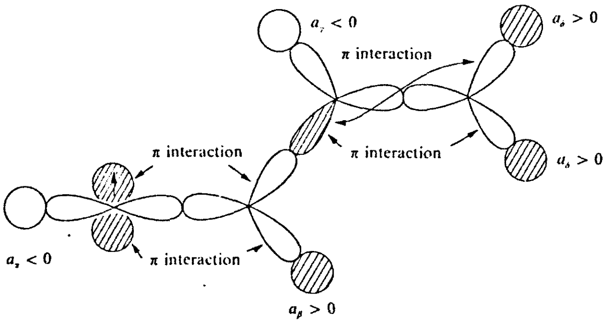
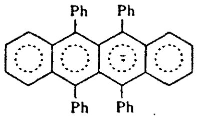


Figure *Diagram showing interactions responsible for transmission of spin density through σ-bonds. Orbitals in which there is relatively high positive spin density are shaded.*



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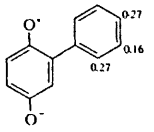

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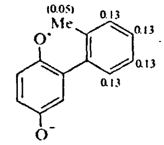

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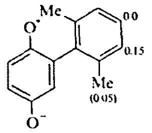

(40)

increasing dihedral angle →

14 Some Miscellanies

There has been some interest in the structure of methyl-lithium, which is a tetramer consisting of a tetrahedran of lithium atoms with a methyl group by

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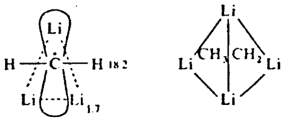
[77] Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *J. Amer. Chem. Soc.*, 1973, 95, 2372.
[78] H. G. Aurich, H. Forster, A. Lotz, and W. Weiss, *Chem. Ber.*, 1973, 103, 2832.
[79] R. Biehl, K. P. Dinse, K. Mobius, M. Plato, and H. Kurreck, *Tetrahedron*, 1973, 29, 363.

14

the centre of each face. The e.s.r. spectrum of the corresponding alkyl radical,[80] in which one hydrogen atom has been removed, has been obtained and shows, as expected, hyperfine coupling with three equivalent ^{7}Li nuclei [$I(^7\mathrm{Li}) = \frac{3}{2}$]. This is consistent with the structure (41). There must be rapid rotation of the methylene group to account for the equivalence of the three lithium nuclei.



end view

(41)

Further examples of emission lines in e.s.r. spectra have been observed[81] which can give information, in particular, about the situation when a radical is actually being formed or possibly destroyed. A report of a reaction which has a measurable dependence on magnetic field[82] strength might well be related to this, for though magnetic energies are much too small, under usual conditions, to have any visible effect on radical reactions, when the singlet–triplet transition probability depends on the field, the latter could have pronounced effects on that step of a reaction. If this result is confirmed it could have important theoretical and practical implications.

Finally it should be noted that the following texts have appeared: a simple introduction to free radical chemistry[83] and a comprehensive monograph.[84]

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[80] K. S. Chen, F. Bertini, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, 95, 1340.

[81] P. W. Atkins, A. J. Dobbs, and K. A. McLauchlan, *Chem. Phys. Letters*, 1973, 23, 204.

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[83] J. I. G. Cadogan, 'Principles of Free Radical Chemistry,' Monographs for Teachers, The Chemical Society, London, 1973, No. 24.

[84] J. K. Kochi, 'Free Radicals: Vol. I. Dynamics of Elementary Processes', Wiley, New York, 1973.

Offprinted from the *Journal of The Chemical Society, Faraday Transactions II*, 1974, vol. 70.

LONG-RANGE ELECTRON SPIN RESONANCE COUPLING CONSTANTS IN RADICAL ADDUCTS OF MALEIC ACID

Long-range Electron Spin Resonance Coupling Constants in Radical Adducts of Maleic Acid

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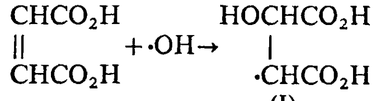
Received 11*th March*, 1974

The e.s.r. spectra of a number of radical adducts of maleic acid have been observed and hyperfine structure arising from γ-, from δ- and from ε-coupling has been revealed. This provides a positive identification of the radicals involved. The origin of the long-range coupling constants is discussed in terms of simple molecular orbital theory and direct magnetic interaction. The difference between spectra observed in acidic and in alkaline conditions, is interpreted in terms of structural changes.

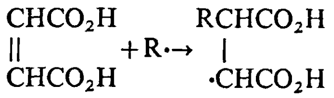
Aliphatic or aryl radicals may be trapped by maleic acid,[1, 2] and the short-lived adducts so-formed detected by means of e.s.r. spectroscopy. The sequence of reactions leading to the observed radicals have generally been as follows:

$$\mathrm{Ti^{III}} + \mathrm{H_2O_2} \rightarrow \mathrm{Ti^{IV}} + \mathrm{OH^-} + \cdot\mathrm{OH} \qquad (1)$$

$$\mathrm{RH} + \cdot\mathrm{OH} \rightarrow \mathrm{R}\cdot + \mathrm{H_2O} \qquad (2)$$



$$\begin{array}{l}\mathrm{CHCO_2H}\\ \|\\ \mathrm{CHCO_2H}\end{array} + \cdot\mathrm{OH} \rightarrow \begin{array}{c}\mathrm{HOCHCO_2H}\\ |\\ \cdot\mathrm{CHCO_2H}\\ \mathrm{(I)}\end{array} \qquad (3)$$



$$\begin{array}{l}\mathrm{CHCO_2H}\\ \|\\ \mathrm{CHCO_2H}\end{array} + \mathrm{R}\cdot \rightarrow \begin{array}{c}\mathrm{RCHCO_2H}\\ |\\ \cdot\mathrm{CHCO_2H}\\ \mathrm{(II)}\end{array} \qquad (4)$$

Phenyl adducts have been generated from the corresponding diazonium salts by reduction.[2] In alkaline or neutral solution the reducing species has been $\mathrm{Ti^{III}}$ and in acidic solution the reduction has been achieved by radicals R· formed in reaction (2) where RH is a primary or secondary alcohol or formic acid.

$$\mathrm{PhN_2^+} + [\mathrm{Ti^{III}(edta)}] \rightarrow [\mathrm{Ti^{IV}(edta)}] + \mathrm{N_2} + \mathrm{Ph}\cdot. \qquad (5)$$

It is easy to arrange the conditions so that the consecutive reactions (2) and (4) dominate, and the e.s.r. spectra of the resulting radicals of type (II) consist of four lines. The two coupling constants obtained from each spectrum characterise the adducts but do not positively identify them. These splittings do not, for example, tell us whether or not the species, which has added to the double bond, is the same as that which would have been observed in the absence of maleic acid from the solutions. We now report successful attempts to improve the resolution of the four line spectra, so that in most cases further small splittings appear, which confirm the assumed nature of the adduct radicals.

In the most straightforward cases each of the four lines was split further into a multiplet as appropriate for the number of γ-protons in the adduct. Thus the e.s.r. spectrum of the methyl radical adduct had a small quartet (1 : 3 : 3 : 1) splitting whereas there were small doublet (1 : 1) splittings when either dioxan or ethylenediaminetetra-acetic acid were the " primary " substrates in the Ti^{III}/H_2O_2 system (see table 1). In neutral or in alkaline solution the spectrum of the hydroxyl radical adduct itself has a small doublet splitting.

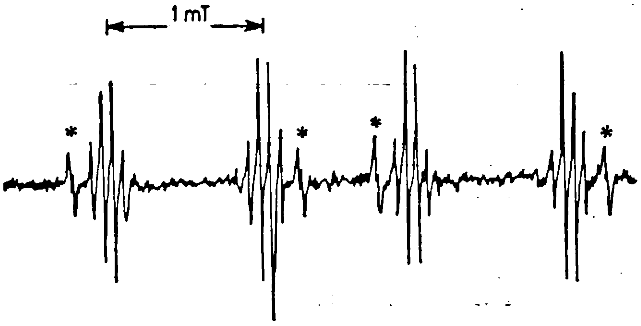


FIG. 1.—E.s.r. spectrum of maleic acid adducts with methyl and hydroxyl (asterisked) radicals.

The spectra obtained from the adducts of radicals of type $RR'\dot{C}OH$ were not so straightforward, since they were less well resolved in neutral or in alkaline solution, but appeared to have small couplings corresponding to the appropriate number of γ- and δ-protons in acid. These " extra " splittings confirm the nature of these radicals. No additional splitting of the four lines was observed in the spectrum ascribed to the phenyl radical adduct, so 2-fluorophenyl was used in the hope that the fluorine splitting might be large enough to observe. In fact a fluorine splitting was observed and it was larger even than that expected from previous studies on aryl semiquinones.[3]

EXPERIMENTAL

The conditions in our experiments were similar to those of Beckwith and Norman [2] except that the flow system was driven by a peristaltic pump which gave a fine control of the flow rate (*ca.* 10 $cm^3 s^{-1}$). The concentrations used were approximately 0.05 mol dm^{-3} for Ti^{III} and peroxide, 0.25 mol dm^{-3} for the diazonium salts and for the substrates about 0.5-1.0 mol dm^{-3}. The acidic solutions contained 0.5 mol dm^{-3} sulphuric acid and the " alkaline " solutions were at pH 7-9.

RESULTS AND DISCUSSION

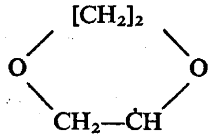
All of the results are summarised in table 1.

THE ORIGIN OF THE LONG-RANGE COUPLING CONSTANTS

(i) δ-SPLITTINGS

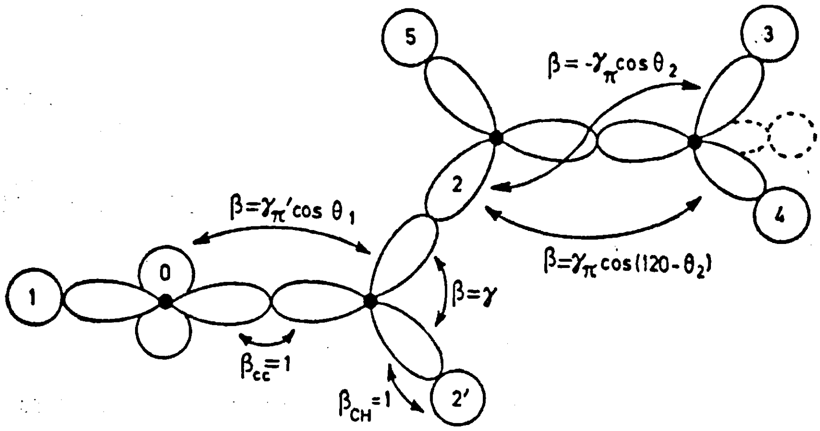
The patterns of the small coupling constants establish convincingly the structures of the adduct radicals. Relatively large γ-coupling constants have been observed many times, e.g. in radicals from t-butyl alcohol, ether, dioxan etc., [1, 4] and it seems likely that they arise from a combination of hyperconjugation and spin polarisation.[5] The observation of δ-splittings is less common, however, and such splitting generally occurs only in rigid systems such as the adamantyl radicals.[6, 7] It is not difficult to see how coupling through so many σ-bonds arises, since the situation is essentially the same as that leading to large *meta*-coupling constants when aryl rings are twisted out of the nodal plane of a single occupied molecular orbital,[3] e.g. as in the rubrene radical ions.[8] The transmission of spin density through σ-bonded systems has already been explained in simple MO terms,[4, 9, 10] but in view of the complexity of the present problems it is rewarding to examine them in some detail.

TABLE 1.—COUPLING CONSTANTS (IN 10 T) OF RADICALS $RCH(CO_2H)\dot{C}HCO_2H$. NUMBER OF PROTONS IN BRACKETS

	acid			alkali		
R	$a_\alpha(1)$	$a_\beta(1)$	further splittings	$a_\alpha(1)$	$a_\beta(1)$	further splittings
•OH	12.7	20.7	—	15.3	20.2	0.2(1)
•(edta—H)†	—	—	—	7.5	19.8	0.9(1) 0.2(N)
•CH_2OH	13.7	20.8	0.6(1) 0.3(1)	9.8	20.2	—
$CH_3\dot{C}HOH$	9.5	20.6	0.4(4)	7.5	20.0	0.3(3)
$(CH_3)_2\dot{C}OH$	10.5	20.5	0.3(6)	5.1	20.0	0.3*
$(CH_3)_2COH{\cdot}CH_2{\cdot}$	9.0	20.3	*	7.1	19.9	0.6(1) 0.3(7)
$CH_3\dot{C}HOEt$	11.5	20.4	0.3*	6.7	20.0	0.3(3)
 	11.2	21.0	0.4(1)	8.0	20.3	0.3*
•CO_2H	15.2	20.9	—	8.4	20.0	—
•CH_3	13.5	20.8	0.6(3)	10.3	20.3	0.7(3)
C_6H_5•	14.6	20.9	—	10.7	20.4	—
o-C_6H_4F•	10.9	20.3	1.6(F)			

* Denotes incomplete resolution.

† Most probably a proton α with respect to one of the carboxyl groups is abstracted.



$$c_1 = 0\,;\; c_2 = c_{2'} = -\gamma'_\pi \cos\theta_1 c_0\,;\; c_5 = -\gamma c_2\,;\; c_3 = (\gamma_\pi \cos\theta_2 + \gamma^2)c_2$$

FIG. 2.—Diagram showing orbitals and interactions mainly responsible for the σ-spin delocalisation with coefficients of non-bonding orbital. Values of the non-zero parameters are

$$\alpha_C = \alpha_H,\ \gamma_\pi \approx \gamma'_\pi \approx \tfrac{1}{4},\ \gamma \approx \tfrac{1}{4}\sqrt{3}$$

θ_1 = dihedral angle of orbital 2 about C_α—C_β bond with respect to axis of orbital 0. θ_2 = dihedral angle about C_γ—C_δ bond, Using the MO parameters given in fig. 2, the average coupling constant of the δ-protons, assuming free rotation about the C_γ—C_δ bond is given approximately by:

$$a_\delta = \tfrac{1}{2}\gamma_\pi^2(\gamma' \cos\theta_1)^2\, 508 Z_{\text{eff}}^3 \times 10^{-4}\ \text{tesla} \qquad (a)$$

where we take the hyperfine splitting due to the nucleus in a free hydrogen atom to be 50.8 mT and Z_{eff} is the effective atomic number for the hydrogen 1*s* orbital in a molecule. There are several ways of obtaining an order of magnitude for a_δ from this. However, we shall take values of γ_π and γ_π' which have been shown to account for the coupling constants in the vinyl radical and also for the n.m.r. coupling constants in butadiene,[11] i.e. $\gamma_\pi \approx \gamma_\pi' \approx \frac{1}{4}$ so that eqn (*a*) becomes:

$$a_\delta \approx \cos^2\theta_1\, Z_{\text{eff}}^2. \qquad (a')$$

If $\cos^2\theta_1$ is about 0.5 then for $Z_{\text{eff}} = 1.0$, $a_\delta \approx 0.5 \times 10^{-4}$ T.

This is of the correct order of magnitude and is close to the limits of resolution of our spectrometer under conditions of flow. If necessary, a_δ can be quickly estimated for any dihedral angle using formula (*a'*). We can even go so far as to deduce the conformation about the C_α—C_β bond. The δ coupling constants observed are of the order of 0.03 mT which corresponds to a dihedral angle of about 60°. Similarly the β coupling of about 1 mT (averaged over the different adducts) corresponds to a dihedral angle of about 60°. The resulting conformation is given in fig. 3.

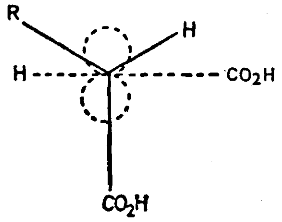


FIG. 3.—One of the two conformations predicted for the $(CH_3)_2\dot{C}OH$ adduct.

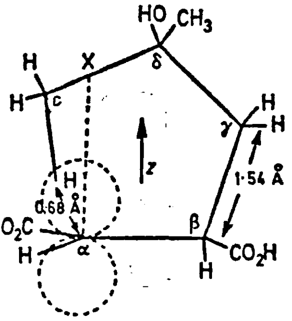


FIG. 4.—Diagram showing nearest approach of an ε proton to the α-carbon atom in adduct $\dot{C}HCO_2H\ CH(CO_2H)CH_2C(OH)(CH_3)_2$.

Point X is nearest approach of a δ proton. Adjacent C—C bonds are all taken to be 1.54 Å.

(ii) ε-COUPLING CONSTANTS

The splittings from protons attached to α-, to β-, to γ- and to δ-carbon atoms can be explained in terms of transmission of spin density through bonds. The mechanisms involved may be separated approximately into two, i.e., (*a*) hyperconjugation and (*b*) spin polarisation. Appreciable splittings from ε-protons have already been observed [12] and they have been ascribed to " through-space " interactions. This term has not yet been clearly defined and in many cases where it has been invoked, an extended theory of hyperconjugation of the type given above for δ-splittings can account for the observations. Also, because of the way spin densities tend to be transmitted to alternate orbitals, direct through-space interaction of a hydrogen orbital with the orbital containing the odd electron would result in spin density appearing not in the hydrogen orbital itself, in the first instance, but on the adjacent carbon atom.

In view of these thoughts we have investigated the possibility that ε-splittings arise not from spin density associated with the ε-hydrogen orbitals, but from a direct *magnetic* interaction between those protons and the cloud of spin density on the α-carbon atom. The hypothetical situation which would give the maximum effect of this kind is shown in fig. 4.

The Slater-type orbital most commonly used for carbon $2p$ orbitals is:

$$\psi(2p_z) = (\tfrac{1}{4}\sqrt{2\pi})(Z/a_0)^{\frac{5}{2}}z\exp(-Zr/2a_0)$$

where the effective atomic number $Z = 3.25$ and a_0 is the Bohr radius of the hydrogen atom.

The magnetic interaction of a proton with an electron in this carbon $2p_z$ orbital is

$$(508/\pi a_0^3)[\psi(2p_z)]^2 = 2.06\times10^3\,z^2\,\mathrm{e}^{-6.13r}\ \mathrm{mT}$$

where distances are measured in Ångstroms.

For the proton in fig. 5 this becomes 10.2 mT. Now we would not expect that the proton could possibly get nearer to the α-carbon atom than a distance somewhat greater than the C—H bond distance, so if we doubled the distance of closest approach the maximum direct coupling is reduced fifty times to 0.2 mT.

Allowing further free rotation of the methyl group and for other possibilities of bending or flapping in the molecule, the estimated ε-splittings are rather less than 0.05 mT. The main point here is that this direct magnetic interaction could be large enough to account for the observed splittings. The effect could be enhanced by steric repulsions of the β-carboxyl group.

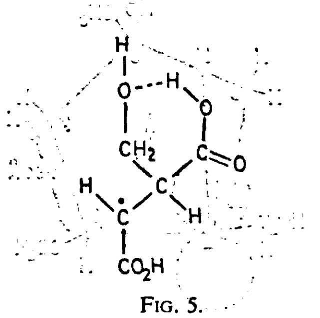


Fig. 5.

The corresponding direct interaction with one of the δ-protons has a maximum value of 0.05 mT. Allowing again for free rotation of methyl groups and for bending within the molecule, this is negligible compared with the coupling due to extended hyperconjugation, and is moreover extremely sensitive to the exact position of the δ carbon atom.

ADDUCTS OF RADICALS DERIVED FROM ALCOHOLS

The pattern of lines in the spectra from the adducts of maleic acid with radicals formed by α-hydrogen abstraction from alcohols, were dependent on the pH of the solutions. The maximum fine structure was observed in strongly acidic solutions and and in the case of the adduct formed from $\cdot CH_2OH$, this fine structure unexpectedly showed two non-equivalent protons. A reasonable way of accounting for this, and for the apparent disappearance of some of the couplings when the solutions are made alkaline, is that there is some rigidity in the molecule, preventing free rotation and the corresponding equivalence of the two methylene protons of the CH_2OH group. This rigidity could arise from hydrogen bonding between the hydroxyl group of CH_2OH and the neighbouring carboxyl group (see fig. 5).

One might expect these structures to break down under alkaline conditions.

The results for simple addition of hydroxyl radicals indicate that the rate of exchange of the hydroxyl proton in the CH_2OH group is much faster in acidic solution than when conditions are more alkaline.

In conclusion it can be stated that the observed hyperfine splittings in the e.s.r. spectra of these adducts of maleic acid confirm their identities more completely than has previously been possible. The long-range δ-coupling constants arise from extended hyperconjugation through the σ-bonds and ε-splittings from direct magnetic interactions. Both are observed because of favourable conformations.

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Electron Spin Resonance Spectra of Hydroxyl Adducts of Some Aromatic Acids

By W. T. Dixon * and D. Murphy, Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

The first e.s.r. spectra of hydroxyl adducts of some naphthalene derivatives are reported. The spin distribution in these radicals resembles those in corresponding naphthoxyl radicals. Further examples of cyclohexadienyl-type radicals are also given and fresh light is shone on the detailed mechanism of the formation of benzyl and phenoxyl radicals in the Ti^{III}–H_2O_2 system.

RADICALS of the cyclohexadienyl type are important intermediates in many homolytic reactions of aromatic compounds and a number have been directly observed by means of e.s.r. spectroscopy.[1-4] Though heterocyclic analogues of these radicals have been studied relatively extensively,[5-7] only one example has been reported of an adduct radical in the naphthalene system, and that was in a single crystal.[8] We have extended the range of hydroxyl adduct radicals by using sulphonic acids which are water soluble, and have also obtained spectra arising from both α- and β-addition to the naphthalene skeleton. Some of the results obtained with sulphonic acids were rather unexpected but not inconsistent with the ideas developed by Norman *et al.*[2,3] for the mechanism of formation of benzyl[2] and of phenoxyl[3] radicals in the Ti^{III}–H_2O_2 system.

RESULTS

Spectra from Naphthalenesulphonic Acids.—Naphthalene compounds are generally much less soluble in water than corresponding benzenoid compounds and this, together with the increased number of sites for possible attack, makes them poor substrates in the Ti^{III}–H_2O_2 system. The naphthalenemonosulphonic acids however are soluble in water but give at best, weak signals due to mixtures of radicals in the flow system. In contrast to this the symmetrical disulphonic acids gave relatively intense spectra in which one component was much stronger than the others and could be picked out with ease. In these cases the signal ascribed to a Ti^{IV}–$HO_2\cdot$ complex [3,9] was entirely quenched, in contrast to the situation with monosulphonic acids, showing the relatively unreactive nature of the latter species.

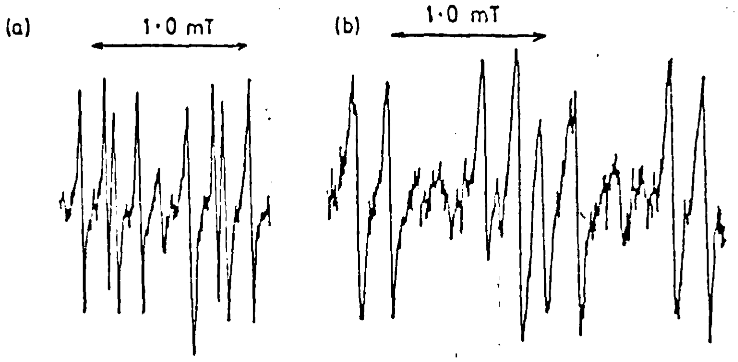
The coupling constants were assigned by comparison with the corresponding naphthoxyl radicals,[10] implying that the geometries of the naphthoxyls are simply related to those of the adduct radicals.

Radicals from Benzene Acids.—In some cases, such as for benzenesulphonic acid, mixtures of radicals were observed but lines due to *meta*-adducts could usually be picked out because their spectra were much wider than those from other isomers. The results for a variety of radicals are given in Table 2.

DISCUSSION

It is clear that carboxy- or sulpho-groups have little effect on the spin distribution in the adduct radicals although the coupling of the methylene proton does change markedly depending on the number of adjacent substituents, ranging from *ca.* 3·6 mT with no adjacent substituent, to *ca.* 2·5 mT when it has substituents on either side. The fused benzo-group can be regarded as a substituent and so the effect can be interpreted as being due only to steric forces. With increasing substitution the hydroxy-group is pushed further from the plane of the ring, moving the methylene proton nearer to that plane hence decreasing hyperconjugation. The electrophilic nature of the hydroxyl radical is shown by a preponderance of addition '*meta*' to a sulpho-group.

Toluene-p-*sulphonic Acid.*—The results using this substrate seemed to be anomalous because at the high acidity of our solutions one would have expected to observe only the substituted benzyl radical.[2,4] Benzyl radicals arise from initial addition of ·OH followed by acid catalysed loss of water.[2] The presence of the electron-withdrawing sulphonic acid group tends to



E.s.r. spectra from 5-sulphosalicylic acid (a) with Co^{IV} and (b) with $Ti-^{III}H_2O_2$ and an excess of substrate

TABLE 1

Coupling constants (10^{-4} T) in hydroxyl adduct radicals of some naphthalenedisulphonic acids (corresponding naphthoxyl coupling constants in parentheses)

Substituent	Position of ·OH attack	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
3,6-$(SO_3H)_2$	1	a_β 24·4	9·4 (6·8)		13·3 (10·8)	3·0 (2·5)		3·5 (2·5)	1·0 (0)
3,7-$(SO_3H)_2$	1	a_β 22·0	10·4 (6·8)		13·4 (10·8)	3·0 (2·5)	1·1 (0·7)		1·1 (0)
4,8-$(SO_3H)_2$	2	11·75 (10·8)	a_β 32·75	2·5 (1·5)		1·9 (1·5)	6·25 (5·4)	1·9 (1·2)	

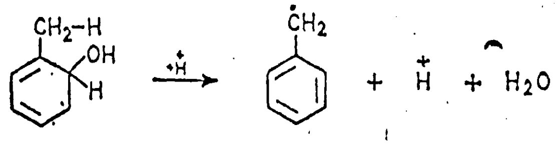
TABLE 2

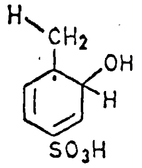
Coupling constants (10^{-4} T) in radicals from attack by ·OH on some benzene acids

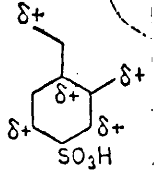
Substituents	Position of ·OH attack	a_1	a_2	a_3	a_4	a_5	a_6
3-SO_3H	1	35·0	8·75		13·25	2·75	9·5
3,5-$(SO_3H)_2$	1	35·5	9·0		13·5		9·0
4,6-(SO_3H)	1	30·75	8·75	2·25		2·25	
3-CO_2H-4-SO_3H	1	36·6	8·5			2·8	9·0
3-SO_3H-4-CO_2H	1	36·0	9·0			2·8	9·5
2,6-$(CO_2H)_2$-4-SO_3H	1	24·5		2·75		2·75	
4,5,6-$(CO_2H)_3$	1	32·0	8·25	2·5			
3,4,5-$(CO_2H)_3$	1	30·25	8·6				
2,3,5,6-$(CO_2H)_4$	1	28·75			12·4		
2-CH_3-5-SO_3H	1	32·5	a_{Me} 9·5	2·75	13·0		8·5
2-CH_3-4-SO_3H-5-EtO_2CO	1	32·75	a_{Me} 9·75	2·25			7·75
1-OH-2-CO_2H-4-SO_3H	2			8·5		12·25	2·25
1-OH-2-CO_2H-4-SO_3H	1 *			1·6		2·2	7·1
1-OH-4-SO_3H	1 *		7·25	2·1		2·1	7·25
1-OH-2,4-$(SO_3H)_2$	1 *			1·75		2·25	6·3
1-OH-2,4,6-$(SO_3H)_3$	1 *			2·0		2·0	
1-CH_3-4-SO_3H	1 †	a_{CH_2} 16·25	5·25	1·75		1·75	5·25

a_1 = Methylene proton splitting.

* Phenoxyl radicals confirmed by Ce^{IV} oxidation in the flow system. † Benzyl-type radical.

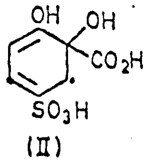


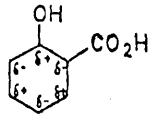

(I)


(Ia)

favour loss of a proton from the methyl group but on the other hand would inhibit proton attack on the hydroxy-group, as we can see from the charge distribution in model (Ia). The observation of an adduct : benzyl radical ratio of *ca.* 2 : 1 (from peak heights) at pH *ca.* 0, suggests that the rate determining step is the attack by a proton.[2] This was confirmed by varying the acidity of the solutions. In $5\,\text{M}$-sulphuric acid a pure spectrum of the sulphonated benzyl radical was obtained, whereas at higher pH (zero sulphuric acid concentration) the benzyl radical could not be detected at all in the presence of a somewhat decreased signal from the adduct radical. It is interesting that the substituent on a *meta*-position is conjugated in the same sense as is the *para*-position of the ring, *i.e.* with the substituent in the 1-position.

Hydroxybenzenesulphonic Acids.—Having observed adduct radicals from toluene-*p*-sulphonic acid under strongly acidic conditions, we investigated the possibility of observing something similar with phenols. From the results it seems that the sulpho-group does not prevent loss of water, from the initially formed adducts [3] so that we only observed phenoxyl radicals except in one special case, 5-sulphosalicylic acid. This compound evidently formed a complex with titanium(III) since when it was present in excess the colour of the solution became dark brown instead of purple. With high Ti$^{\text{III}}$ concentrations a mixture of radicals was observed, the main one being the aryloxyl radical. When the Ti$^{\text{III}}$ concentration was reduced with respect to the substrate concentration, a pure spectrum (Figure) was obtained which could only be interpreted in terms of adduct (II). It seems that when the Ti$^{\text{III}}$ complex reacts with H_2O_2 the hydroxyl radical formed attacks the nearest accessible site. This particular site would probably be favoured because it would initially carry a small negative charge [see (III)].


(II)


(III)

EXPERIMENTAL

The spectra were obtained using the flow system reported previously[10] and the signals were best obtained at the maximum flow rate we could achieve (*ca.* 15 ml s^{-1}). In the oxidations by Ti^{III}–H_2O_2 the substrates were in the range 0·1—0·3M. The experimental conditions were as in ref. 1, but the solutions were made strongly acid with sulphuric acid (pH *ca.* 0). Attempts to purify the commercial samples of the sulphonic acids by recrystallization led to no improvement in the spectra obtained and sometimes led to worse results. We attribute this to the lability/ of the sulpho-group.

y.

[4/147 *Received, 25th January*, 1974]

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