

A Study of the E.S.R. Spectra
of Radicals Related to Phenoxyl

by

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ABSTRACT

Short-lived phenoxyl radicals were formed by the oxidation of phenols with Ce^{IV} ions, using a flow method, and their e.s.r. spectra were obtained.

From regularities observed in the coupling constants of many o-, m- and p-substituted phenoxyl radicals, unambiguous assignments could be made as well as the determination of relative signs. This was achieved by means of appropriate graphs. Semiquinone anions can be classed as phenoxyl radicals as can the radicals derived from the oxidation of trihydroxy benzene derivatives.

Hydroxylated derivatives of γ -pyrone such as kojic acid, maltol, flavones and also coumarins were oxidised by Ce^{IV} in acidic solutions to give radicals analogous to phenoxyl radicals. These were also observed by means of e.s.r. spectroscopy and the patterns of coupling constants obey some simple rules which are given in terms of non-bonding orbital coefficients. With suitable parameters, the patterns of splittings in all of these radicals can be rationalised by means of McLachlan's S.C.F. theory. For substituted phenoxyl radicals, a heteroatom model and an inductive model both explain most of the observed trends.

I.N.D.O. calculations gave rather poor account of the splittings in phenoxyl and those in naphthoxyl radicals.

The e.s.r. spectra of radicals formed by the oxidation of hydroxycinnamic acid derivatives were obtained, and

McLachlan's S.C.F. Theory used for assignment of the coupling constants. The dihedral angle between the double bond and the ring seems to be of the order of 30° .

ACKNOWLEDGEMENT

I wish to express my sincere appreciation of the help and encouragement received from Dr. W. T. Dixon during every aspect of this work.

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PUBLICATIONS

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J. Chem. Soc. Faraday II, 1974, 70, 1713.

(ii) An E.S.R. Study of Radicals Obtained from the Oxidation of Naturally Occuring Hydroxypyrones.

J. Chem. Soc. Perkin II, in the press.

(iii) An E.S.R. Study of the Stereochemistry of Radicals Related to Cinnamic Acid.

J. Chem. Soc. Perkin II, in the press.

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CHAPTER 1

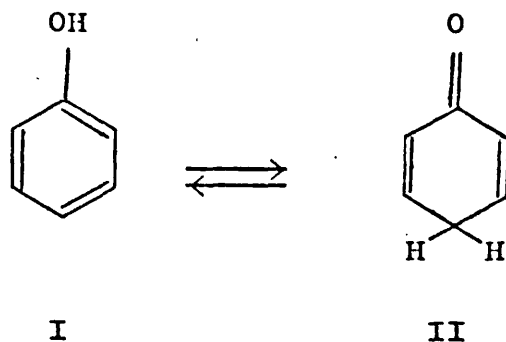
A survey of the chemistry of phenoxyl and related radicals

Although the term "phenol" signifies the monohydric derivative of benzene, it is also applied generally to all derivatives of benzene and its homologues having nuclear hydroxyl group(s).

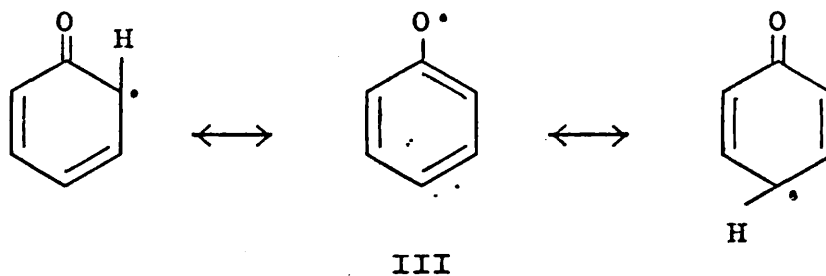
According to the number of hydroxyl groups present the compounds are termed mono, di-, tri-hydric phenols. One reason why there has been much interest shown in the oxidation products of phenols is that they occur widely in plants in the form of glucosides, chromones, coumarins, flavanoids, lignins, tannins and so on.^{1,2}

The extensive use of phenols as antioxidants for oils and fats and realisation that many naturally occurring compounds and certain alkaloids are the result of oxidative coupling of relatively simple phenols, has led to numerous and intensive studies. In general autoxidations, which are believed to occur in nature, take place by radical mechanisms and the first intermediates are in fact phenoxyl-type radicals.

Simple phenols exist exclusively in the enolic form (I) rearrangement to a keto form (II) being accompanied by a decrease in resonance energy.

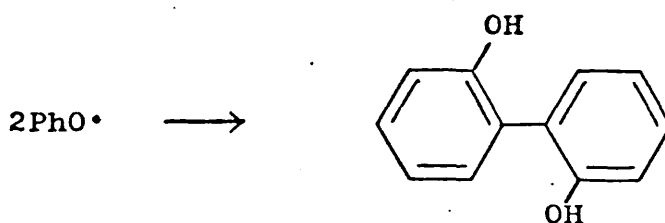


Phenoxy radicals (III) are resonance stabilised and once formed they may react in a number of ways:-³

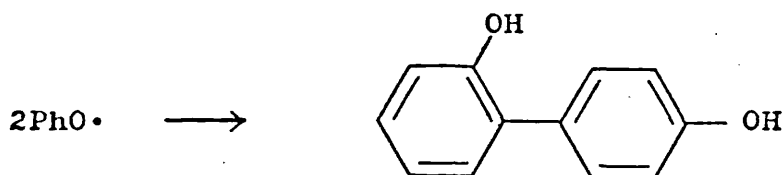


(a) They may dimerise through C-C to give dihydroxybiphenyls or diphenoquinones.

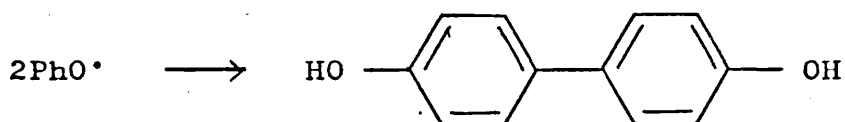
(1) ortho-ortho C-C coupling



(2) ortho-para C-C coupling

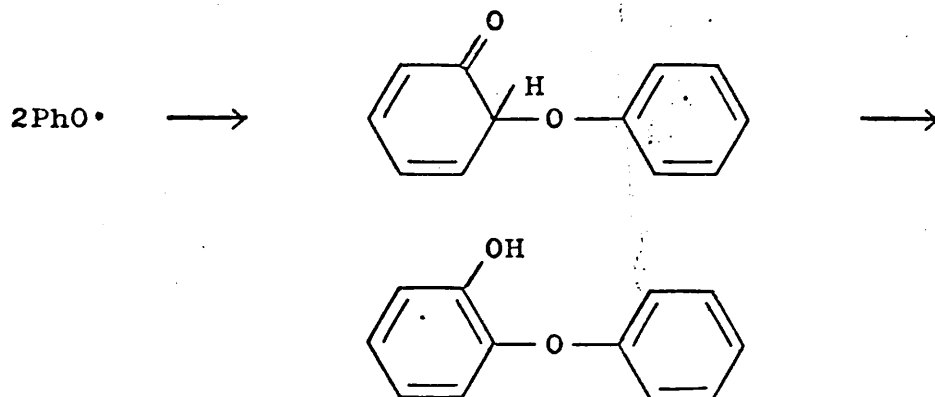


(3) para-para C-C coupling

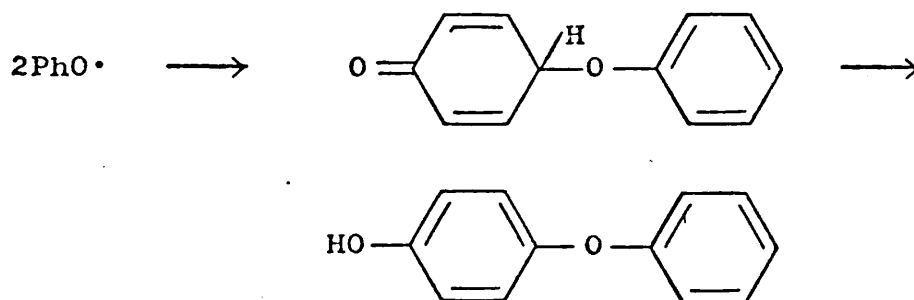


(b) They can couple through C-O to give diaryl ethers or polymeric ethers

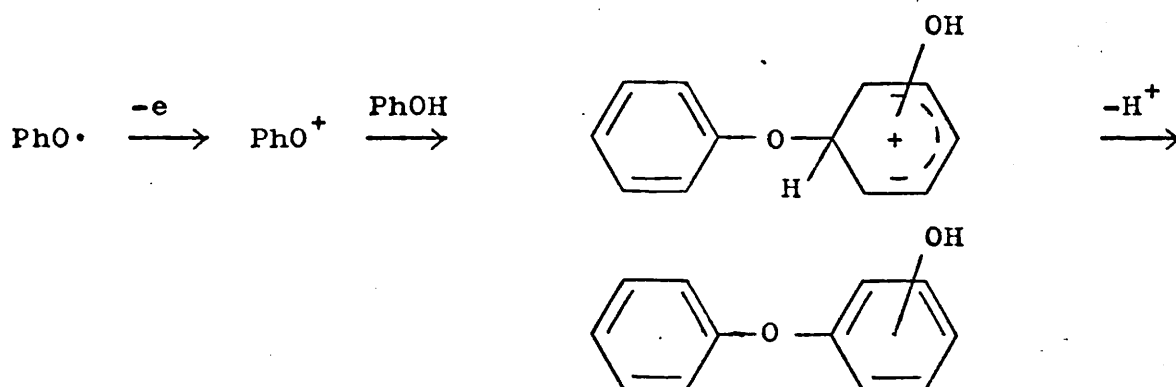
(1) ortho C-O coupling



(2) para C-O coupling



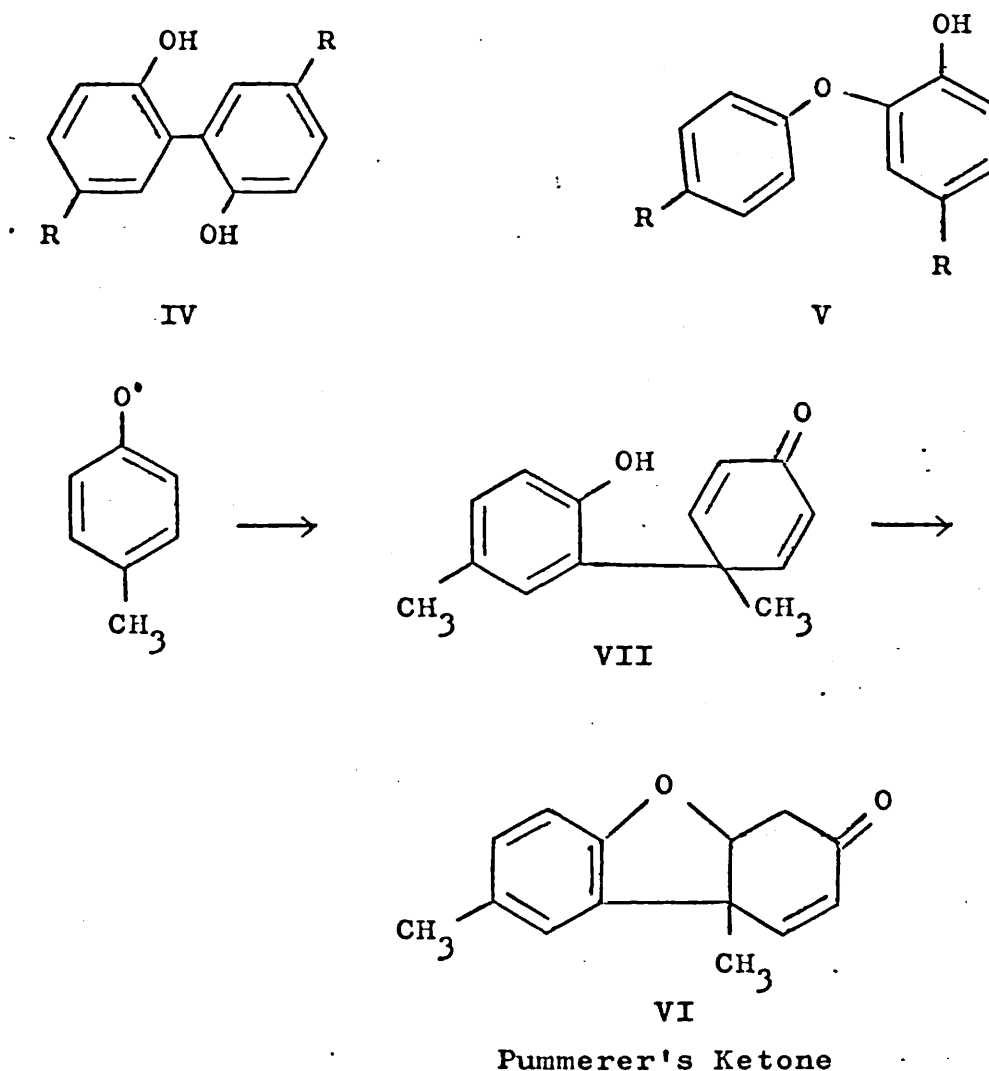
The phenoxy radical could undergo further oxidation to the phenoxonium ion and then could substitute a phenol molecule.



Phenoxonium ion is formed to a limited extent in phenol ox-

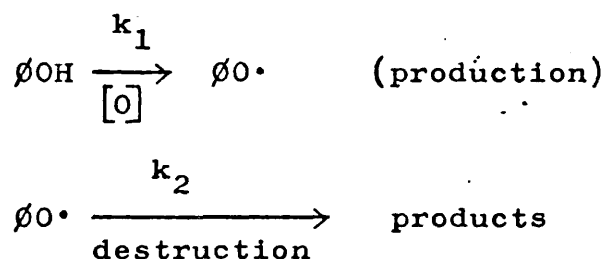
dation when a strong oxidant such as Ce^{IV} is used, weaker oxidants do not oxidize phenols beyond the phenoxyl radical.⁴

Oxidation of p-alkyl phenols are interesting, they lead to the typical C-C and C-O coupled products IV, V. In the case of p-cresol, these products are accompanied by a third product, Pummerer's ketone VI, formed by ortho-para C-C coupling followed by an intramolecular Michael addition of the phenolic hydroxyl to the cyclohexadienone VII.⁵



The phenoxyl radicals in which we are interested, are very reactive and so were difficult to observe in appreciable concentrations.

Consider the following rate reactions:-



In a drastically simplified form the rate equation can be written:-

$$\frac{d(\text{pO}\cdot)}{dt} = k_1(\text{pOH}) - k_2(\text{pO}\cdot)$$

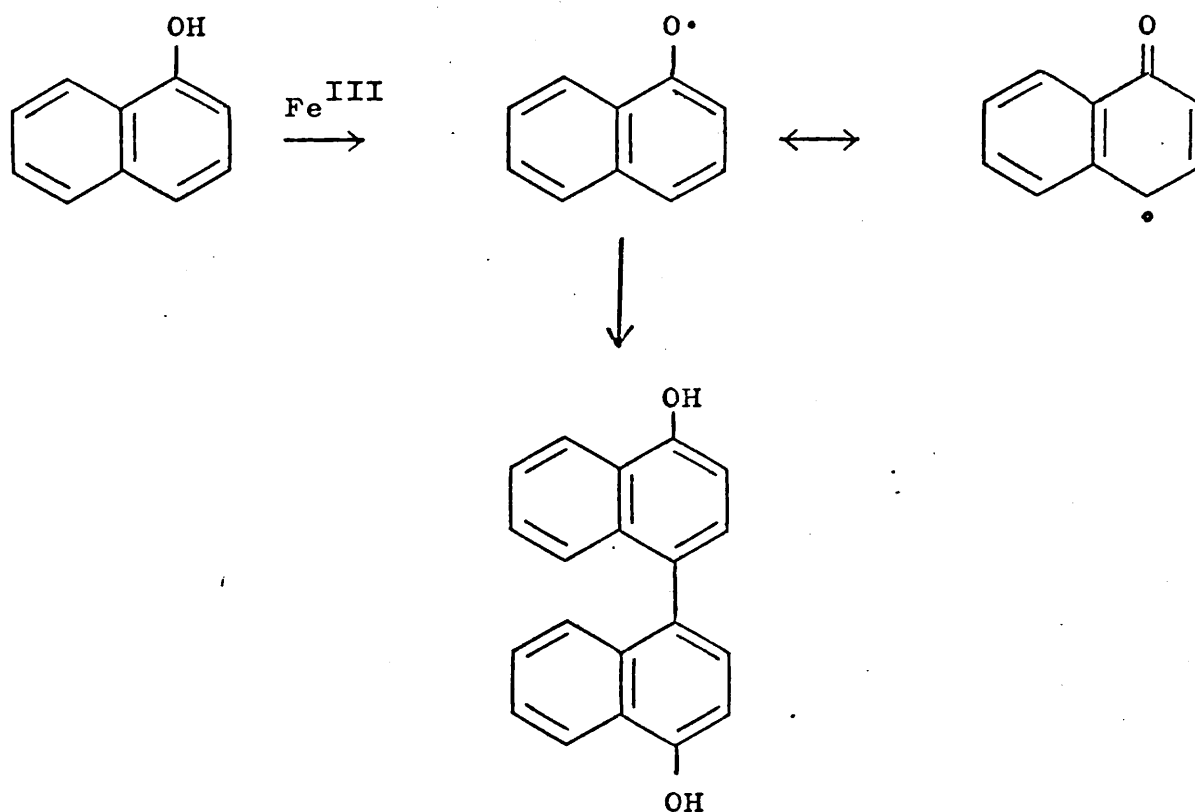
At maximum radical concentration i.e. under steady conditions we have

$$\begin{aligned} k_1 [\text{pOH}] &= k_2 [\text{pO}\cdot] \\ \text{or } [\text{pO}\cdot] &= \frac{k_1}{k_2} [\text{pOH}] \end{aligned}$$

Since k_2 is large then concentration of $\text{pO}\cdot$ can only be large if rate of production i.e. $k_1(\text{pOH})$, is large also. However because of this high rate of destruction the state in which there is a large radical concentration is necessarily short-lived, because of this fact we had to use flow system originally designed by Dixon and Norman.⁶

With this technique radicals with half-lives in the range of 10^{-2} to 10^{-4} seconds can be generated and their e.s.r. spectra recorded.

Free phenoxy radicals are produced by the oxidation of phenols by one-electron abstracting reagents. eg. oxidation of 1-naphthol with ferric chloride gives free naphthoxy radicals, subsequent reactions lead to dimeric and other product.



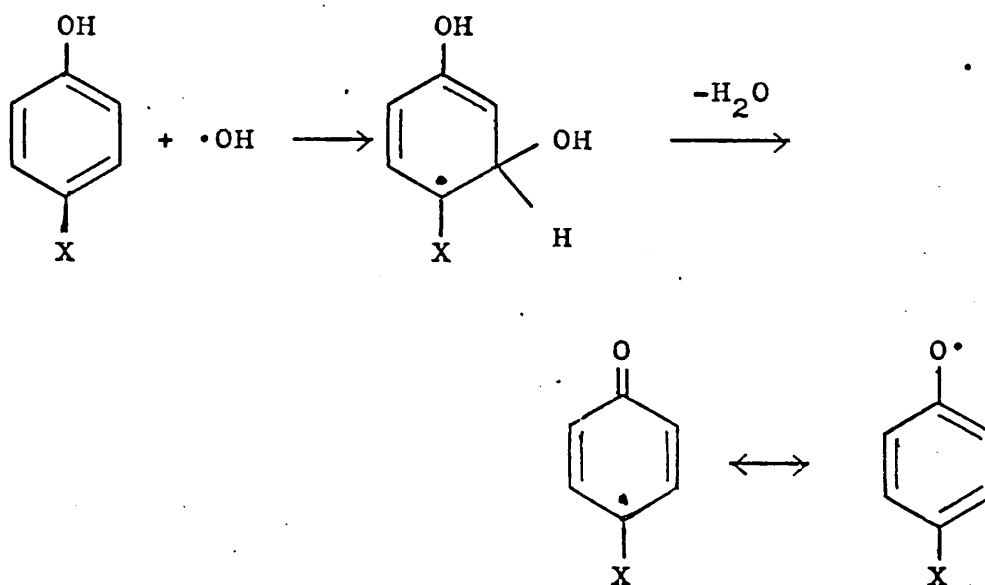
In 1958, Müller et al,⁷ obtained for the first time the e.s.r. spectra of 2,4,6 trisubstituted phenoxy radicals which when they contained bulky substituents having no α -hydrogen eg. (Me_3C) are of long life time.

Scott et al,⁸ examined a number of less stable phenoxy

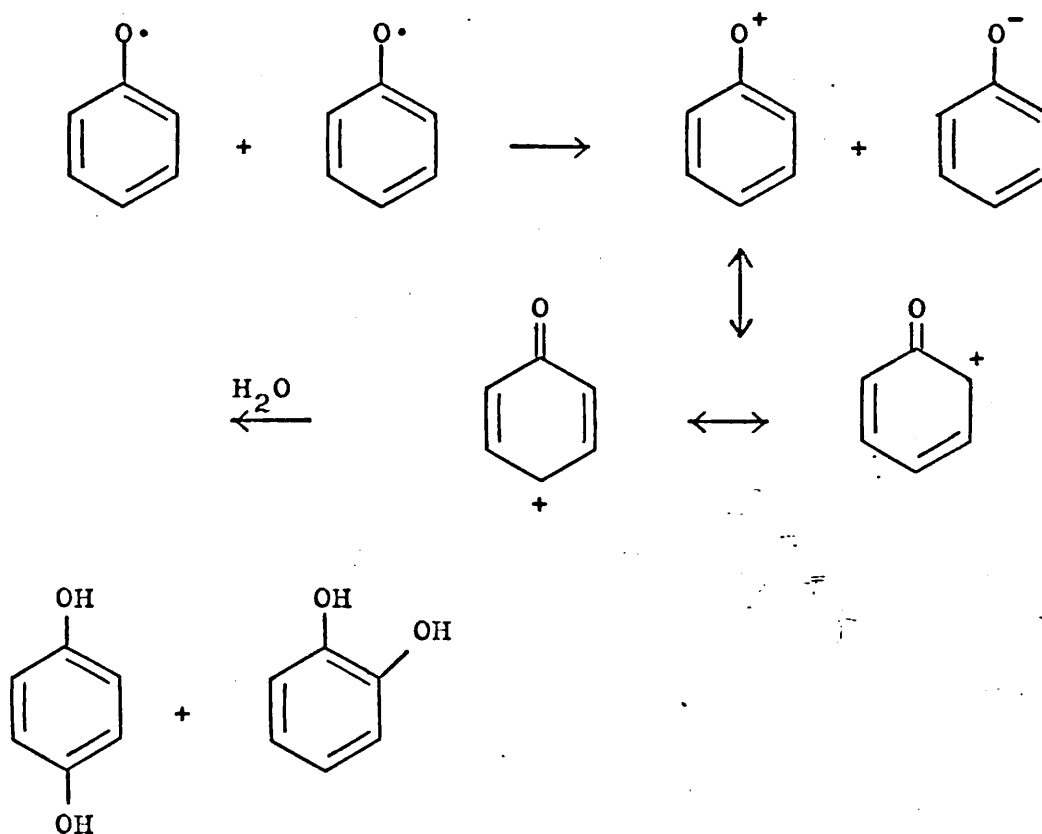
radicals by using a freezing technique. Rieker et al,⁴ in 1963, Reiker and Scheffler,¹⁰ 1965, Dimroth et al,⁵⁶ 1965, used lead dioxide and alkaline ferricyanide to generate phenoxy radicals from hindered phenols.

Another method due to Pannell⁵⁷ involves the oxidation of phenols by t-butoxy radicals formed within the e.s.r. apparatus by u.v. irradiation of cooled solutions containing t-butylperoxide.

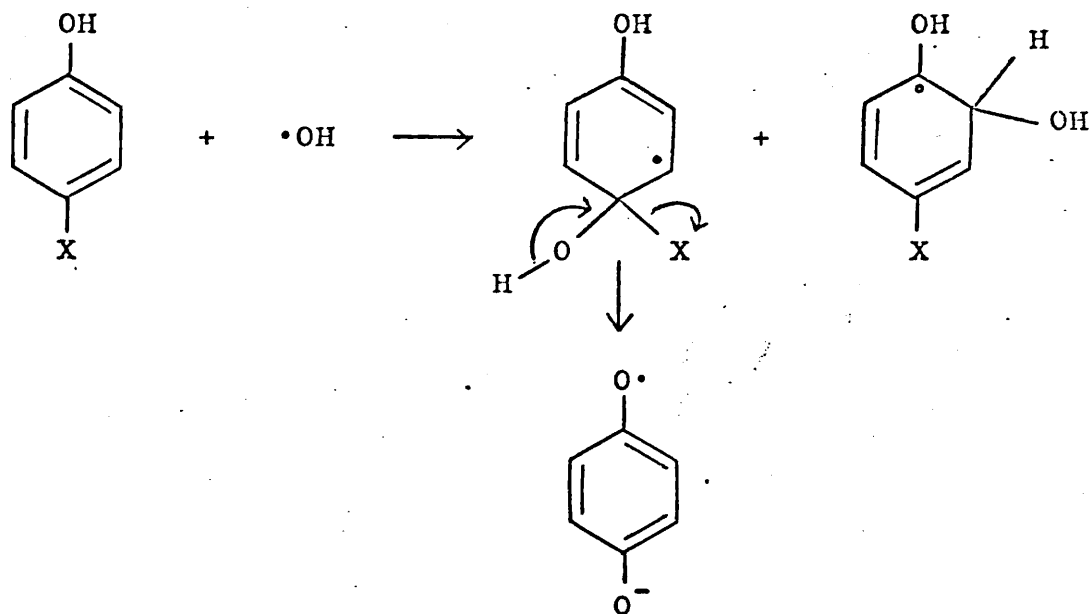
The titanous/peroxide system oxidises phenol to the phenoxy radical. The mechanism of this reaction is not a simple abstraction of hydrogen atom ($\text{PhOH} + \cdot\text{OH} \rightarrow \text{PhO}\cdot + \text{H}_2\text{O}$), but instead occurs through an addition - elimination mechanism as indicated originally by Adams et al.⁵⁸ More recently Neta and Fessenden⁵⁹ used radiolysis e.s.r. technique to produce phenoxy radicals by reaction of $\cdot\text{OH}$ with a number of carboxy substituted phenols and amino phenols in alkaline solution. The radicals are formed as above by addition of $\cdot\text{OH}$ to the ring followed by acid catalysed elimination of water.



Also they found that in the e.s.r. spectra of phenoxyls there were signals from corresponding ortho, and para semiquinone radical anions. These latter radicals are believed to be produced in secondary reactions from dihydroxy compounds formed by a bimolecular reaction of the phenoxyl radicals. The secondary reactions are suggested to take place by electron transfer from a negative ion (phenoxide) and a positive ion, then to be neutralized by reaction of water.

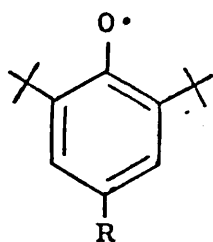


Various workers^{60,11} have studied the hydroxylation of substituted phenols with the $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ system. They found that in alkaline solution benzo-semiquinone was produced.



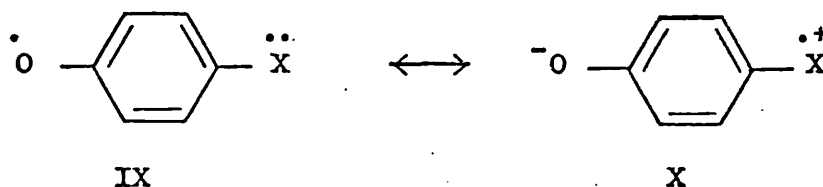
The kinetics of the decay of some of these radicals have been followed.¹² When positions of high spin densities are not blocked the radicals are short lived. The first workers who obtained the e.s.r. spectra of transient phenoxyls were Stone and Waters,^{13,14,15} using a flow technique. Acidified ceric sulphate solution was employed as the oxidising agent, and the reactants were allowed to mix just before entering the cavity of an e.s.r. spectrometer. They found that in short lived phenoxyl radicals electron-repelling para-substituents lower the coupling constants associated with the ortho- and meta-protons while for electron-attracting groups the reverse is true.

Analogous observations have been made in the series of stable radicals of type (VIII)



VIII

Where the meta-proton coupling constant is sensitive to the nature of p-substituent R.⁶¹ In these cases the meta coupling constants increase with increasing inductive power of R. It has been pointed out¹³ that for radicals which can be described by canonical structure of the type IX and X.



much of the electron spin is apparently associated with the oxygen atom and the p-substituent.

Stone and Waters made the important observation that the algebraic sum of the ortho and meta coupling constants in a p-substituted phenoxyl radical is approximately independent of the substituent. This simple rule enabled them to deduce empirically that these two coupling constants must generally have opposite signs, since $|a_o + a_m| = 4.7 \pm 0.2$ G. Presumably the large coupling constants correspond to positive spin densities and so that the small splittings (meta) usually correspond to negative spin densities. In fact the relationship also holds good for p-benzosemiquinone where the two

splittings are equal and of the same sign. The coupling constants of phenoxyl radicals are :

$$a_p = 10.1 \qquad a_o = 6.6 \qquad a_m = -1.8$$

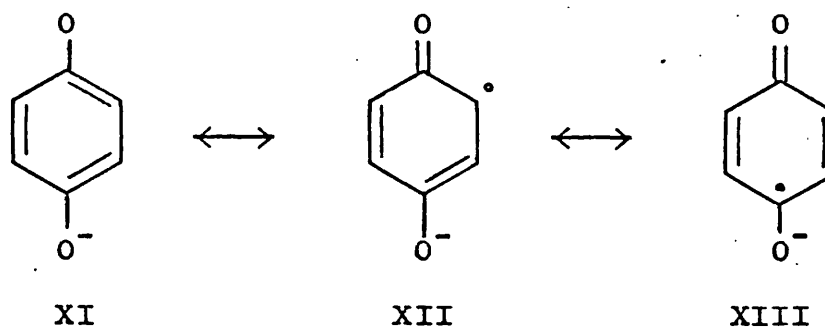
The large value of coupling constant at p-position is to be expected since phenoxyls are mesomeric systems in which the unpaired electron is largely associated with the π -electrons.

The effect of a methoxy substituent on the coupling constants in phenoxyl is drastic, thus in the case of p-methoxy phenoxyl the meta-coupling constant is reduced to zero.

Semiquinones

Semiquinones constitute a special class of phenoxyl radical. The anion XI has a high degree of mesomeric stabilisation and can exist for several hours.

In Valence Bond terms this stability is attributed to resonance between the canonical structures types XI- XIII.

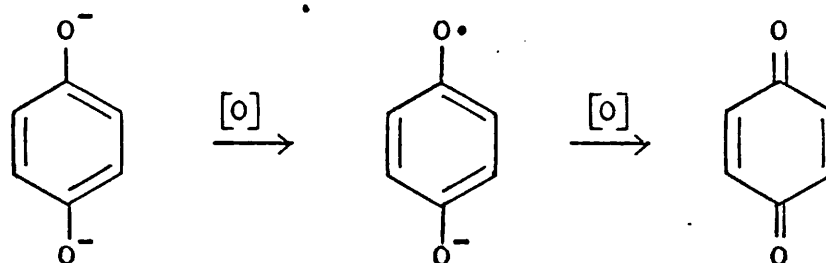


Because of their relative stability semiquinones were among the first radicals to be studied by e.s.r. and a wide range of

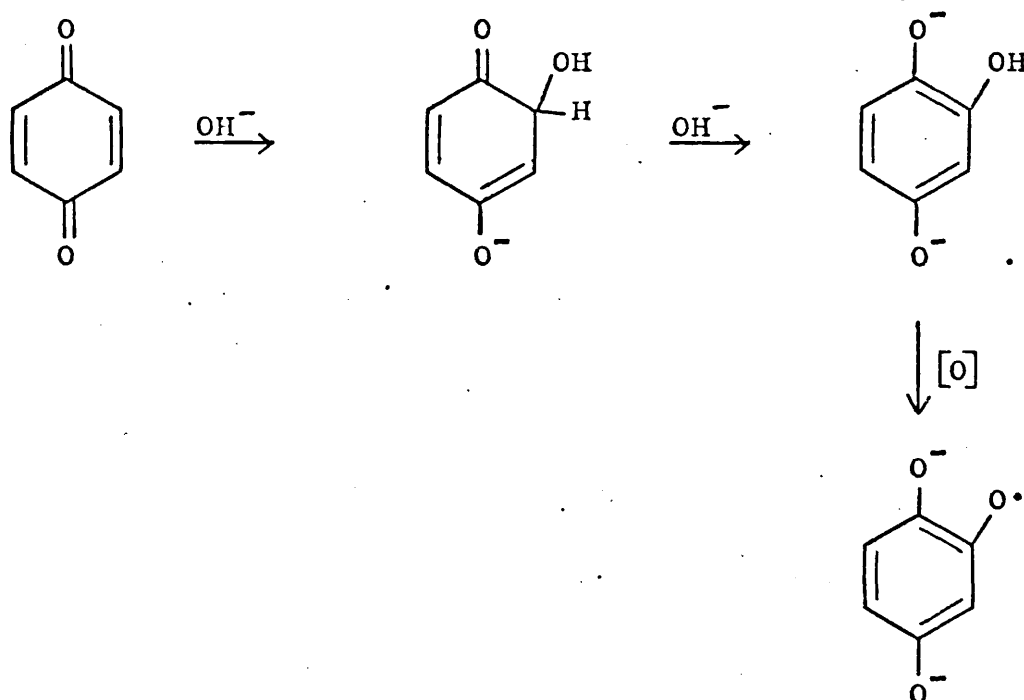
p-semiquinones have been studied in detail.¹⁶⁻²⁴

The formation of semiquinone radicals is however only an initial step in the autoxidation of dihydric phenols, and for example the formation of various secondary radicals in the autoxidation of hydroquinones have been observed.^{44,25} These secondary radicals are derived from 1,2,4-trihydroxybenzenes and the reaction scheme is as follows:-

(1) The autoxidation of hydroquinones lead to benzoquinone.



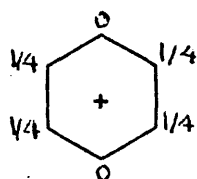
(2) Neglecting the coupling products, the next stage is the introduction of a further oxygen atom into the ring.



A number of well defined spectra due to coupled products have also been obtained. M.O. calculations of the spin distribution of the semiquinone radicals have received a great deal of attention.²⁶⁻²⁹ Vincow and Fraenkel³⁰ calculated unpaired electron densities of the p-semiquinone radical by the H.M.O. method and obtained good agreement with experiment. Latter Vincow³¹ used McLachlan's approximate self-consistent field theory to calculate the spin densities of para and ortho semiquinones and in pyrogallol, and obtained an agreement with the experimental e.s.r. splittings which was a considerably improved calculation relative to those predicted from H.M.O.

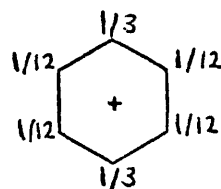
Lott, Short and Waters³² used both Hückel and McLachlan's S.C.F. method to calculate the spin distribution in 1,2,4-trihydroxybenzene and obtained good results. However the number of parameters they used was large compared with number of experimental results they explained.

The spin densities of semiquinones can be explained semi-quantitatively by the perturbation of benzene orbitals.^{33,53} One can regard each of these ion-radicals as a benzene positive ion perturbed by two (\bar{O}) or OH substituents. For p-semiquinone the unpaired electron will occupy the symmetric orbital XV, because the orbital used for odd electron is that with largest probability adjacent to \bar{O} .



XIV

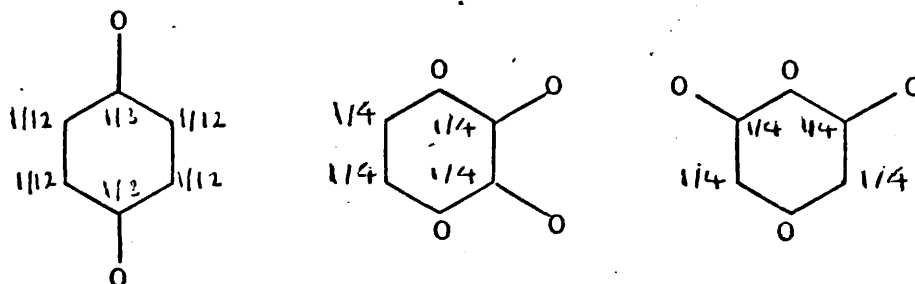
Antisymmetric



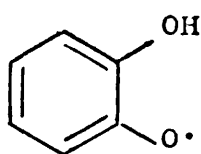
XV

Symmetric

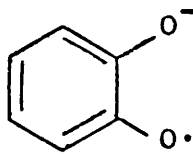
For ortho- and meta-semiquinones, the unpaired electron will occupy the antisymmetric orbital XIV. Experimental coupling constants are in fair qualitative agreement with these models. It is interesting to note that the spin densities in the phenoxyl radical itself cannot be satisfactorily explained in this manner.



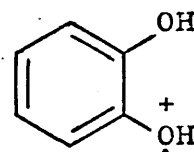
Closely related ortho-semiquinones have been rather less intensively investigated by e.s.r. The first step in the oxidation of catechol is the formation of radical XVI. In strong alkaline solution the resonance stabilised symmetrical anion XVII is formed, whereas in strongly acidic media, the diprotonated radical XVIII is produced.



XVI



XVII

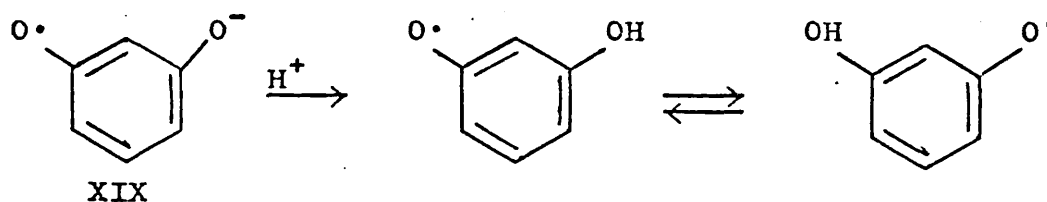


XVIII

Hewgill et al.³⁴ suggested, the mechanism of dimerisation of XVII Smith and Carrington^{22,35} studied the e.s.r. spectra of semiquinone radicals derived from hydroquinone and catechol in aqueous solution of varying pH in a rapid flow system.

They found the spectra changed drastically with pH. These effects arise from the different rates of protonation of these semiquinones.

Resorcinol and substituted resorcinols give us meta-semiquinone radicals when oxidised in alkaline (ferricyanide) solution or acidic solution (ceric ion), in the latter condition the radical anion XIX is protonated.¹⁴



The spectra from the acid oxidation indicate that the number of interacting hydrogen nuclei are the same as the anion obtained from alkaline oxidation of resorcinol thus no splitting from the hydroxyl proton is observed, due to rapid exchange with the solvent.

Theories of spin densities

Theories of different levels of complexity have been applied to some of these radicals. Apart from extremely simplified qualitative perturbation models Hückel and McLachlan's method have been most successfully used for semi-quinones. The main points of these theories are as follows:

M.O. Theory

A molecular orbital is generally chosen as a linear combination of the atomic orbitals.

$$\text{i.e. } \Psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \dots c_n\phi_n \quad (1)$$

The coefficients c_1 are adjustable parameters. The energy corresponding to this wave function is defined by equation (2)^{36,37}

$$E = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau} \quad (2)$$

To find set of coefficients that gives the best values for the energy of the M.O. we make use of the variation principle, which is summed up by the relation (3)

$$E = \frac{\int \Psi H \Psi d\tau}{\int \Psi^2 d\tau} \geq E_0 \quad (3)$$

where E_0 is the actual ground state energy of the molecule. The problem of finding least energy is solved by minimizing the function (3) with respect to the coefficients

i.e. using the relations

$$\frac{dE}{dc_i} = 0 \quad (4)$$

Substituting (1) into (2) and differentiating with respect to c_i we obtain the secular equations

$$\sum_r c_r (H_{rt} - S_{rt}) = 0 \quad (t = 1, \dots, n)$$

There are n equations here.

H_{rr} is called coulomb integral denoted by α_r where

$$\alpha_r = H_{rr} = \int \phi_r H \phi_r d\tau$$

H_{rt} is called the resonance integral denoted by β_{rt}

$$\beta_{rt} = H_{rt} = \int \phi_r H \phi_t d\tau$$

S_{rt} is called overlap integral

$$S_{rt} = \int \phi_r \phi_t d\tau$$

and $S_{rr} = \int \phi_r \phi_r d\tau = 1$

For these equations to apply the secular determinant has to be zero.

$$\begin{vmatrix} \alpha_{11} - E & \beta_{12} - ES_{12} & \beta_{13} - ES_{13} & \dots & \beta_{1n} - ES_{1n} \\ \beta_{21} - ES_{21} & \alpha_{22} - E & \beta_{23} - ES_{23} & \dots & \beta_{2n} - ES_{2n} \\ \dots & \dots & \dots & \dots & \dots \\ \beta_{n1} - ES_{n1} & \beta_{n2} - ES_{n2} & \dots & \dots & \alpha_{nn} - E \end{vmatrix} = 0$$

In the Hückel approximation the following conditions are applied.

- (1) Zero overlap between atomic orbitals

$$\text{i.e. } S_{rs} = 0 \\ r \neq s$$

- (2) H_{rr} is assumed to be the same for each atom

$$H_{rr} = \alpha$$

- (3) The resonance integral H_{rs} is assumed to be the same for any pairing of atoms directly bonded to each other

$$H_{rs} = \beta$$

- (4) H_{rs} is assumed to be zero if the atoms r, s are not directly bonded to each other

By solving these equations, Eigen values and Eigen vectors are calculated, which are the energy and the coefficients of the molecular orbitals. Squares of the coefficients are then spin densities when the orbital contains the unpaired electron, and are positive for every atom.

Alternant Hydrocarbons

A compound possessing a π -electron system which does not contain an odd membered ring is said to be alternant. An alternant compound is further classed as 'even' or 'odd' according to the number of conjugated π -centers in it.

Many useful generalizations are applicable to the Hückel or modified Hückel π -orbitals of alternant hydrocarbons, they

have been established as a series of formal theorems,^{38,39} we refer to some of the appropriate ones here:-

(1) All the M-orbital energies of an even alternant hydrocarbon occur in pairs, lying symmetrically above and below the non bonding energy α . That is if there is a bonding π -orbital Ψ_{+m} of energy $\alpha - \omega_{+m}\beta$ there is an antibonding π orbital Ψ_{-m} of energy $\alpha + \omega_{-m}\beta$ where $\omega_{-m} = -\omega_{+m}$.

(2) An odd alternant hydrocarbon has a non-bonding π -orbital, whose energy is equal to α , in addition to pairs of bonding and antibonding π -orbitals.

(3) In the non-bonding orbital the coefficients of one set of alternant atomic orbitals are zero. Accordingly, the non-bonding orbital can be expressed as $\Psi_0 = \sum_{\pm} c_{0i}^* \phi_i^*$ where the set of alternate orbitals some of which are not zero are starred.

(4) If j is an unstarred atom and i is a starred atom directly linked to j , the coefficients of atomic orbitals in the non-bonding orbital satisfy the following relation

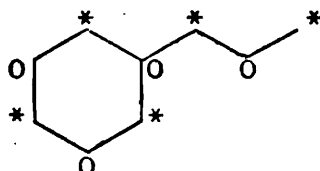
$$\sum_i c_i \beta_{ij} = 0$$

In the Hückle approximation in which all the resonance integrals with this atom β_{ij} are the same then

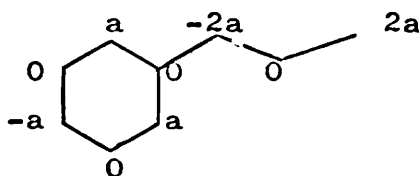
$$\sum_i c_j = 0$$

This theorem enables one to write down the coefficients of atomic orbitals in the L.C.A.O. expression of the non-bonding molecular orbital, without solving secular equations, i.e.

in any alternant hydrocarbon the sum of the coefficients must be zero around any orbital position (zero-sum-rule).³⁶ In a chain of orbitals a zero coefficient is required at penultimate position eg.



Other zero coefficients are assigned according to the zero-sum-rule, one remaining coefficient is given an arbitrary value of a , using this rule other coefficients are given consistent values in units of a as far as possible



To find the value of a , they are normalized.

$$(2a)^2 + (-2a)^2 + a^2 + a^2 + (-a)^2 = 1$$

$$a = \frac{1}{\sqrt{11}}$$

In Figure 1 the 1-naphthylmethyl and benzyl systems are shown

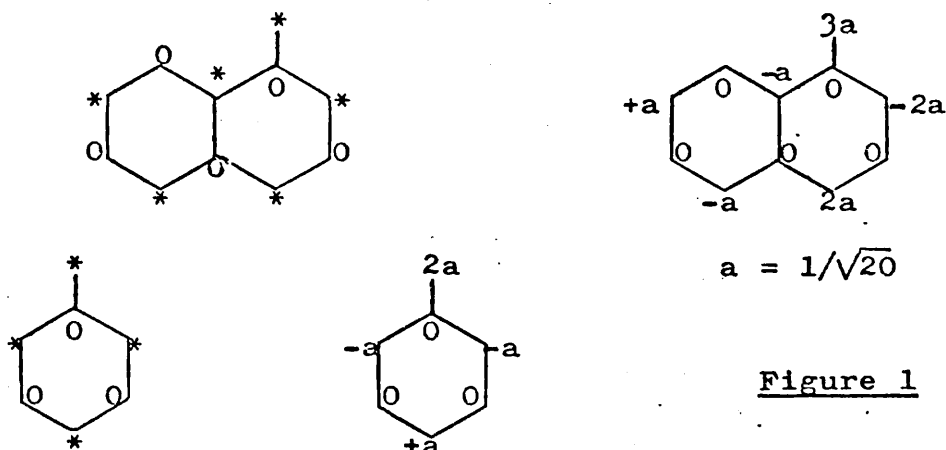


Figure 1

McLachlan S.C.F. Theory

Simple H.M.O. theory is not appropriate for discussing negative spin densities. The easiest way of introducing the possibility of negative spin density into M.O. theory is by means of perturbation technique suggested by McLachlan.⁴⁰

In effect there are differential repulsions between α and β electrons. If the total spin is α then the repulsion between an α electron and the other electrons will on average be different from that of a β electron and the others.

The effect of a spin density in a π atomic orbital is to spin-polarize the nearby σ -bonds as well as other π -M.O.'s and thus lead to a change in the overall electron repulsions acting on it. In McLachlan's theory we simply use the Hückel spin density on a position to modify the coulomb integral of that orbital. Thus if α is the coulomb integral appropriate to β electron, then the coulomb integral for α electron will be

$$\alpha + k'\beta$$

where $k' = 2\lambda e$, λ is a constant, e = Hückel spin density.

For the problem of parameterisation we used the definitions^{36,37}

$$\alpha_x = \alpha_c + h_x \beta_{cc}$$

$$\beta_{cx} = k_{cx} \beta_{cc}$$

α_x is the coulomb integral of heteroatoms

α_c is the coulomb integral of carbon atoms

β_{cc} is the resonance integral between carbon atoms

The spin density at each atom is given by⁴⁰

$$c_r = c_{Or}^2 - \lambda \sum_{s=1}^n \pi_{rs} c_{Os}^2$$

where: c_{Or} is the Hückel coefficient of the odd orbital on atom r .

π_{rs} is the mutual polarizability of atoms r and s .

λ is a constant, gives value between 1.0 and 1.2.

and

$$\pi_{rs} = -4\beta \sum_j^{\text{filled}} \sum_k^{\text{empty}} \frac{(c_{jr}c_{kr})(c_{js}c_{ks})}{E_k - E_j} \quad \text{Ref.40}$$

where c 's are Hückel coefficients for atoms s and r in the molecular orbital j and k .

E_k, E_j are the Hückel energies for k and j levels.

As an example, the spin densities of allyl radical will be calculated, using above formula. Hückel molecular orbitals for allyl radical are:

$$\Psi_1 = \frac{1}{2}\rho_1 + \frac{1}{\sqrt{2}}\rho_2 + \frac{1}{2}\rho_3$$

$$\Psi_2 = \frac{1}{\sqrt{2}}\rho_1 + 0\rho_2 - \frac{1}{\sqrt{2}}\rho_3$$

$$\Psi_3 = \frac{1}{2}\rho_1 - \frac{1}{\sqrt{2}}\rho_2 + \frac{1}{2}\rho_3$$

and the energies are:

$$E_1 = \alpha + \sqrt{2}\beta$$

$$E_2 = 0$$

$$E_3 = \alpha - \sqrt{2}\beta$$

McLachlan's formula for spin densities will be:-

$$e_1 = c_{21}^2 + 1.0(\pi_{11}c_{21}^2 + \pi_{13}c_{23}^2)$$

$$e_2 = 0 + 1.0(2\pi_{21}c_{21}^2)$$

where we have taken $\lambda = 1.0$

and
$$\pi_{11} = -4\beta \frac{\frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2}}{(\alpha - 2\beta) - (\alpha + 2\beta)} = \frac{1}{8\sqrt{2}} = \pi_{13}$$

$$\pi_{21} = -4\beta \frac{(\frac{1}{2}) (\frac{1}{2}) (-1) (\frac{1}{2})}{(\alpha - 2\beta) - (\alpha + 2\beta)} = \frac{-1}{4\sqrt{2}}$$

therefore
$$e_1 = 0.5 + 0.088 = 0.588$$

$$e_2 = 0.0 - 0.176 = -0.176$$

In this calculation mutual polarizabilities π_{rs} should be calculated each time. McLachlan suggested that e_r can be directly found without taking π_{rs} into direct account from the expression

$$e = \psi_0^2 + \sum_1^n \left\{ \psi_i^2 - \psi_i'^2 \right\}$$

where ψ_0 is the coefficients of the odd orbital

ψ_i' is the Hückel coefficients

and ψ_i is the modified coefficients which are derived from secular equations by changing

$$\alpha_r \longrightarrow \alpha_r + 2\lambda c_{0r}^2 \beta$$

and keeping β_{rs} unchanged.

For an example of this method we use allyl radical again.

The secular determination for allyl is:-

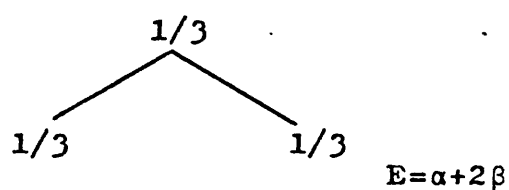
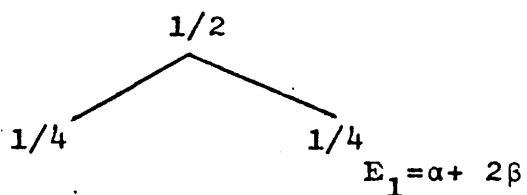
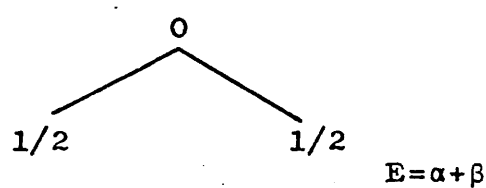
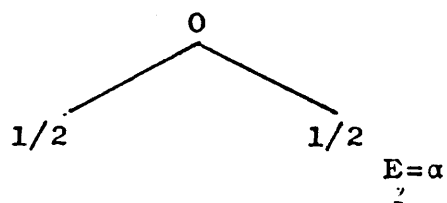
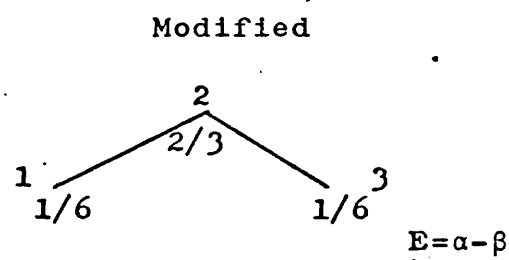
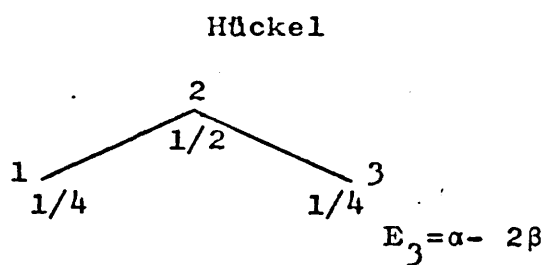
$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

The energy levels and coefficients are as previously. To modify the coulomb integral by $2\lambda c_0^2 \beta$ where $\lambda = 1.0$, c_0^2 the square of the coefficients of the orbital with unpaired electron. The modified equation will become.

$$\begin{vmatrix} x+1 & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x+1 \end{vmatrix} = 0$$

$$x = +1 \text{ or } -2$$

The square of coefficients are shown



Spin densities are:-

$$e_1 = e_3 = \frac{1}{2} + (1/3 - 1/4) = 7/12 = .583$$

$$e_2 = 0 + 1/3 - \frac{1}{2} = -1/6 = -.166$$

and when $\lambda = 1.2$

$$e_1 = e_3 = .593$$

$$e_2 = -.185$$

Experimental spin densities for $Q = 25$ are:-⁶⁷

$$e_1 = e_3 = .592$$

$$e_2 = .184$$

The Theory of e.s.r. Spectroscopy

Electron-spin Resonance Spectroscopy is a branch of microwave spectroscopy which is applied to molecules possessing electrons with unpaired spins. A free electron has a spin S of $\frac{1}{2}$ and can exist in two states of equal energy said to be degenerate. This degeneracy is only removed by the application of an external magnetic field and two separate levels characterised by the spin quantum numbers $M_s = -\frac{1}{2}$ or $+\frac{1}{2}$ result. The lower level corresponds to parallel alignment of the electron spin magnetic moment with the external field, the upper level corresponds to anti-parallel alignment. The separation between the levels is equal to $g\beta H$ where H is the strength of the applied magnetic field, β is the Bohr magneton and g is a dimensionless quantity having the value 2.0023 for a free electron. The application of a microwave field of the appropriate frequency causes the electron spin to change its orientation, and the resulting transition is detected as an absorption of energy.

The magnetic interaction term for an electron i.e. the spin Hamiltonian is:-^{41,42}

$$H_e = g\beta B_Z S_Z$$

and for a nucleus is:-

$$H_n = -\gamma_n B_Z I_Z$$

If α and β are the functions describing the spin of odd electron we can write

$$H_{\alpha} = g\beta B_Z S_Z \alpha = \frac{1}{2}g\beta B_Z \alpha$$

$$H_{\beta} = g\beta B_Z S_Z \beta = -\frac{1}{2}g\beta B_Z \beta$$

where S_Z is the Z component of the spin angular momentum operator s , with $\pm\frac{1}{2}$ eigen value.

i.e. $S_Z \alpha = \frac{1}{2}\alpha$

$$S_Z \beta = -\frac{1}{2}\beta$$

First order perturbation energy is given by:-

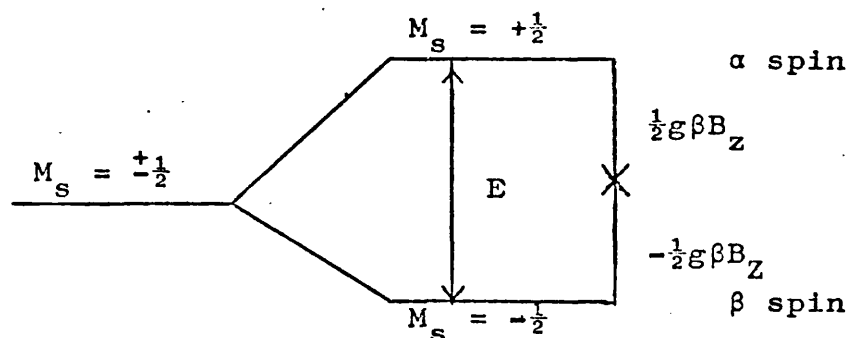
$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

and $\langle \Psi | \Psi \rangle = 1$ when normalized

Energies are:-

$$\langle \alpha | H | \alpha \rangle = \frac{1}{2}g\beta B_Z \langle \alpha | \alpha \rangle = \frac{1}{2}g\beta B_Z$$

$$\langle \beta | H | \beta \rangle = -\frac{1}{2}g\beta B_Z \langle \beta | \beta \rangle = -\frac{1}{2}g\beta B_Z$$



$$\Delta E = h\nu = g\beta B_Z$$

Figure 2

Hyperfine splittings

The nucleus in a radical interacts with the field and also with the odd electron. The interaction with the odd electron averaged on all angles is A.S.I. which can be simplified for our purposes to $aS_Z I_Z$. The magnetic interaction then becomes:-

$$H = g\beta B_Z S_Z - \gamma \hbar B_Z I_Z + a S_Z I_Z$$

The combinations of spin states which are possible are as follows:-

$$\Psi_1 = \alpha_e \alpha_N, \quad \Psi_2 = \alpha_e \beta_N, \quad \Psi_3 = \beta_e \beta_N, \quad \Psi_4 = \beta_e \alpha_N$$

where α_e, β_e are spin w/f of electron

α_N, β_N are spin w/f of nucleus

The corresponding energy levels are shown in Figure 3.

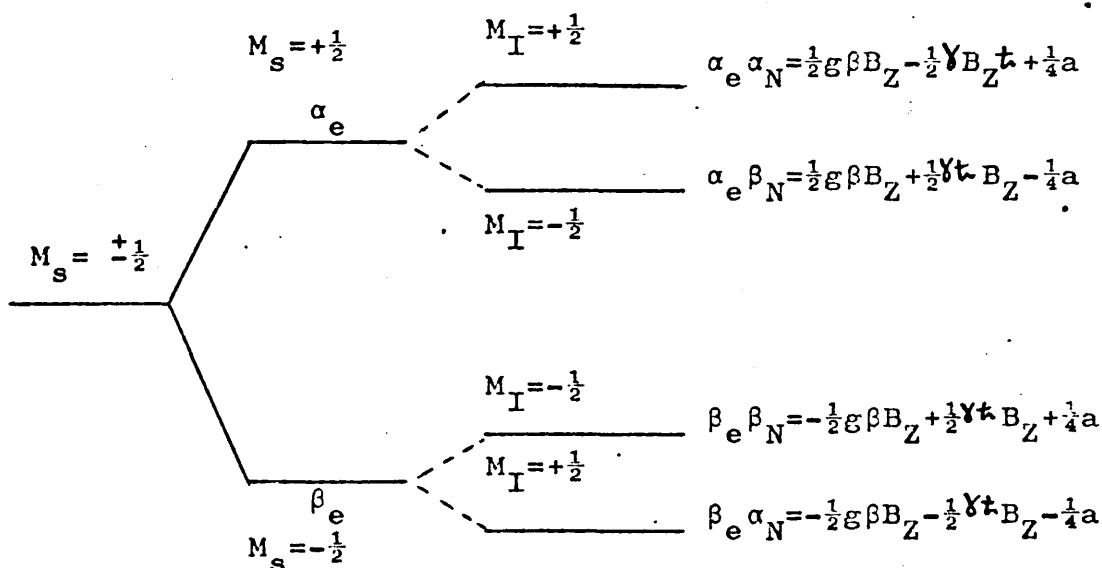


Figure 3

Transition probability

The selection rule for an electron spin transition is $\Delta M_S = \pm 1$. With magnetic interaction between electron and nucleus the selection rules are:-

$$\Delta M_S = \pm 1, \quad \Delta M_I = 0$$

The energy of the two transitions are

$$\Delta E_1 = g\beta B_Z + \frac{1}{2}a$$

$$\Delta E_2 = g\beta B_Z - \frac{1}{2}a$$

so in an electron resonance situation the presence of a proton of spin $\frac{1}{2}$ leads to two absorptions separated by $\frac{1}{2}a - (-\frac{1}{2}a) = a$ which is called the coupling constant of the proton.

The magnetic interaction of electron with a number of protons can be seen diagrammatically in Figure 4. When electron interacts with two equivalent protons each electron spin level is split into three sublevels, the central one being doubly degenerate. For this system the spectrum would consist of three equally spaced lines with relative intensities 1:2:1. It follows when there are n-equivalent protons it gives rise to a hyperfine pattern with (n+1) lines whose relative intensities are proportional to the coefficients of the binomial of order n.

For the case when there are non equivalent protons (Figure 5) the procedure is to consider the splittings due to each proton in turn, For example when the electron couples

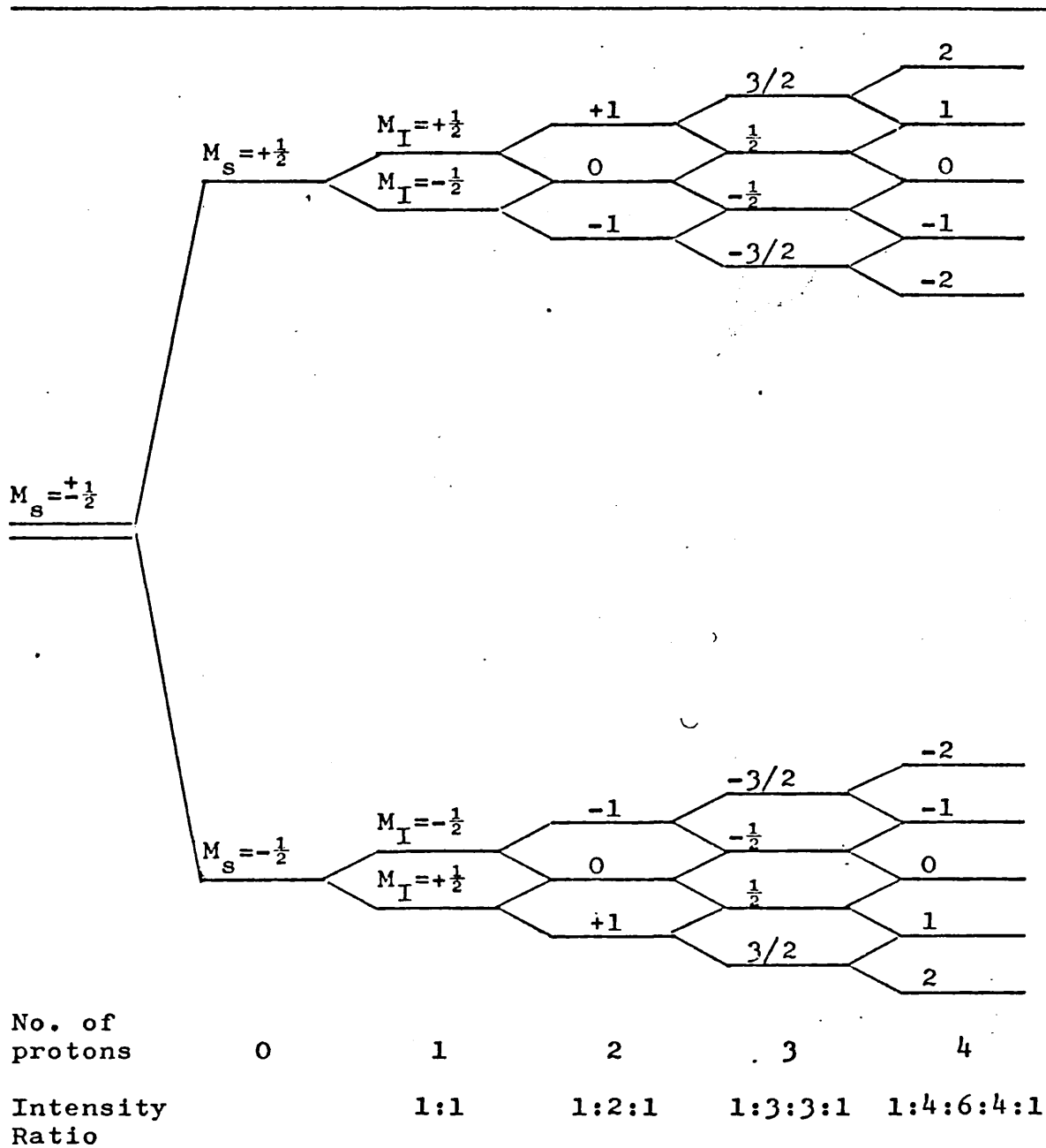


Figure 4

with one proton (A) more strongly than with proton (B). The larger interaction will split the single electronic absorption line into two lines separated by $a_A G$ while the weaker interaction will split each of these into two lines separated by $a_B G$.

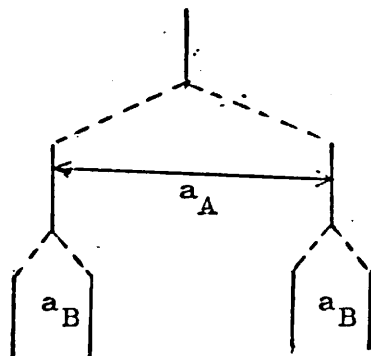
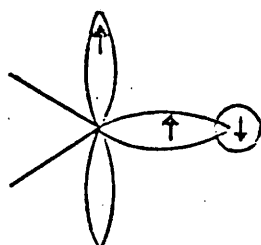


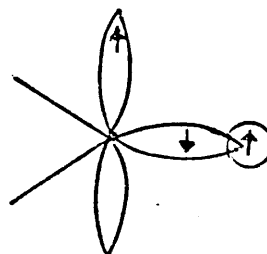
Figure 5

Origin of negative spin densities

In order to explain the negative spin density, consider a C-H fragment of a conjugated system.⁴³ If spin α is assigned to the one electron in the $2p_z$ orbital on the carbon atom, there are two possibilities for assigning the spins in the C-H σ bond, these are shown.



A



B

If there is no electron in $2p_z$ orbital the electron configurations A and B are equally probable. However when $2p_z$

electron is present according to Hund's Rule (maximum multiplicity) configuration A is more stable in which the two electrons on the carbon atom have parallel spins and hence a negative spin density at the proton.

McConnell⁵⁰ showed that the negative spin density at an aromatic proton is proportional to the spin density on the adjacent carbon atom

$$\text{i.e.} \quad a_{\text{H}} = +Q\rho_{\text{C}}$$

$$Q(\sim -3.0 \text{ mT})$$

$$\rho_{\text{C}} = \text{spin density in } \pi \text{ A.O. of adjacent carbon atom}$$

$$a_{\text{H}} = \text{coupling constant}$$

When Stone and Waters studied phenoxyl radicals they obtained a relation between the coupling constants of some p-substituted phenoxyl. In this work, we have extended this approach to a larger variety of radicals and have developed methods for assigning unambiguously the signs and magnitudes of coupling constants by graphical methods. We have also explained these coupling constants and confirmed the assignments using the different theoretical models which are discussed in this thesis. Finally we have applied the successful theory to other, related systems such as those derived from hydroxypyrones.

CHAPTER 2

Experimental

The spectra were observed using a Varian E4 spectrometer. Most of the radicals were produced by flowing 10^{-2} M solutions in 0.5 M sulphuric acid against 10^{-2} M Ce^{IV} solutions, using the flow system and modifying the coaxial mixing device,⁶ so that the reactant solutions mixed virtually inside the cavity of 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} . 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.

Analysis of spectra

The spectra of substituted phenoxy radicals are shown following page 49. We will discuss analysis of some of the more important ones here. The spectrum from phenoxy radical is derived from two triplets splittings giving rise to 1:2:1:2:4:2:1:2:1, which is repeated twice due to the para-hydrogen, the measured coupling constants are 6.6 and 1.8 for two triplets and 10.2 for the doublet.

All spectra from para-substituted phenoxy radicals are easily analysed due to their symmetry, but the analysis of spectra of ortho and meta substituted phenoxy radicals are more complex. The smaller splittings can be measured straight away from the wings of the spectrum. p- NO_2 phenoxy radical has coupling constant for nitrogen 2.44 which is deduced from the fact that the small triplet of two equivalent hydrogens have the same coupling of nitrogen giving rise to 1:3:4:3:1. i.e.

$$\begin{array}{cccc}
 1 & 1 & 1 & \\
 & 2 & 2 & 2 \\
 & & 1 & 1 & 1 \\
 \hline
 1 & : & 3 & : & 4 & : & 3 & : & 1
 \end{array}$$

o-NO₂ phenoxy, the nitrogen splitting 1:1:1 is 2.1 G which is repeated twice for each proton. m-NO₂ phenoxy, very small splitting for nitrogen, 0.5 G as expected from the small spin density at meta position of phenoxy. p-CHO phenoxy, has very small splitting of 0.3 G due to the proton of CHO group. When CHO at ortho and meta position this splitting is too small to be resolved. p-CHMe₂ has six equivalent protons of small splittings of 0.4 G giving lines of intensities 1:6:15:20:15:6:1. The doublet splitting of the β-proton is 4.5 G. o-CHMe₂:-the coupling constant of β-proton of the isopropyl group is 4.0 G no splitting from methyl groups observed. m-CHMe₂:-no splitting for methyl hydrogens and the coupling constant of the β-proton is 0.8 G. It is interesting that the β-proton of the isopropyl group has a coupling constant which is approximately half that observed for corresponding methyl protons whereas the ring coupling constants are approximately the same.

p-Fluorophenoxy has a large coupling constant attributed to fluorine atom of 27.5 G. o-Fluorophenoxy has large fluorine coupling constant of 16.8 G. m-Fluorophenoxy the coupling constant of fluorine is 5.8 G. Thus, as in other cases the fluorine splittings are about twice corresponding

proton splitting.^{54,55}

p-Cl phenoxy, in this case each triplet of two hydrogens are further split by chlorine ($I=3/2$) giving rise to 1:3:4:4:3:1 which is

$$\begin{array}{cccccc}
 1 & 1 & 1 & 1 & & \\
 & 2 & 2 & 2 & 2 & \\
 & & 1 & 1 & 1 & 1 \\
 \hline
 1 & : & 3 & : & 4 & : & 4 & : & 3 & : & 1
 \end{array}$$

for o- and m- chloro phenoxy the chlorine coupling constant is relatively small 1.05 and 0.25 respectively.

p-OMe has only a triplet of 4.9 G and a quartet 1:3:3:1 of 2.1 G thus the meta proton splitting is apparently zero. In o- and m-OMe phenoxy the quartet splittings are 1.8 and 0.6 respectively.

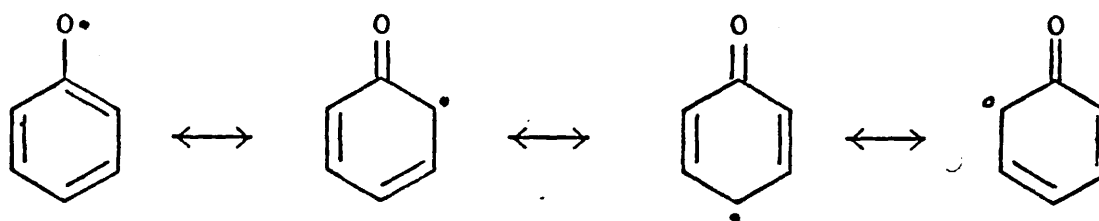
p-NH₂, the nitrogen coupling constant is 6.6 G and there are three triplets 1:2:1 of 4.0, 0.5 and 8.0 G. o-NH₂, nitrogen coupling constant is 6.62 G and the triplet attributed to the NH₂ protons is 8.13 G. m-NH₂, the nitrogen splitting is 6.9 G and that of the NH₂ protons appears to be 8.1 G.

Assignment of coupling constants

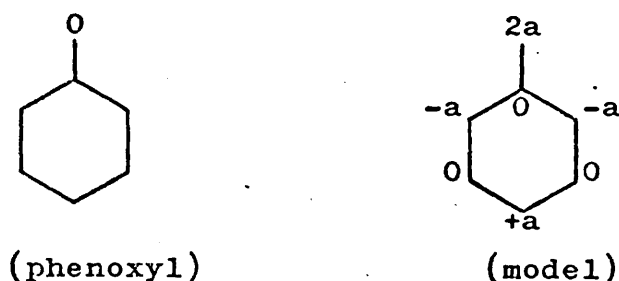
From the analysis of the spectra we have a set of coupling constants, and these now have to be assigned correctly to the various positions. For this purpose we have used a graphical

method which will be explained below. Tables (1,2,3) are for the p-, o- and m-substituted phenoxy radicals respectively. The coupling constants have been tabulated according to the final assignments which were arrived at by a sequence of steps.

Before considering in detail the empirical method of assignment, let us first look at simple theories which account qualitatively for the pattern of spin densities in these radicals. The spin delocalisation in phenoxy radical can be rationalised in terms of V.B. theory quite adequately. The most important canonical structures are as follows:-



These lead one to expect relatively large positive spin densities in the o- and p-positions. One can also deduce from these structures that small negative spin densities should appear at the meta positions. Using a simple M.O. model (i.e. put $\alpha_o = \alpha_c$, which makes it, in fact, the benzyl system) the N.B.O. coefficients are as in the diagram:-



where $a^2 + (-a)^2 + (-a)^2 + (2a)^2 = 1$

$$a = \frac{1}{\sqrt{7}}$$

Again large spin densities are initially expected at the o- and p- positions. Thus both pictures lead to the same general conclusion. The coupling constants in phenoxyl are 10.4 (doublet) 6.6 (triplet) and 1.8 (triplet). We therefore assign the small coupling to meta positions. Now the largest splitting observed is a doublet so there is no ambiguity in placing 10.2 to para position for there is only one para proton, and 6.6 to ortho position because there are two ortho protons which give a 1:2:1 splitting pattern.

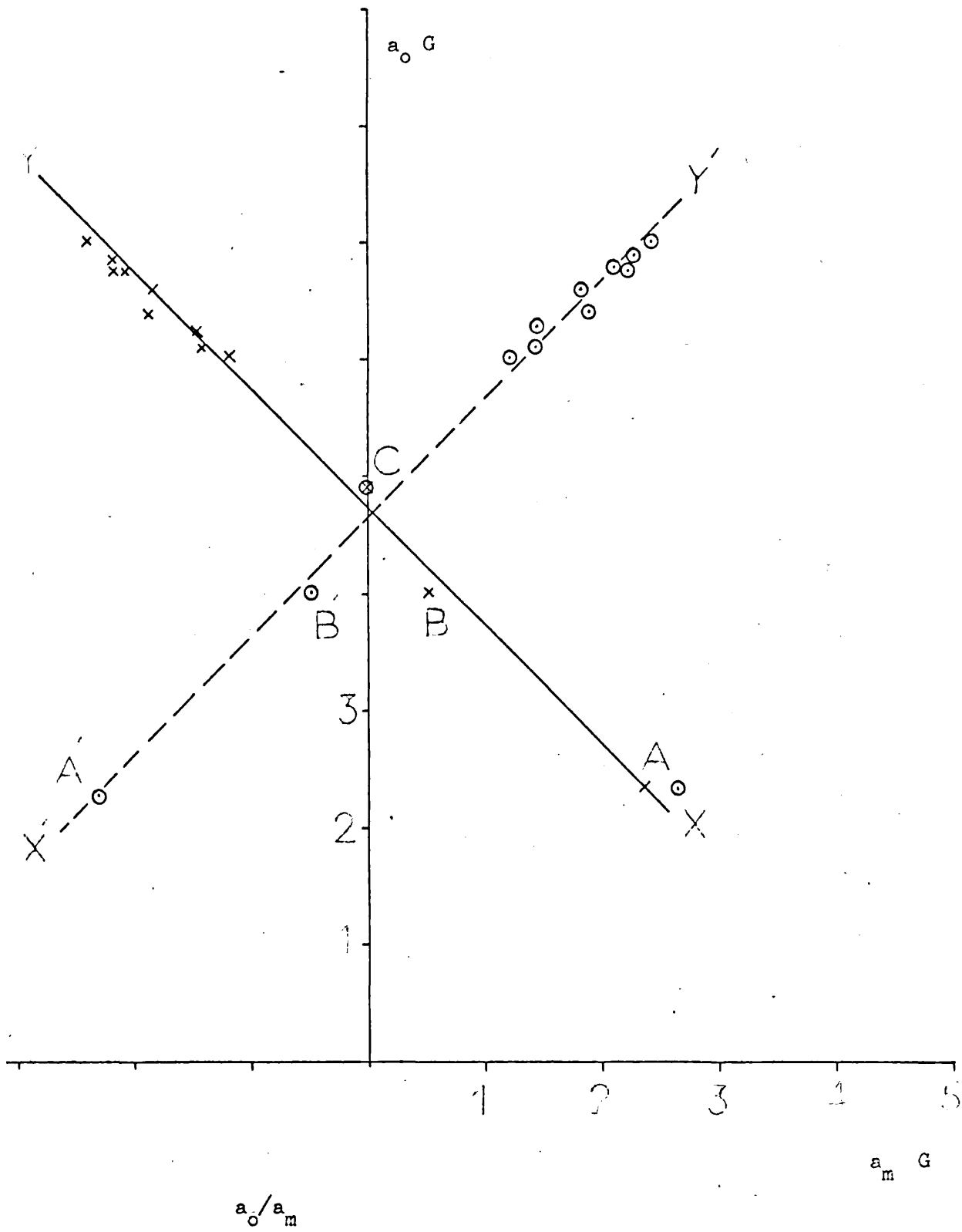
In all the para substituted phenoxyls there are two sets of two equivalent protons as expected from the symmetry. The correctness of this assignment is illustrated by the methyl and carboxy substituted phenols eg. p-CO₂H causes the largest coupling constant to disappear, whilst with p-CH₃ the large doublet splitting is replaced by a quartet of 12.5 G due to the equivalent protons. The ortho and meta splittings in these cases change only a little. Similar empirical confirmation is obtained for the assignments when these two substituents are in the ortho or meta positions. We are stressing this point because the assignments (and their relative signs) of the coupling constants can be made without reference to theory, for our series of experiments form a completely self contained set.

Para-substituted phenoxy radicals

Graph (I) is a plot of a_0 against a_m . The points on the lines xy and $x'y'$ represent two possibilities. In the former the two coupling constants are of the same sign and in the latter they have opposite signs.

Point A(2.37, 2.37) representing semiquinone is to be regarded as a fixed point, because semiquinone is a symmetrical molecule, so that all four protons are equivalent. They therefore have the same sign as well as the same magnitude. Point A' (2.37, -2.37) is not valid as the two coupling constants for two symmetrical protons are not of the same sign. Point C (0, 4.9) which is on the y axis, corresponds to $X \equiv -\text{OMe}$. Both lines xy , $x'y'$ should pass through (or near) this point. We presume that all large coupling constants have the same sign because the overall spin density has to be positive. In that case cy' passes through A' which is not a valid point, whereas cy passes through A. Therefore the line xy is acceptable, indicating that the meta proton splitting generally have opposite signs to the ortho protons.

Point B (4.0, 0.5) corresponds to $X \equiv -\text{NH}_2$ is an exceptional case: B and B' cover two possibilities, only B lies on xy so that we can deduce that in this case the ortho and meta protons have the same sign, otherwise a_0 would not vary smoothly with a_m or even be related to it in a non-arbitrary manner. Another way of looking at this particular problem is to take the difference of a_0 and a_m , which is virtually constant, as pointed out by Stone and Waters. In view of this constancy



P-substituted phenoxy

- a_o, a_m The same sign
- a_o, a_m The opposite sign

GRAPH I

in a large number of cases, one can expect that the relationship should hold in the other examples too, i.e. in the case of semiquinone in which the two coupling constants must be identical. Hence a_m must in general have the opposite sign to a_o . This addition or arithmetic approach is only valid because the curves shown in graph (I) happen to be straight lines. The variations in coupling constants in other cases need not be so simple (i.e. linear) so that such addition rules are simply not forthcoming.

Ortho-substituted phenoxy radicals

As it has been explained before there is no problem in placing the largest coupling constant to the para position, and the second largest to the ortho position.

Following on from this we now look at more exact assignments in the ortho-substituted phenoxy radicals. There are now two non-equivalent meta protons to be considered, and the two small coupling constants usually must be ascribed to these positions. However the situation is more complicated than the case for para-substituted radicals. When $X \equiv O^-$ (o-semiquinone) the protons on the 3 and 6 positions have smaller coupling constants than the other two. We know this from work on substituted catechols. (See substituted catechols - Table 14). There is also a much greater number of possibilities to consider due to lack of symmetry, making all four positions inequivalent in most cases.

To make a start we take two examples which we can regard as known.

- (a) Phenoxy itself, whose coupling constants, relative signs and magnitudes have been determined above.
- (b) Catechol^{derived} radical, for which we can say $a_4 = a_5 = 3.75$ and $a_3 = a_6 = 0.75$. This last coupling constant is small and therefore could correspond to either positive or negative spin density, so there is some ambiguity here to be resolved.

With substituents such as Me, F, CO₂H we can be reasonably sure that the pattern is not very different from that in phenoxy and so the second largest doublet splitting can be assumed to be due to the ortho proton. The main problem in assignment is to distinguish between the two meta positions. When X = OMe, NH₂ one also should distinguish between ortho and meta positions too, because the ortho changes from 6.6 to 0.75, whereas the meta goes with increasing electron donating power of X from -1.8 to +3.75. When the assignments are correct then the points for a given combination of coupling constants should lie on a smooth curve.

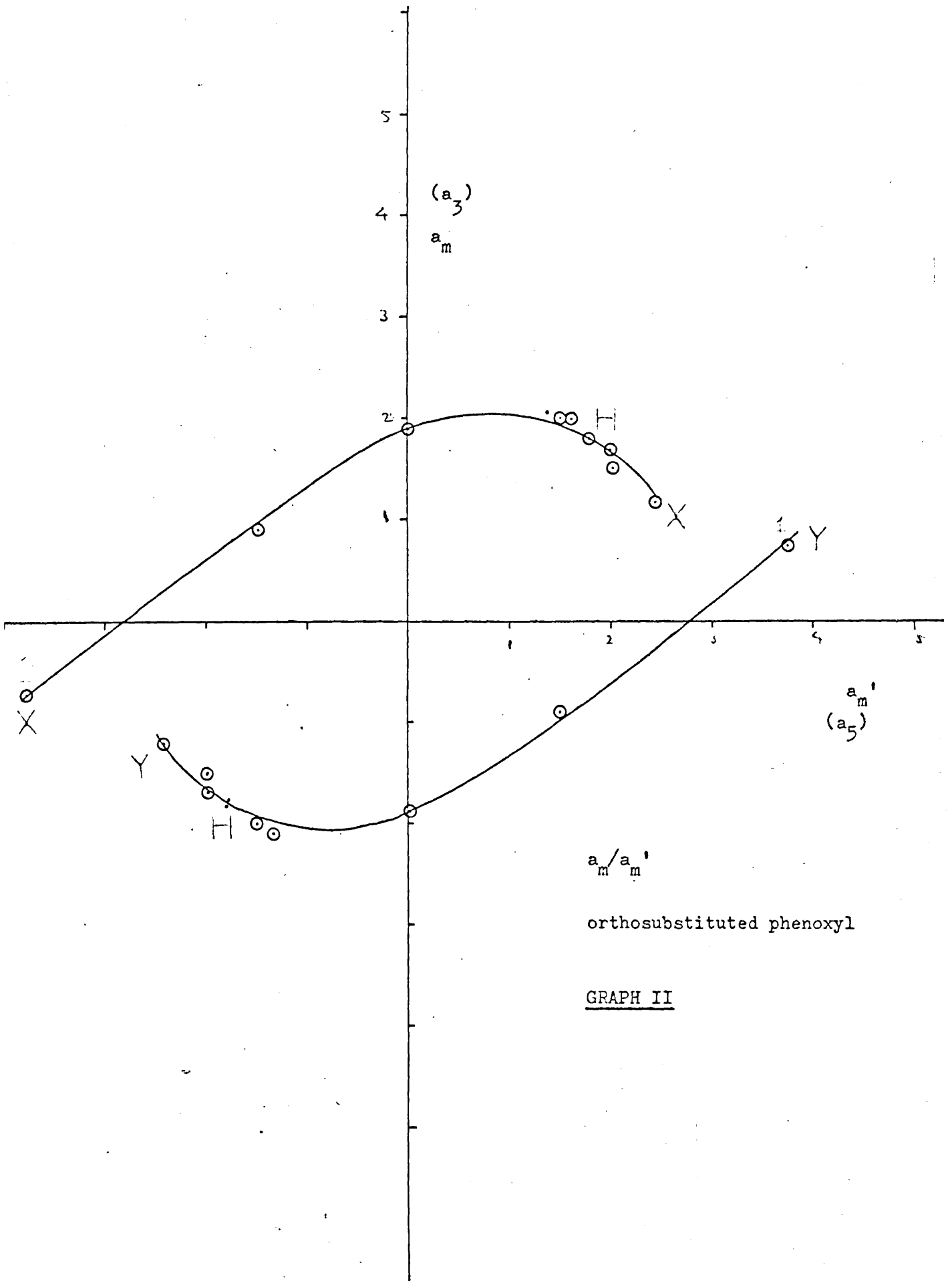
To separate the meta splittings i.e. assigning them either to a_3 or a_5 we look at graph (II) which is a plot of a_m against a_o . Two curves xx and yy are obtained point (1) (0.75, 3.75) corresponding to catechol is fixed. Other possibilities are point (2) (-0.75, -3.75) and (-0.75, +3.75) these are not on the curve yy so this is strong evidence supporting our assumption that a_m normally has the opposite sign to a_o and the corresponding splitting in o-semiquinone. We deduce further that the meta coupling constants in o-amino phenoxy are -0.9, and

1.5 as in Table 2.

Graph (III) contains plots of a_6 against a_5 and a_6 against a_3 , shown by curves yy and xx respectively. These two curves also enable us to distinguish between the two meta coupling constants.

Curve xkx will bring one set of meta coupling constants together, while yy brings together the other meta couplings, because, of all the other possibilities which have been plotted, these are the only ones which give a smooth and regular pattern to changes in the coupling constants for the different substituents. Point H (0.75, 0.75) represents catechol, which presumes positive spin densities for the two hydrogens 3 and 6. Point H' (0.75, -0.75) is not valid due to symmetry, another possibility remaining is point H'' (-0.75, -0.75), by drawing graph (III) it can be seen that this point is not on the same curve which represents a smooth change with certain amount of regularity. Point A (0.75, 3.75) lies on the curve yy. Another possibility is point A' (0.75, -3.75) which is not a valid point, because then the total negative spin density will be too large. Point B₂ (2.6, 1.5) and B₁ (2.6, -0.9) representing NH₂ group are the final assignment of coupling constants while B' and B'' are the other possibilities which are not acceptable. All the other points from a_6 against a_5 lies on yy. Two conclusions arise from this graph

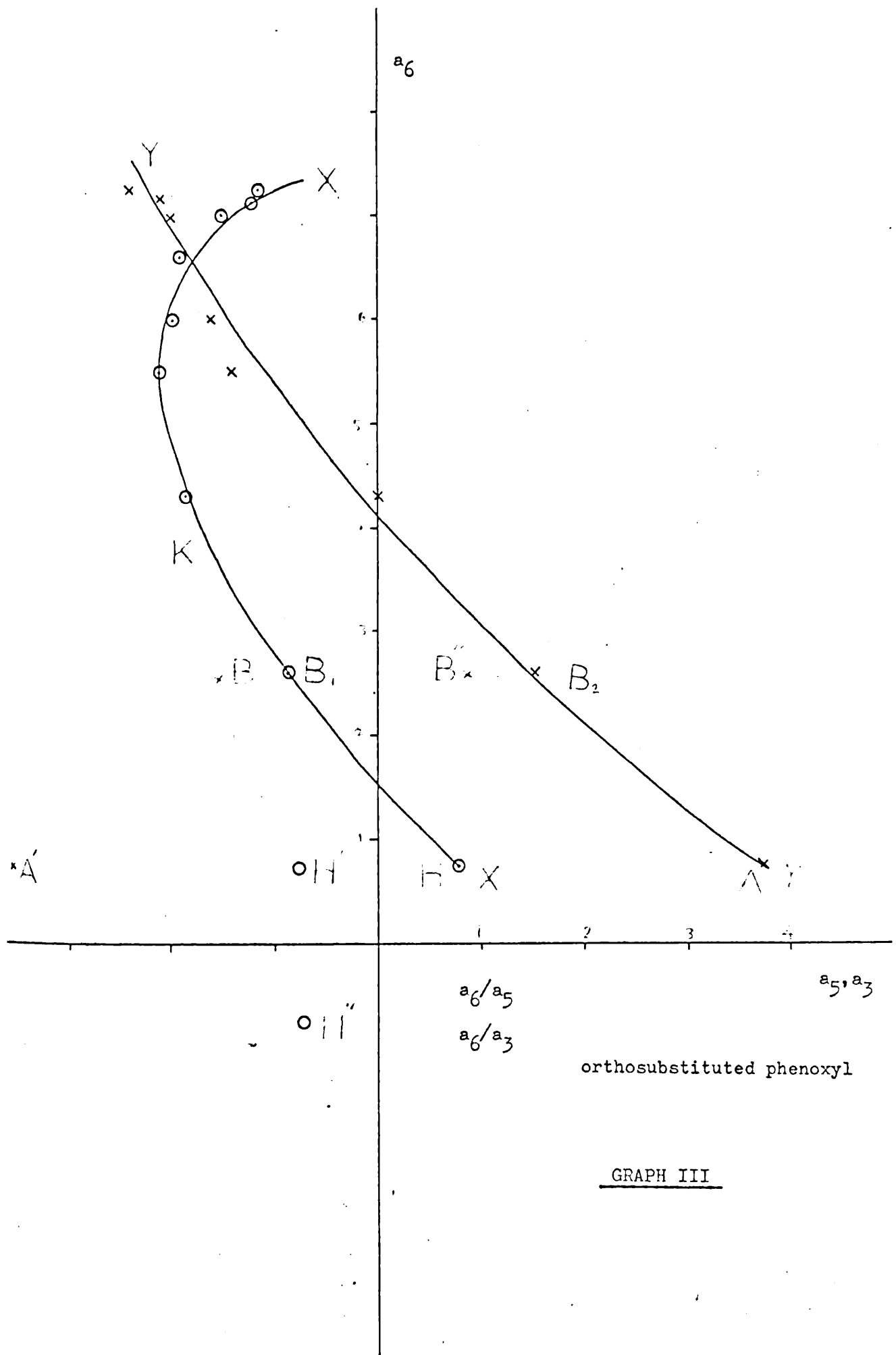
- (i) a_6 and a_5 in catechol are of the same signs and a_6 and a_5 in o-amino phenoxy also are of the same sign.



a_m / a_m'

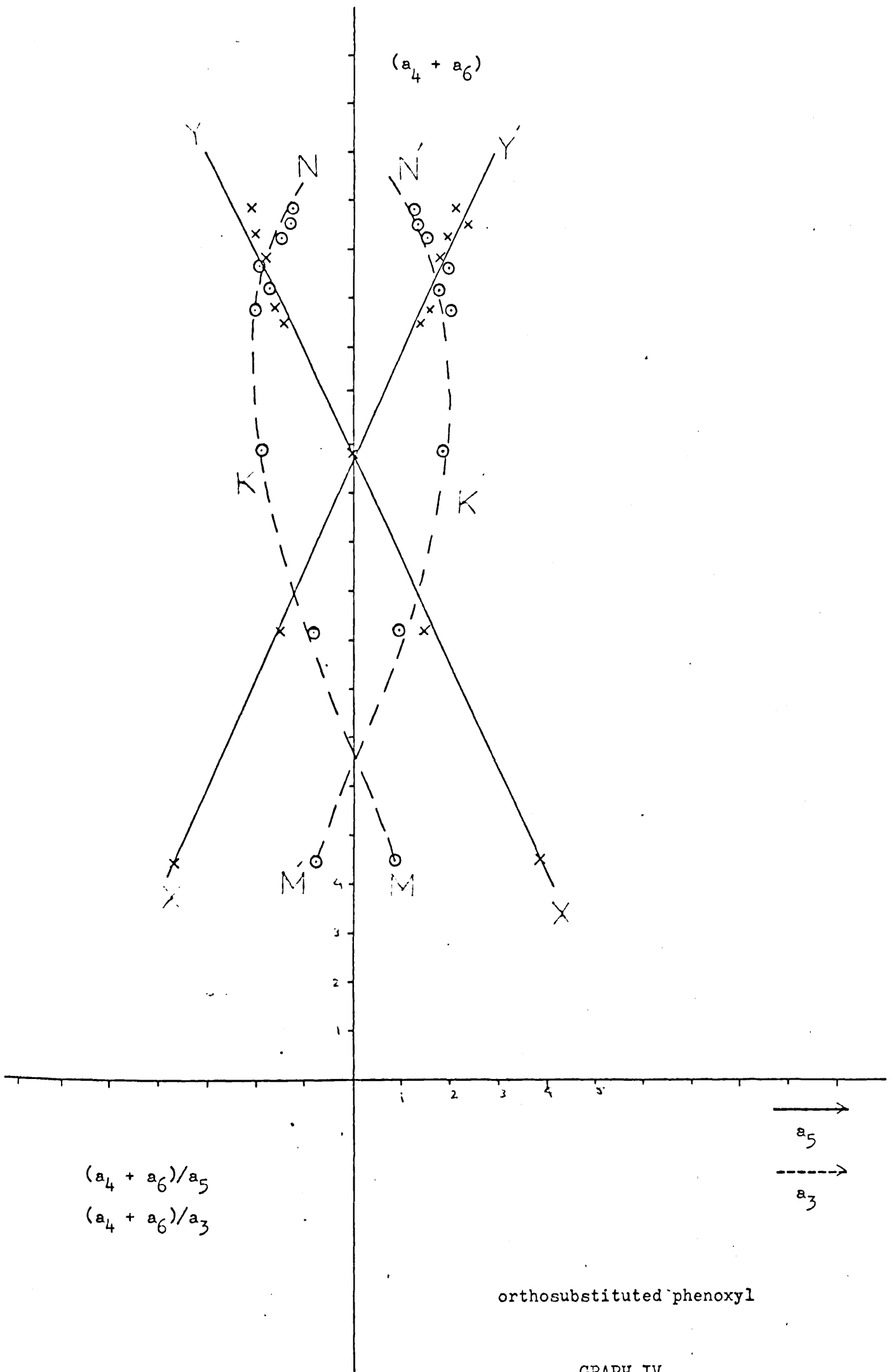
orthosubstituted phenoxyl

GRAPH II



orthosubstituted phenoxyl

GRAPH III



GRAPH IV

(ii) For all the other substituents a_5 and a_6 are of the opposite sign.

Point B_1 (2.6, -0.9) proves opposite signs for a_6 and a_3 in order to stay in line with all the other points of the series. Point A of this series is a fixed point as shown by graph (III).

For graph ($a_4 + a_6$) against a_5 and a_3 there are two sets of possibilities, first when a_6 and a_4 are of the same sign as a_5 and a_3 and second when they are of opposite sign, graph (IV) shows the two possible trends. Clearly in order to obtain curve MKN we have to assign all a_3 's negative and a_4 and a_6 positive except the point M for catechol, and also xy is obtained when all the a_5 's are negative except for catechol and o-amino phenoxy.

Curves M'K'N' and x'y' are the other possibility gives catechol negative a_5 and a_3 , not being valid with respect to the symmetry of the molecule. Therefore by fixing catechol this assignment is unambiguous.

Meta-substituted phenoxy radicals

Most of the substituents in this group of radicals do not make appreciable changes on the coupling constants at o-, m-, and p-positions, a_5 changes but little along the series so it follows from the assignment of phenoxy that a_5 must be negative for all the substituents i.e. negative spin

density at this position.

The coupling constant at p- position changes from 10.2 to either 9.8 or 11.4 while the ortho splitting changes from 6.6 to 11.2 or ± 0.7 . This suggests strongly that these coupling constants are all of the same sign. Positions 2 and 5 can be distinguished by a suitable substitution in resorcinol eg.

Radicals from:

$$\text{2-Nitroresorcinol} \quad a_{\text{NO}_2} = 0.5 \quad a_4 = a_6 = 10.75 \quad a_5 = 2.5$$

$$\text{2-COOHresorcinol} \quad a_4 = a_6 = 11.25 \quad \text{and} \quad a_5 = 2.5$$

$$\text{5-COOHresorcinol} \quad a_2 = 4.0 \quad a_4 = a_6 = 10.0$$

For groups such as OMe and NH_2 there is more or less no ambiguity in assigning the two ortho coupling constants, because they are both sufficiently different from those in phenoxyl.

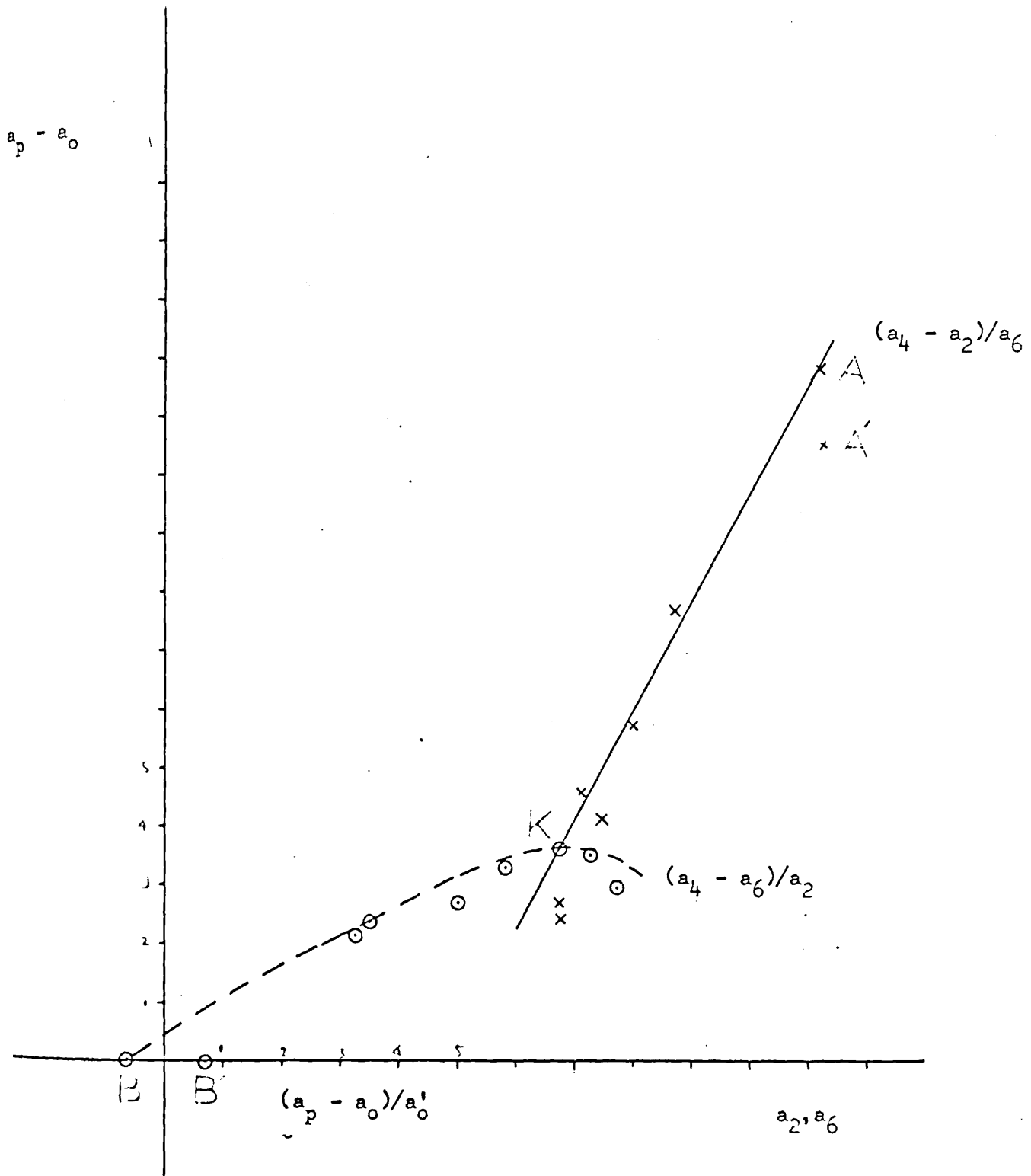
However in other cases it is not easy to make a definite assignment so we again resort to a graphical method. Graph (V) is the plot of $a_p - a_0$ against a_0 , for clarity we use the final assignments.

As expected the radical from resorcinol can be treated as a meta-substituted phenoxyl radical and the smallest coupling constant appears to be due to negative spin density on the position 2. Points A' and B' are the other possibilities when a_2 is assigned to have the positive coupling constant in resorcinol. In fact the parameters of the resorcinol give one fixed point on the graph. Point K, a point on both curves, is that for phenoxyl so that is also a fixed point. From this

graph we confirm that a_6 is always positive and a_2 is positive also for every substituent, except for the case where $X = O^-$.

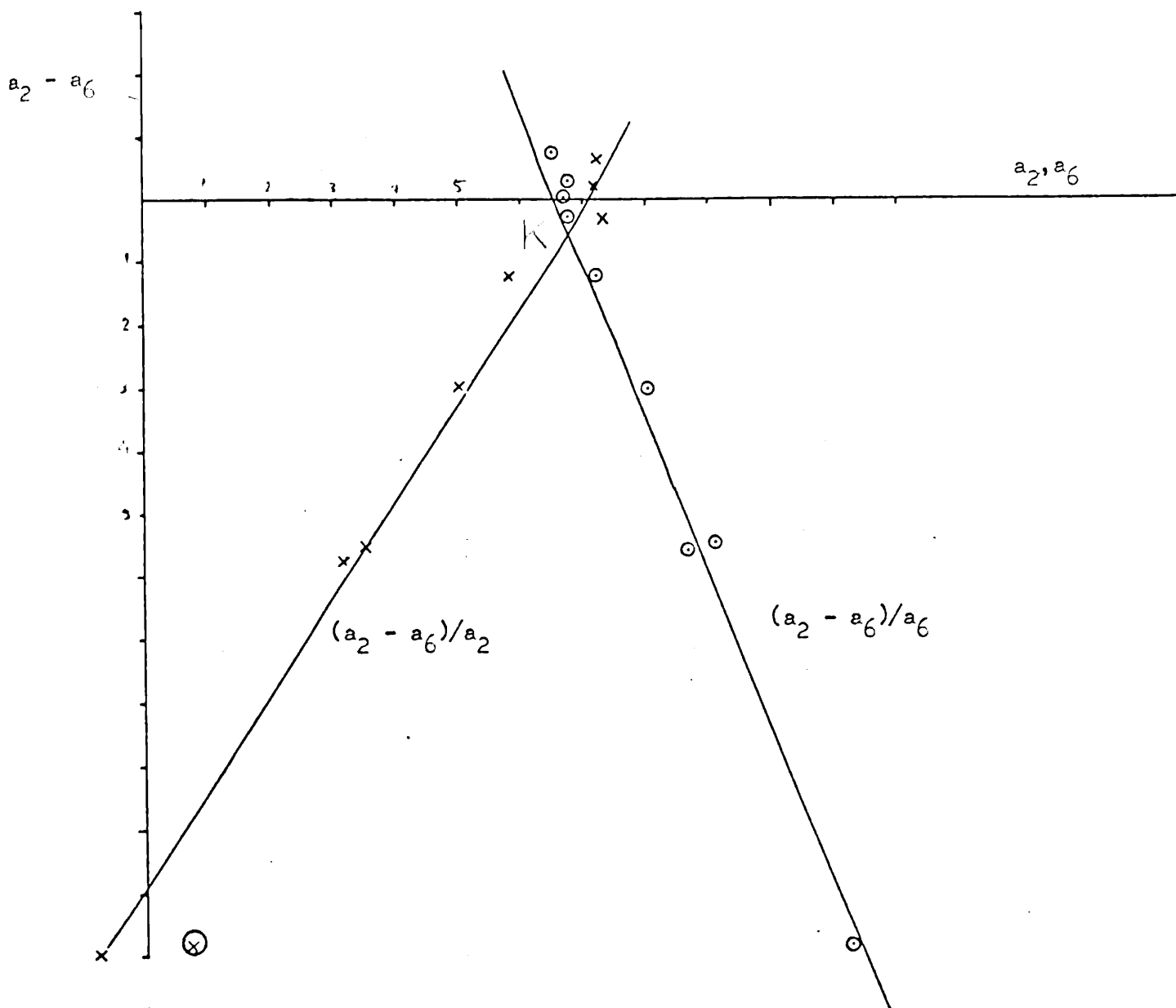
Graph (VI) is $a_0 - a'_0$ against a_0 or a'_0 i.e. $a_2 - a_6$ against a_2 or $a_2 - a_6$ against a_6 . This graph is to confirm the above assignment. The two curves pass through point K of phenoxyl. The small splitting for resorcinol again appears to be due to negative spin density.

Graph (VII) is the plot of a_6 against a_5 . In this graph we have two fixed points, phenoxyl and resorcinol. We have obtained negative spin densities for meta positions in phenoxyl and also at positions 2 and 5 of resorcinol we have negative spin densities. Graph (VII) also shows that a_5 for all the substituents must be negative in order to keep the points on the same smooth curve.



meta-substituted phenoxyl

GRAPH V



meta-substituted phenoxy

GRAPH VI

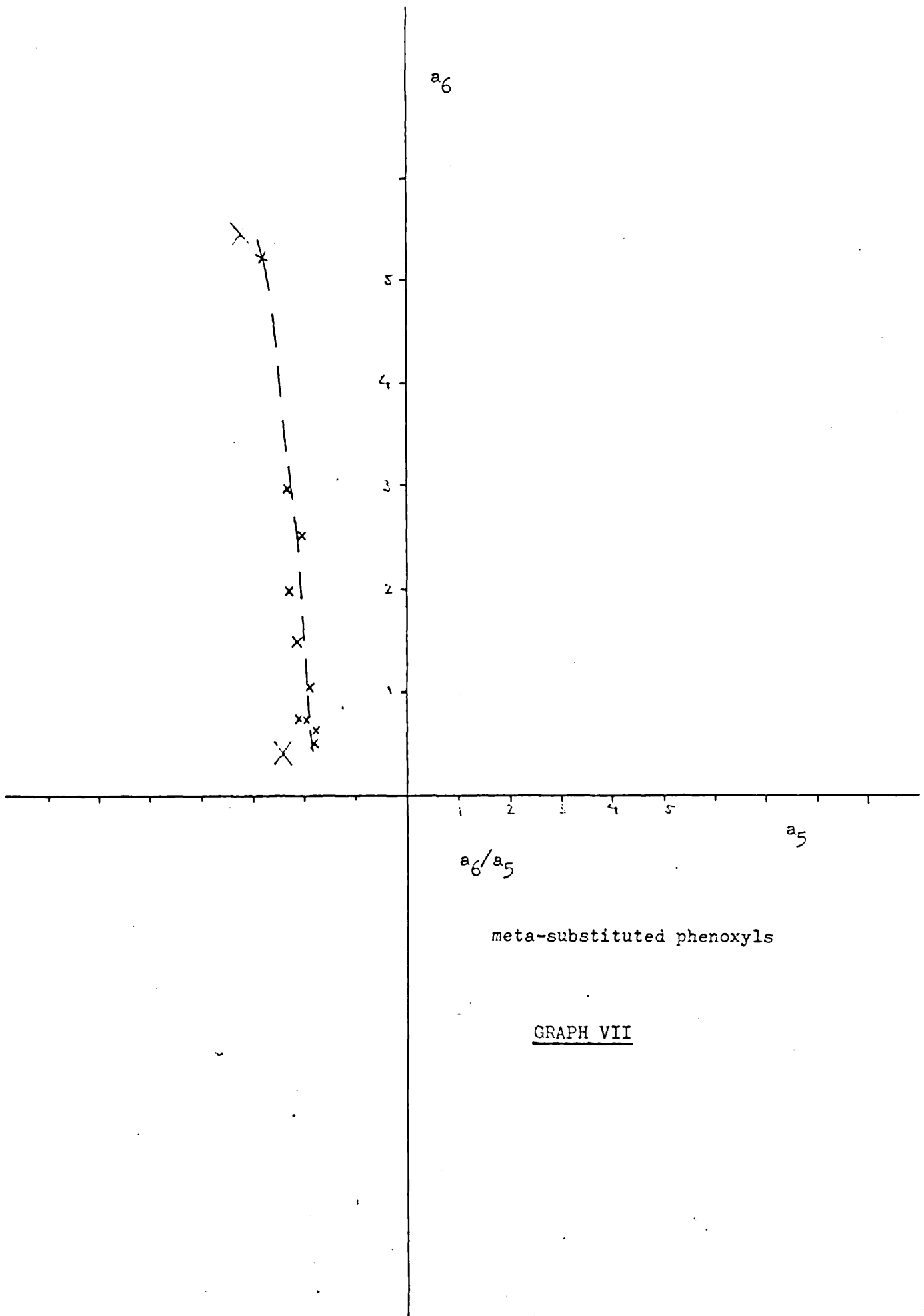


Table 1
Coupling Constants (in -10^{-4} T) of Protons in para-substituted
Phenoxy Radicals

Substituents	a_2	a_3	a_4	a_5	a_6
NO_2	7.0	-2.4	$a_{\text{N}} = 2.4$	-2.4	7.0
COOH	6.75	-2.2	-	-2.2	6.75
CHO	6.8	-2.2	$a_{\text{H}} = 0.3$	-2.2	6.8
COCH_3	6.75	-2.1	-	-2.1	6.75
H	6.6	-1.8	10.2	-1.8	6.6
CH_3	6.1	-1.4	$a_{\text{CH}_3} = 12.5$	-1.4	6.1
CHMe_2	6.0	-1.2	$a_{\text{CH}_3} = 0.4$	-1.2	6.0
			$a_{\text{H}} = 4.5$		
Cl	6.4	-1.9	$a_{\text{Cl}} = 1.9$	-1.9	6.4
F	6.25	-1.45	$a_{\text{F}} = 27.5$	-1.45	6.25
OCH_3	4.9	0.0	$a_{\text{OMe}} = 2.1$	0.0	4.9
NH_2	4.0	0.5	$a_{\text{N}} = 6.6$	0.5	4.0
			$a_{\text{NH}} = 8.0$		
- O	2.37	2.37	-	2.37	2.37

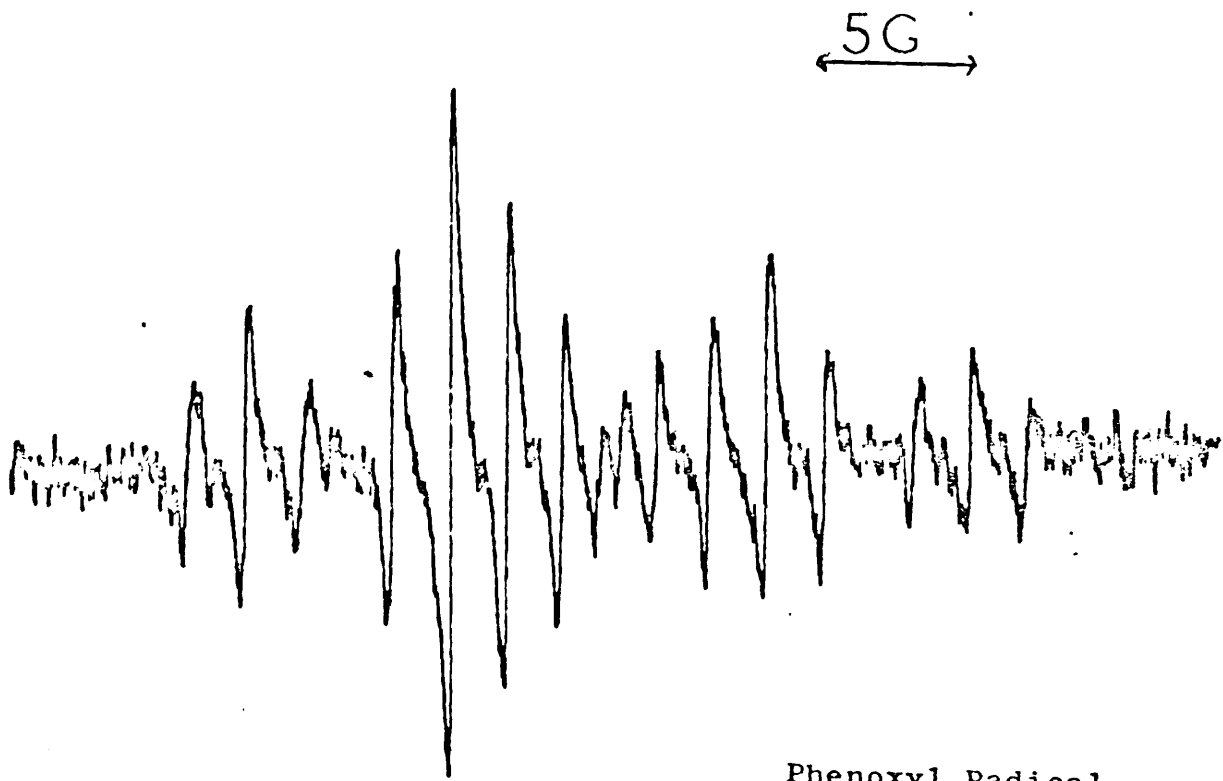
Table 2

Coupling Constants (-10^{-4} T) in ortho-substituted
Phenoxy Radicals

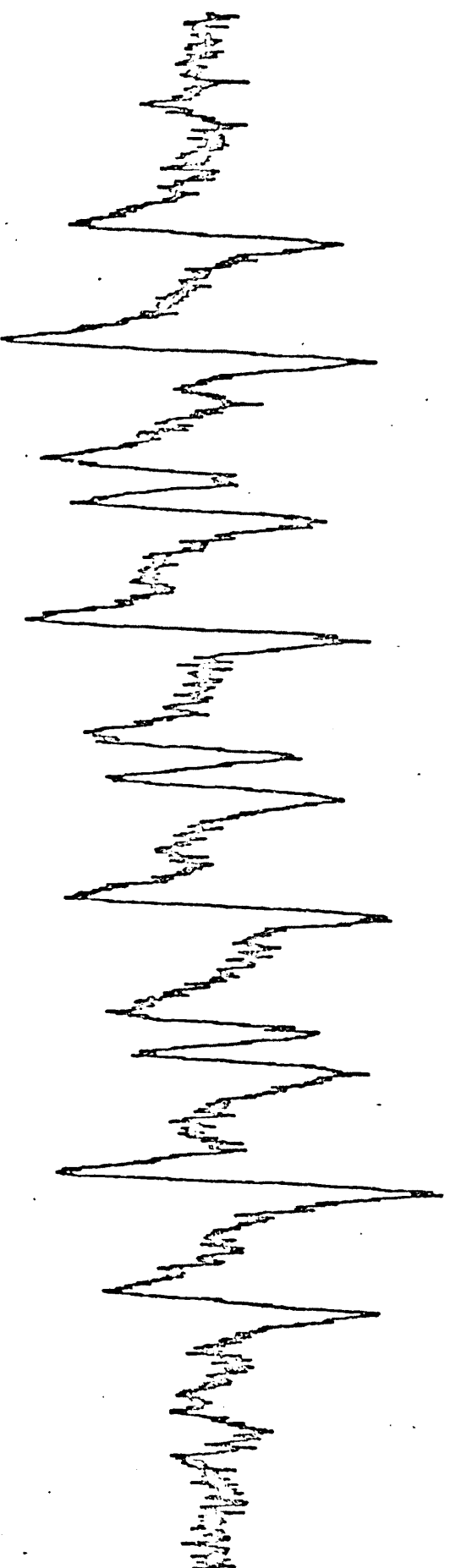
Substituents	a_2	a_3	a_4	a_5	a_6
NO ₂	$a_N = 2.1$	-1.2	10.25	-2.4	7.25
COOH	Δ	-1.25	10.7	-2.1	7.15
CHO	-	-1.7	10.0	-2.0	7.1
COCH ₃	-	-1.5	10.25	-2.0	7.0
H	6.6	-1.8	10.2	-1.8	6.6
CH ₃	$a_{CH_3} = 7.5$	-2.0	9.7	-1.5	6.0
CHMe ₂	$a_{CH} = 4.0$	-2.0	9.6	-1.5	6.0
Cl	$a_{Cl} = 1.05$	-2.0	9.8	-1.6	6.0
F	$a_F = 16.8$	-2.1	10.0	-1.4	5.5
OCH ₃	$a_{OCH_3} = 1.8$	-1.9	8.5	0.0	4.3
NH ₂	$a_N = 6.62$ $a_{NH} = 8.13$	-0.9	6.62	1.5	2.6
\bar{O}	-	0.75	3.75	3.75	0.75

Table 3
Coupling Constants (in -10^{-4} T) in meta-substituted
Phenoxy Radicals

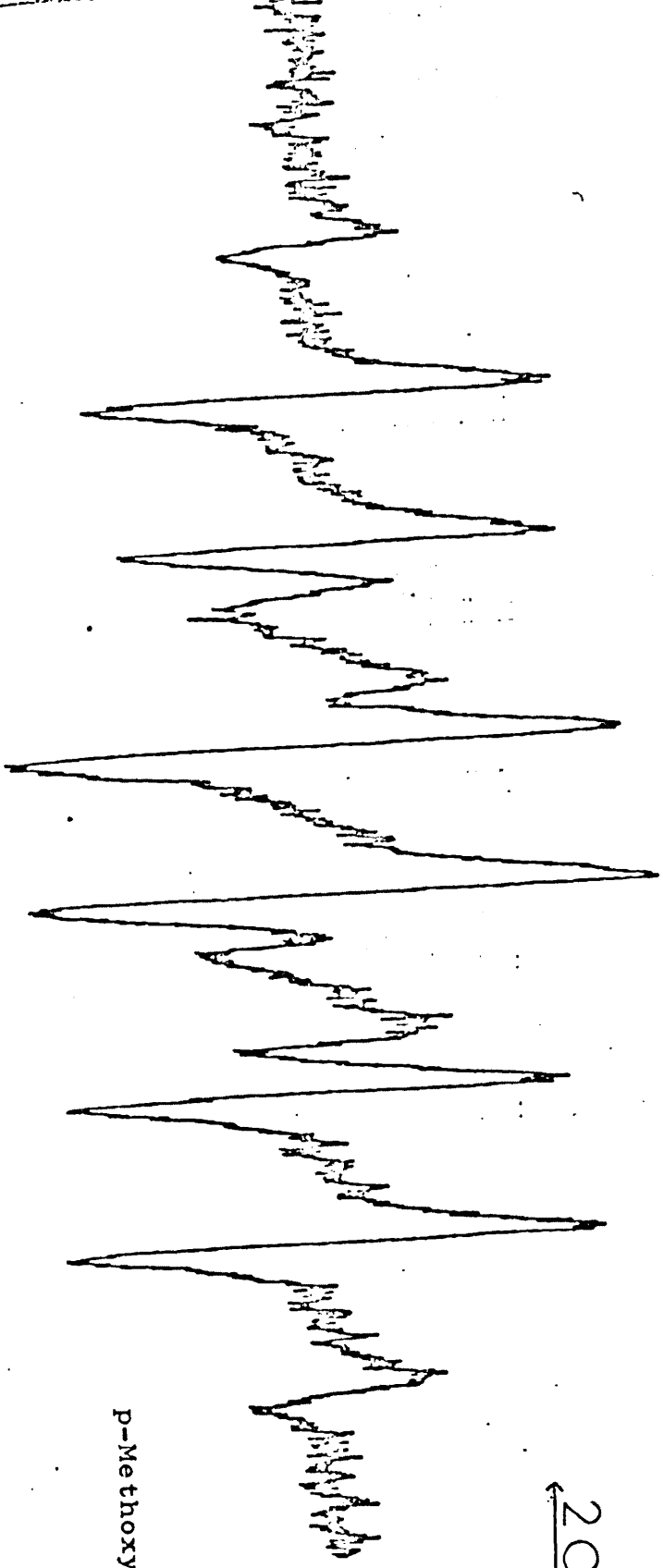
Substituents	a_2	a_3	a_4	a_5	a_6
NO ₂	7.35	$a_H = 0.4$	9.8	-2.1	6.75
COOH	7.25	-	9.9	-1.9	6.5
CHO	7.1	-	9.8	-2.0	6.75
COCH ₃	7.1	-	9.9	-1.9	6.5
H	6.6	-1.8	10.2	-1.8	6.6
CH ₃	5.9	$a_{CH_3} = 1.5$	10.5	-1.9	7.1
CHMe ₂	5.9	$a_H = 0.8$	10.3	-1.9	7.0
Cl	6.2	$a_{Cl} = .25$	10.5	-2.1	7.5
F	5	$a_F = 5.8$	10.75	-2.25	8
OCH ₃	3.5	$a_{OCH_3} = 0.6$	11.4	-2.5	9.0
NH ₂	3.1	$a_N = 6.9$	10.9	-2.0	8.6
		$a_{NH} = 8.1$	10.9	-2.0	8.6
\bar{O}	-0.7	-	11.2	-2.8	11.2



Phenoxy Radical



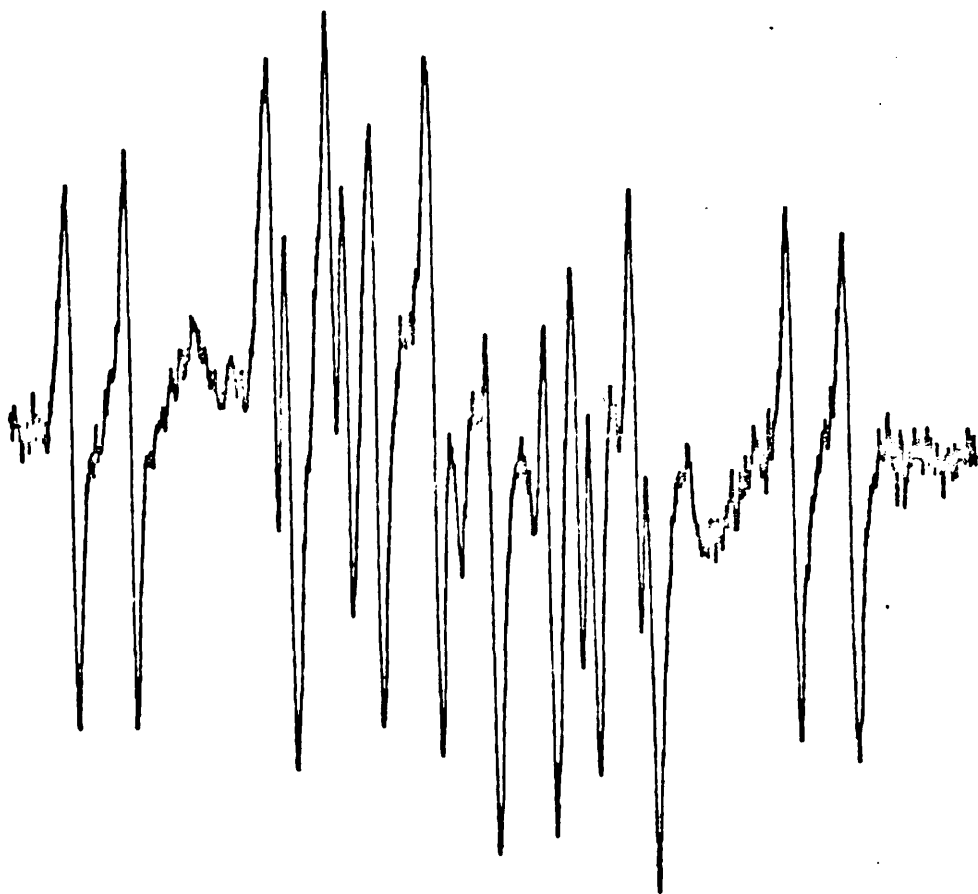
o-Methoxyphenoxyl Radical



p-Methoxyphenoxyl Radical

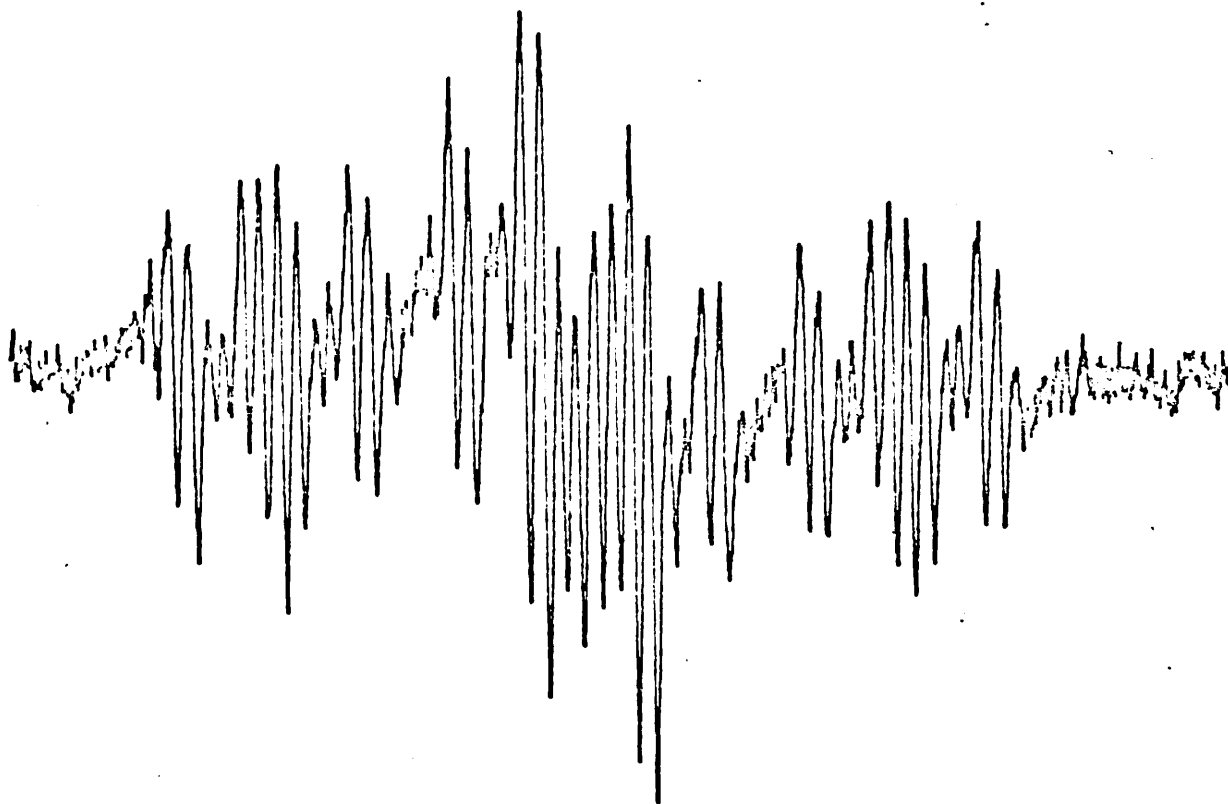
← 2G →

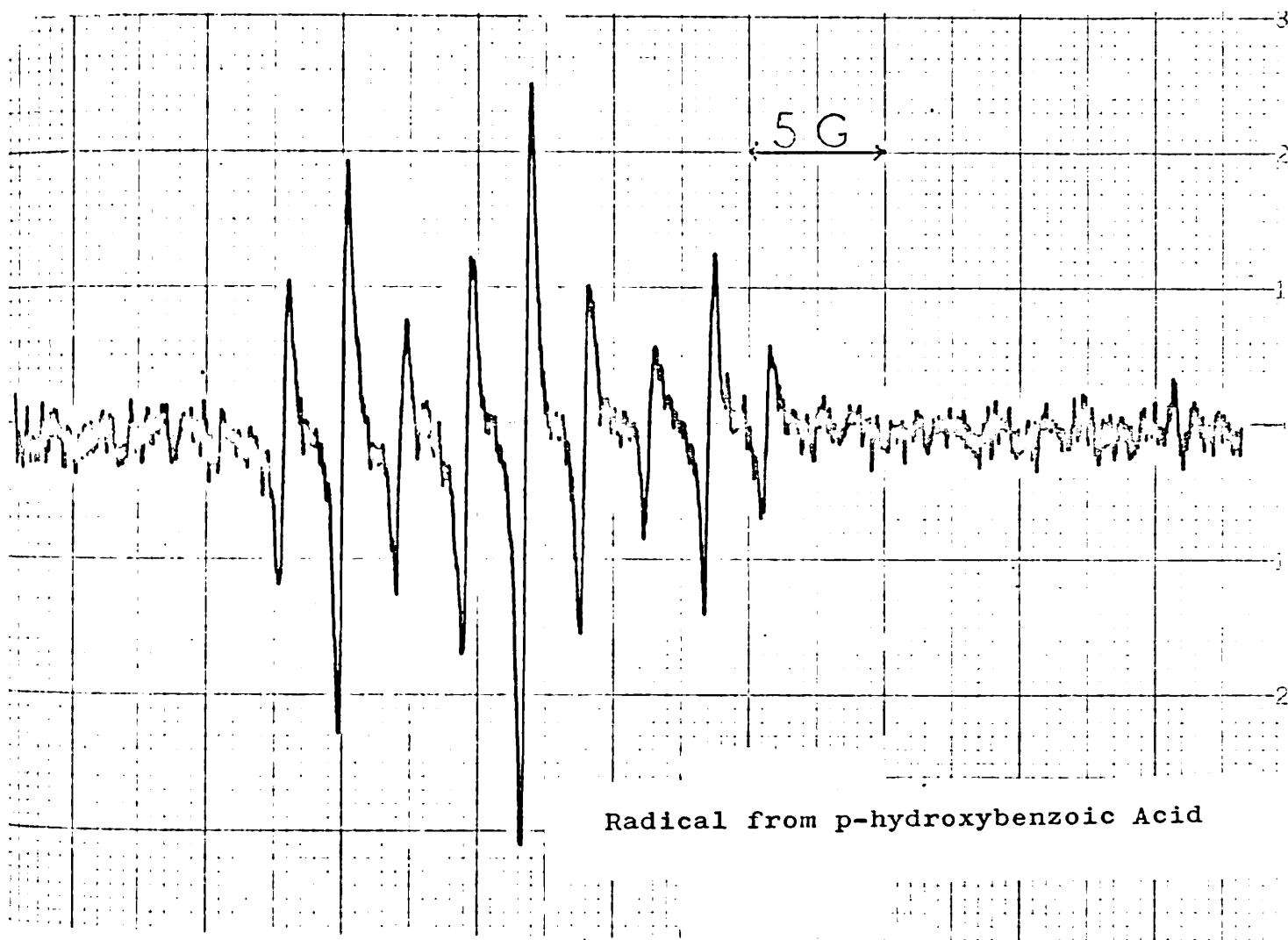
Radical from *m*-Hydroxyacetophenone



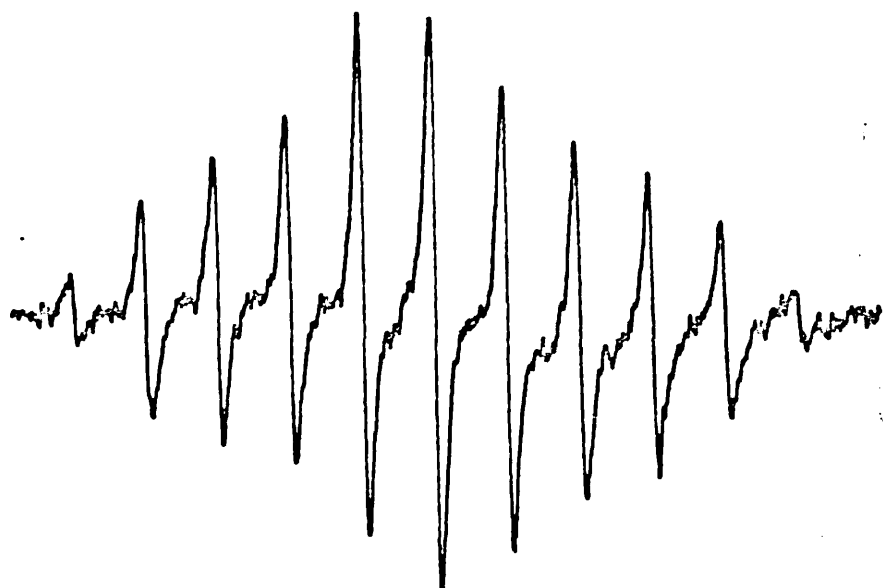
m-Methoxyphenoxy Radical

5G

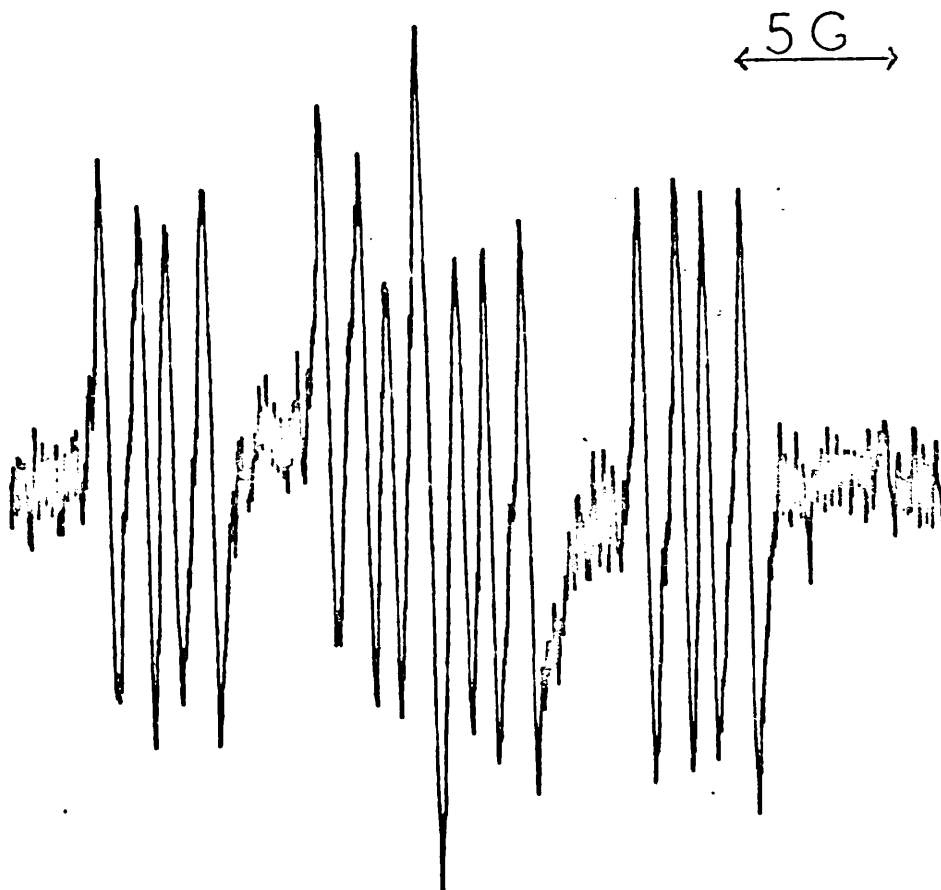




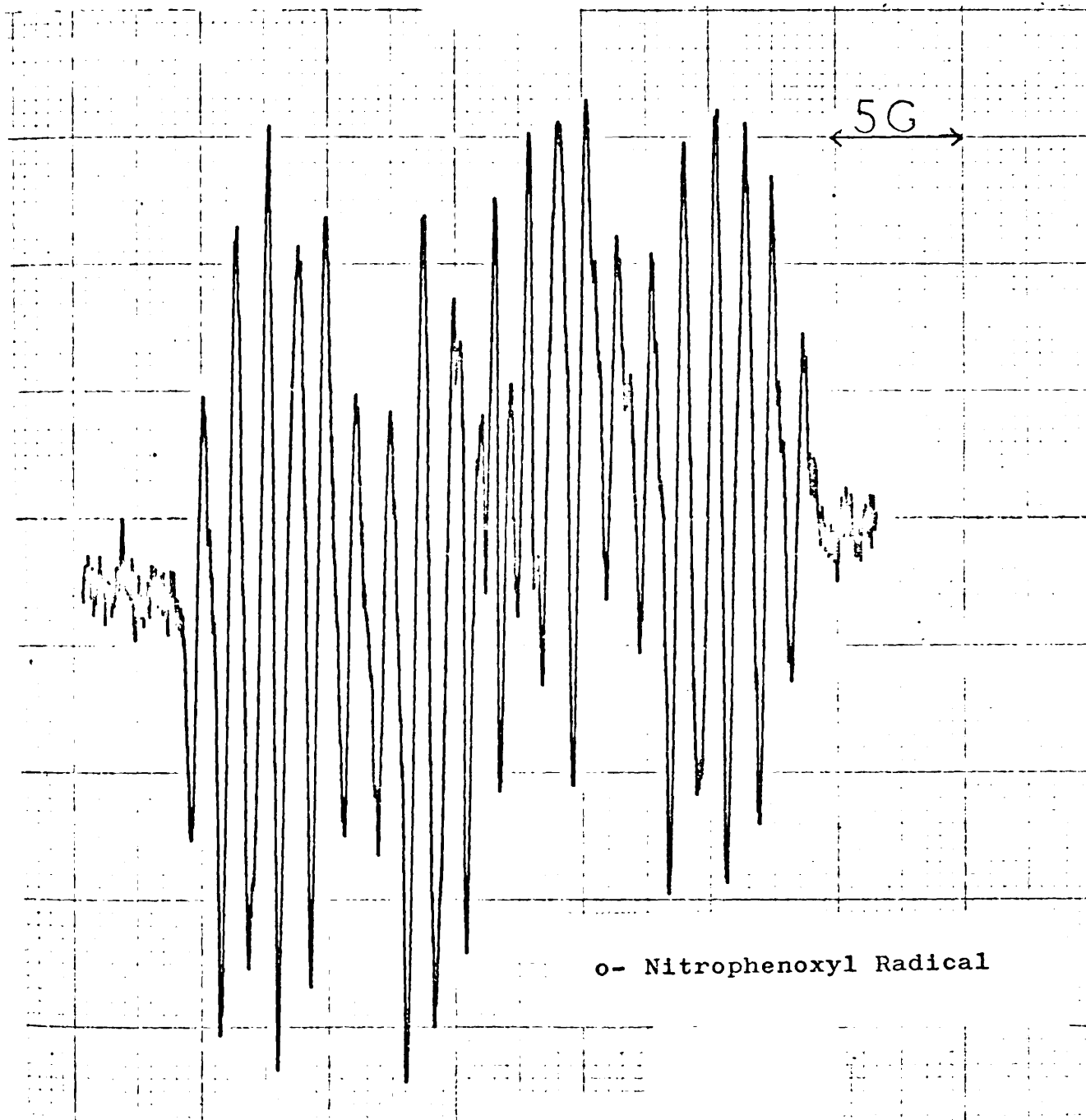
Radical from p-hydroxybenzoic Acid



p-Nitrophenoxyl Radical

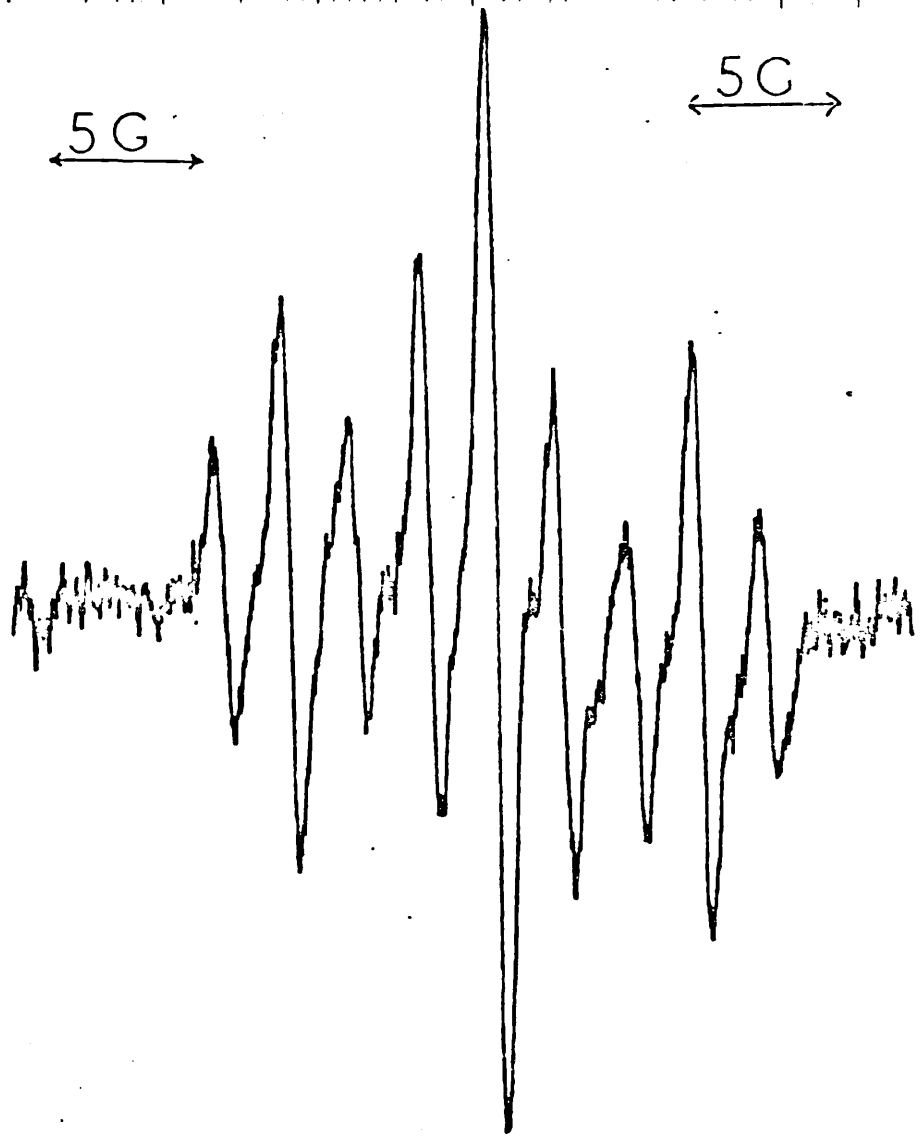


Radical from o-Hydroxybenzoic Acid

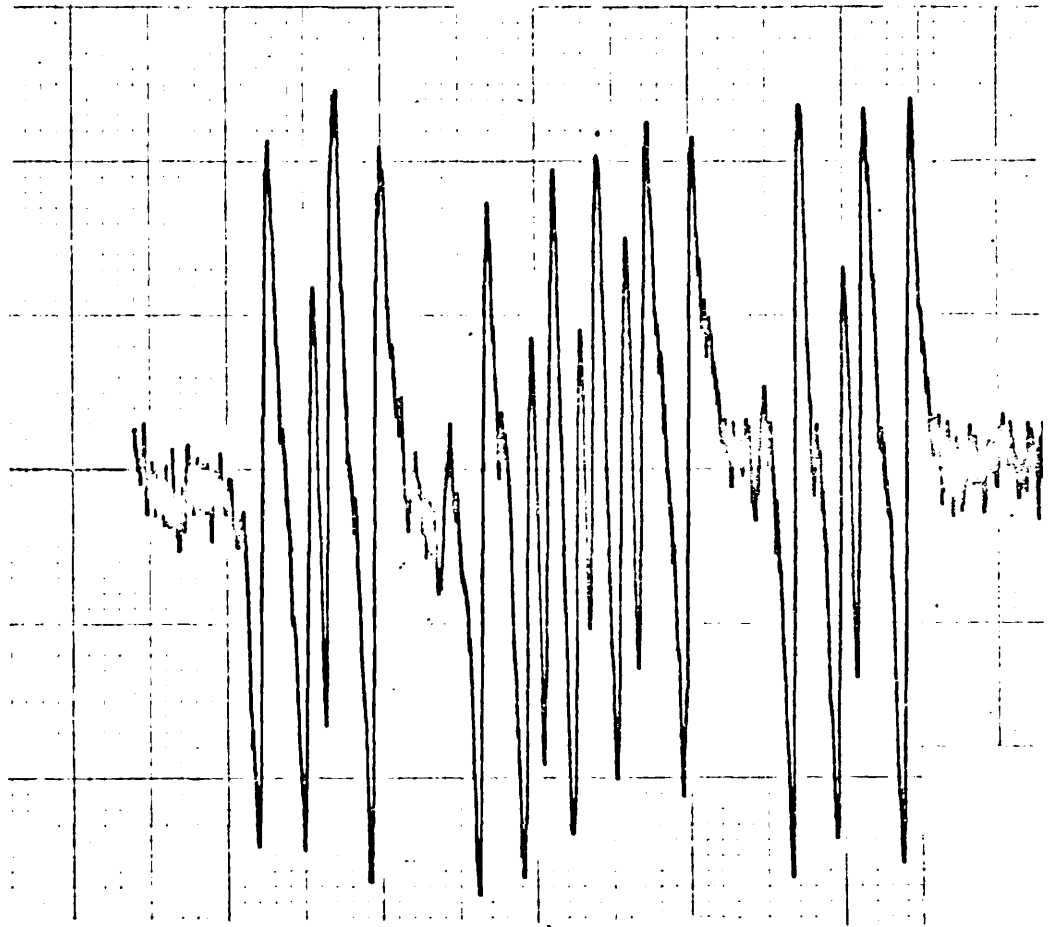


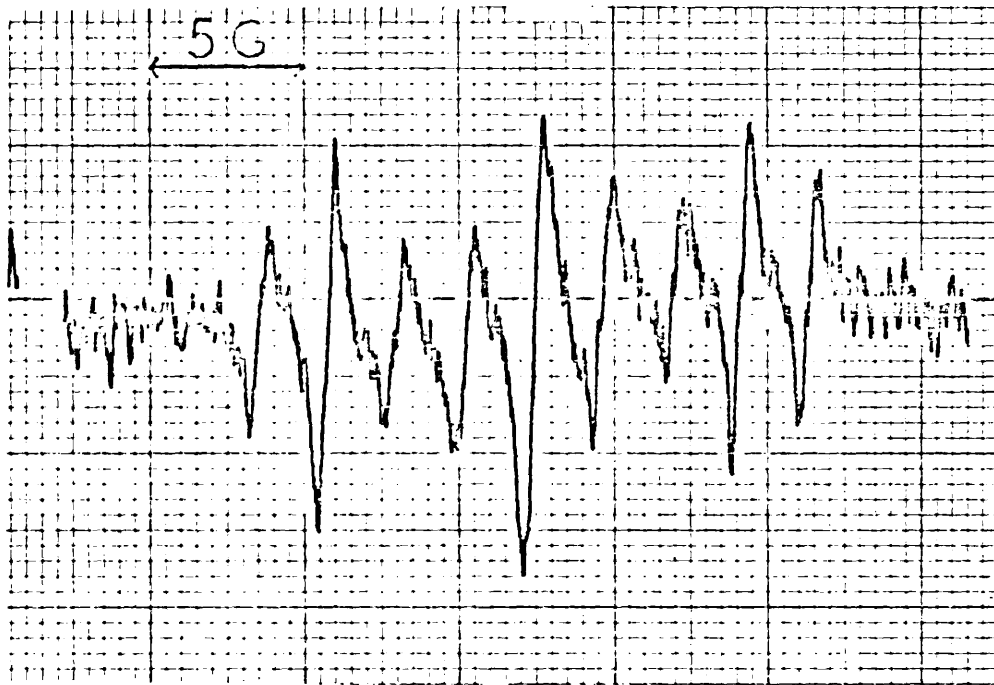
o- Nitrophenoxyl Radical

Radical from p-Hydroxyacetophenone

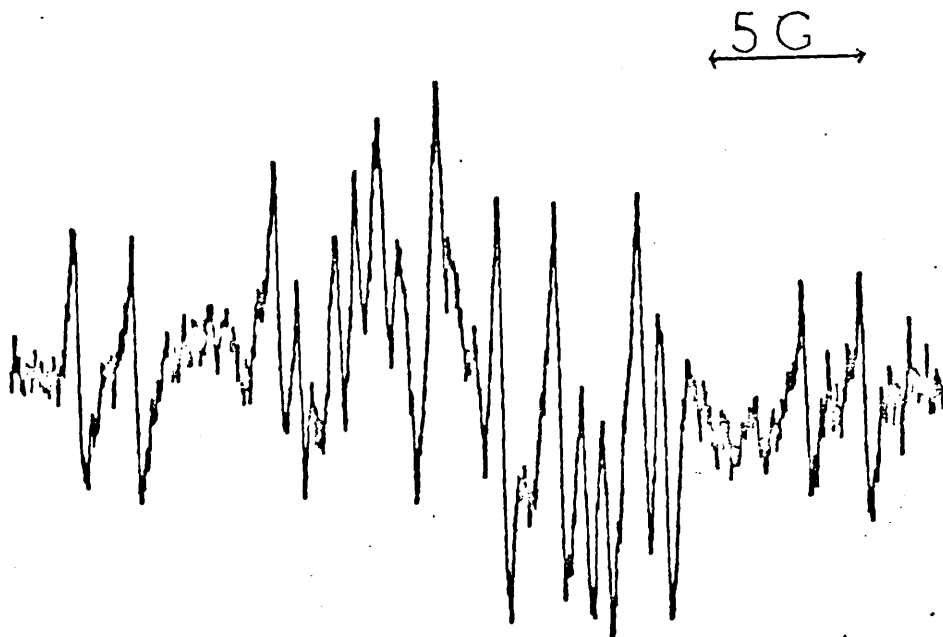


Radical from o-Hydroxyacetophenone

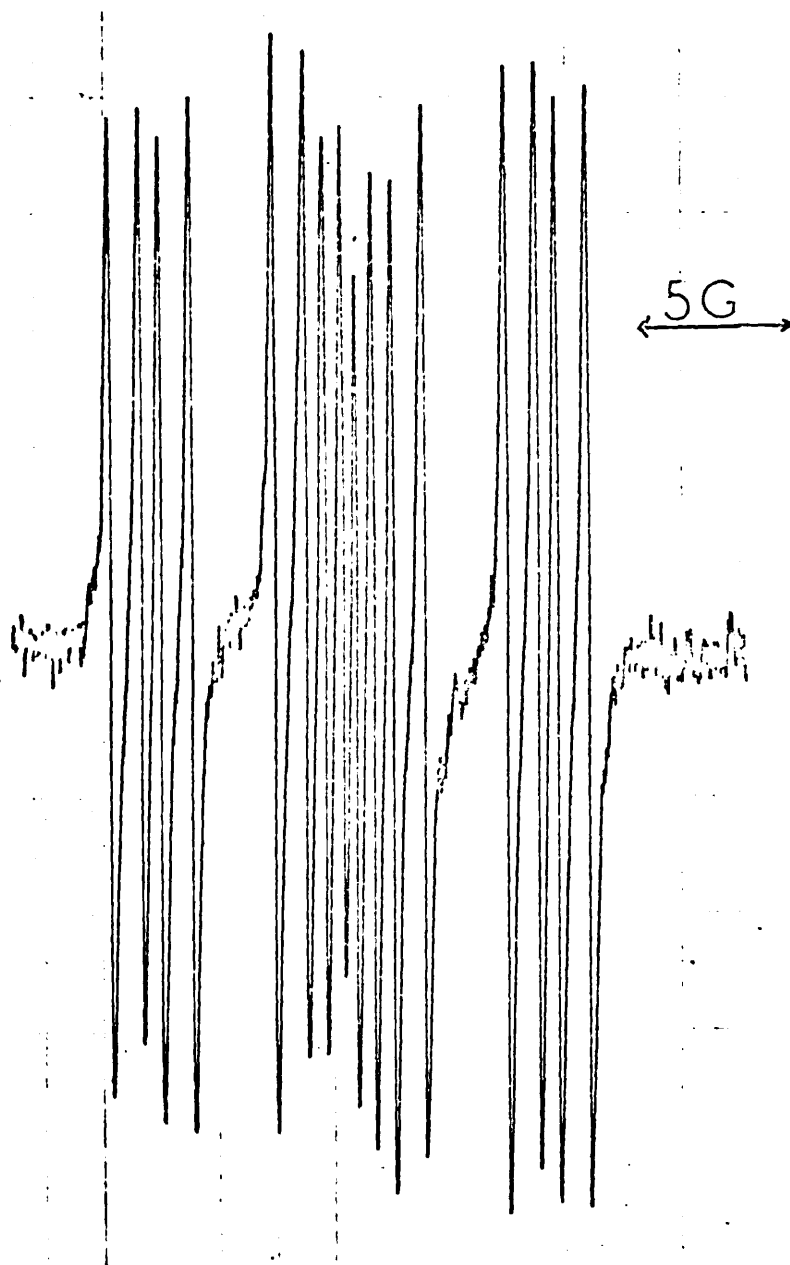




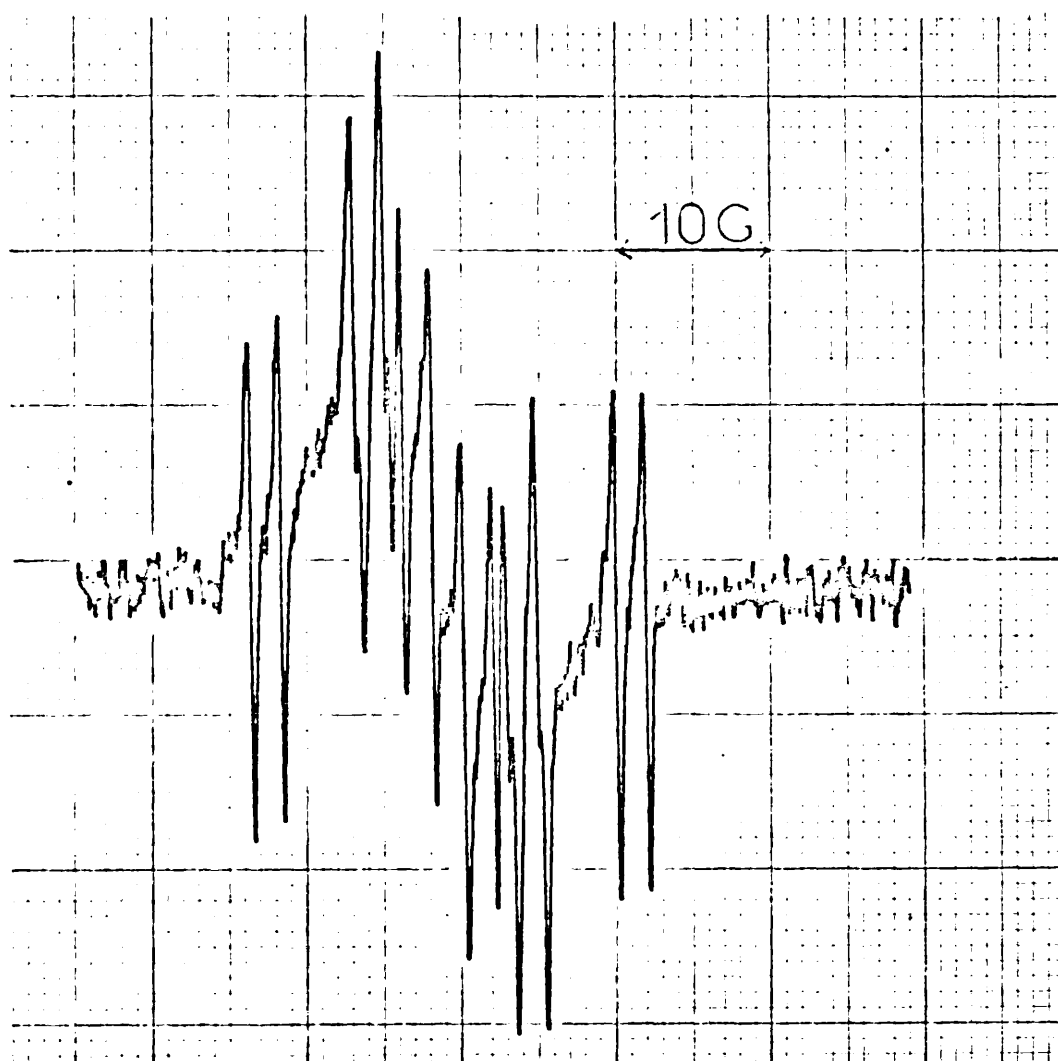
Radical from p-Hydroxybenzaldehyde



Radical from m-Hydroxybenzoic Acid

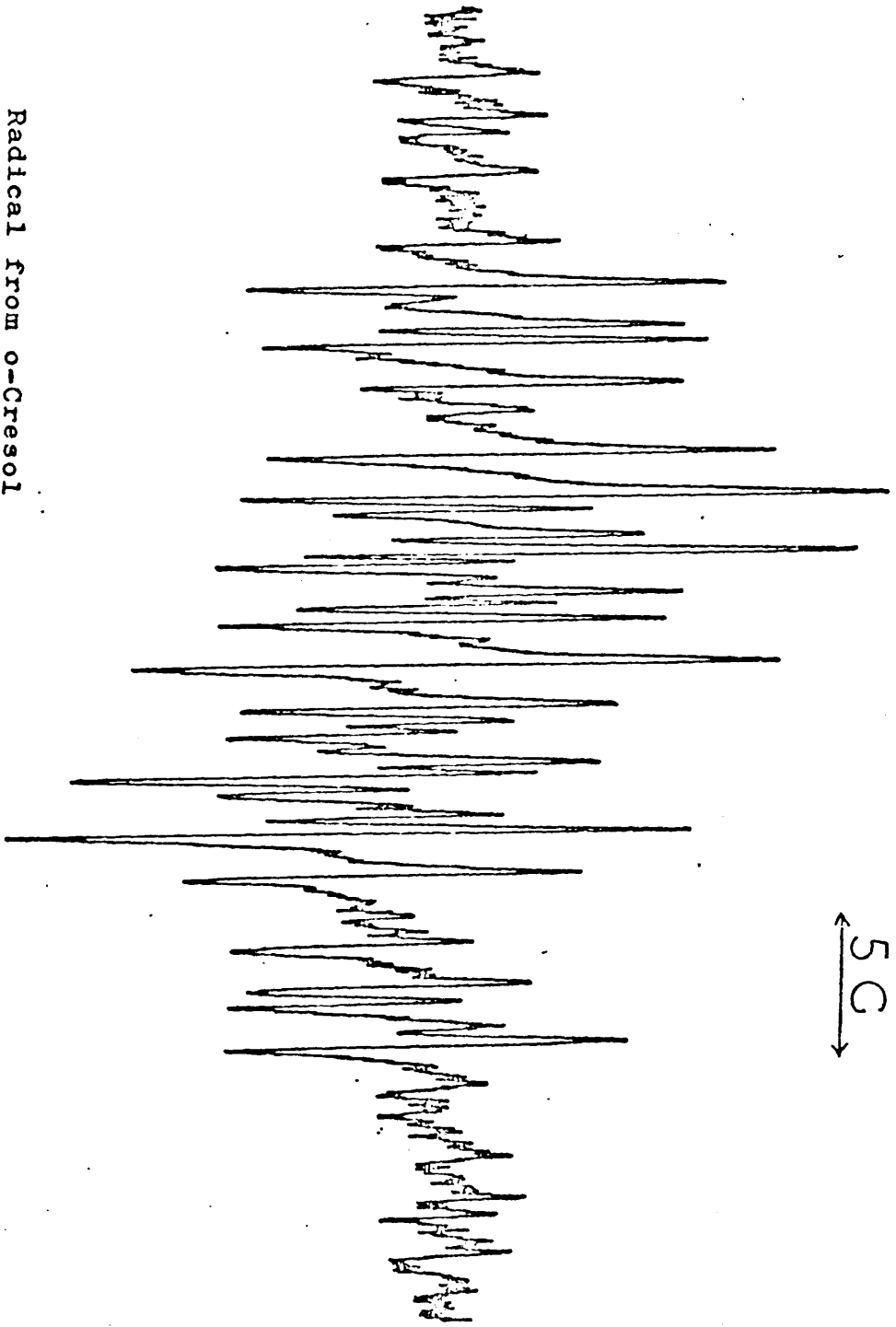


Radical from o-Hydroxybenzaldehyde



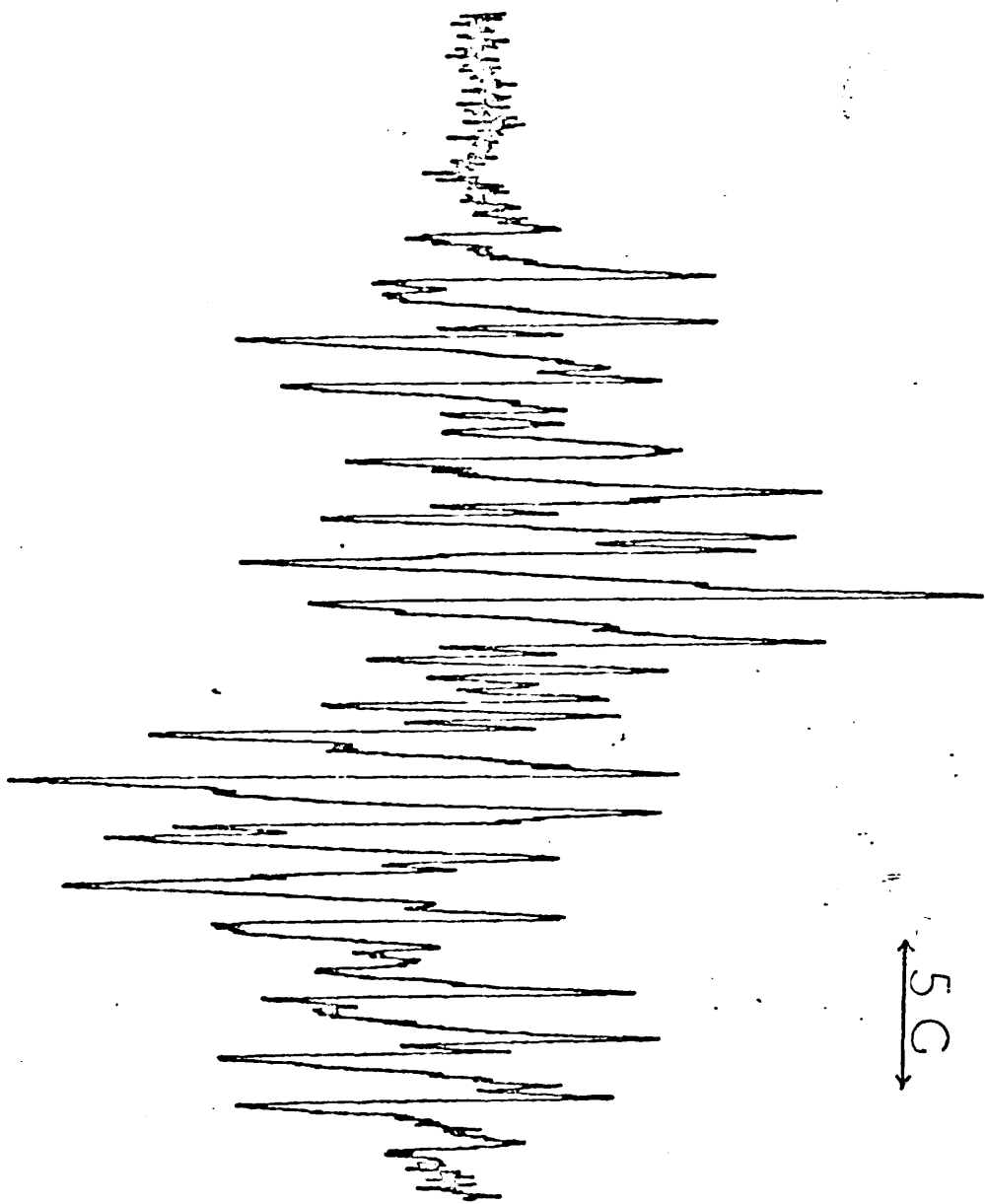
Radical from m-Hydroxybenzaldehyde

Radical from o-Cresol

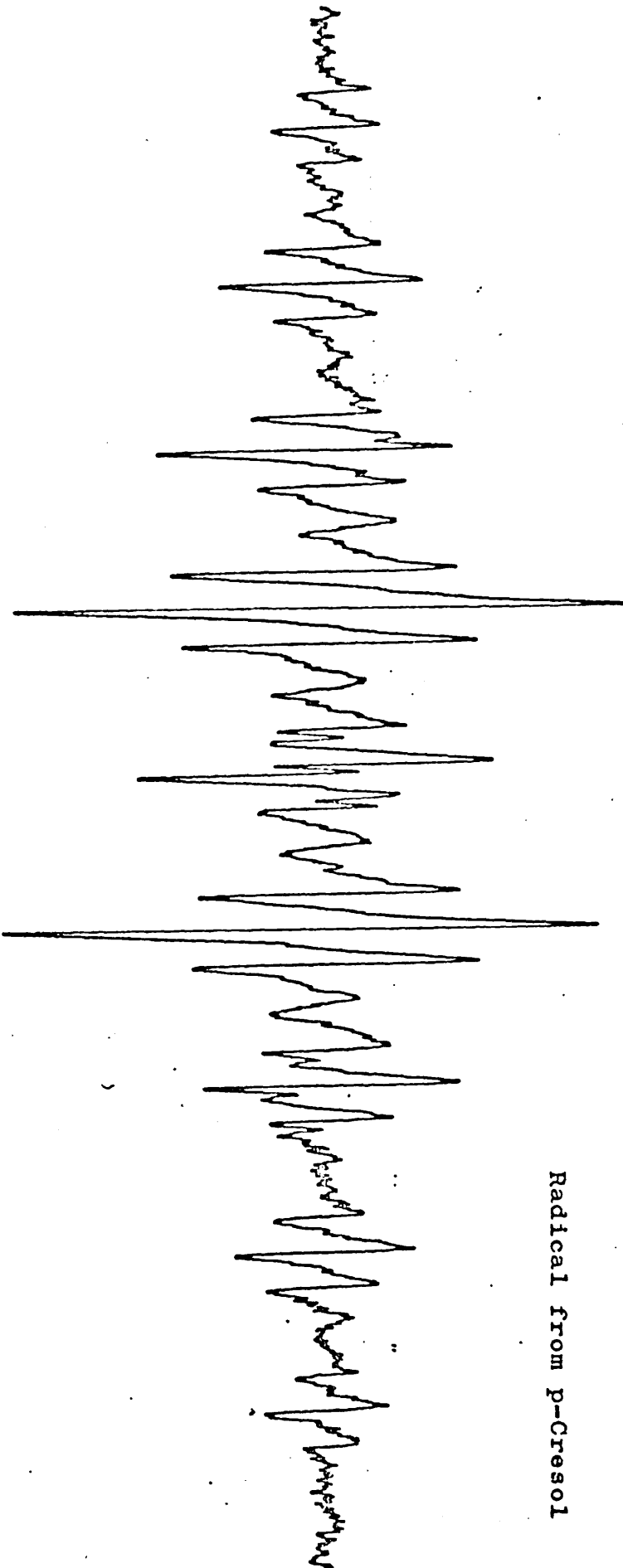


5 G

Radical from m-Cresol

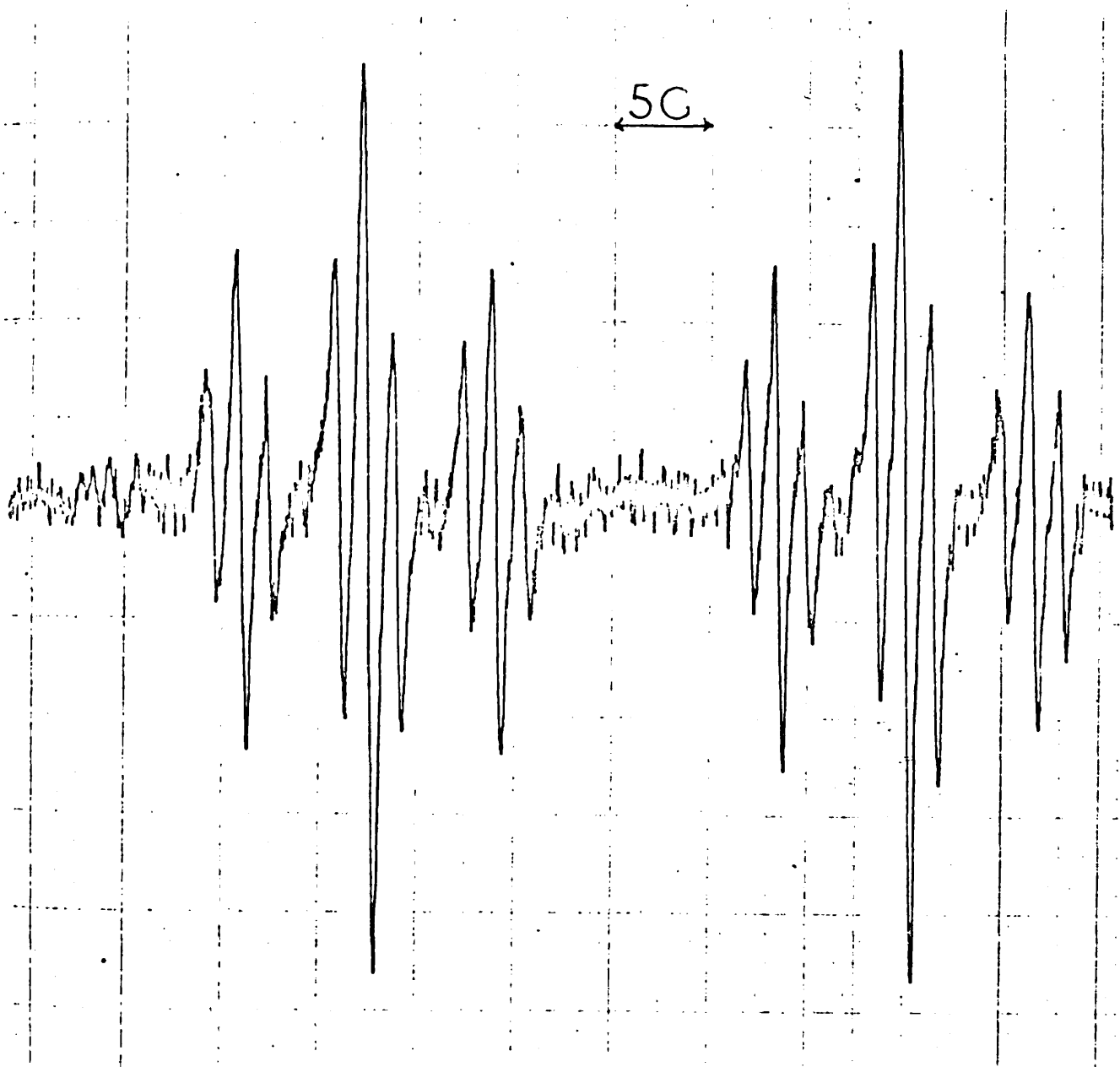


5 G

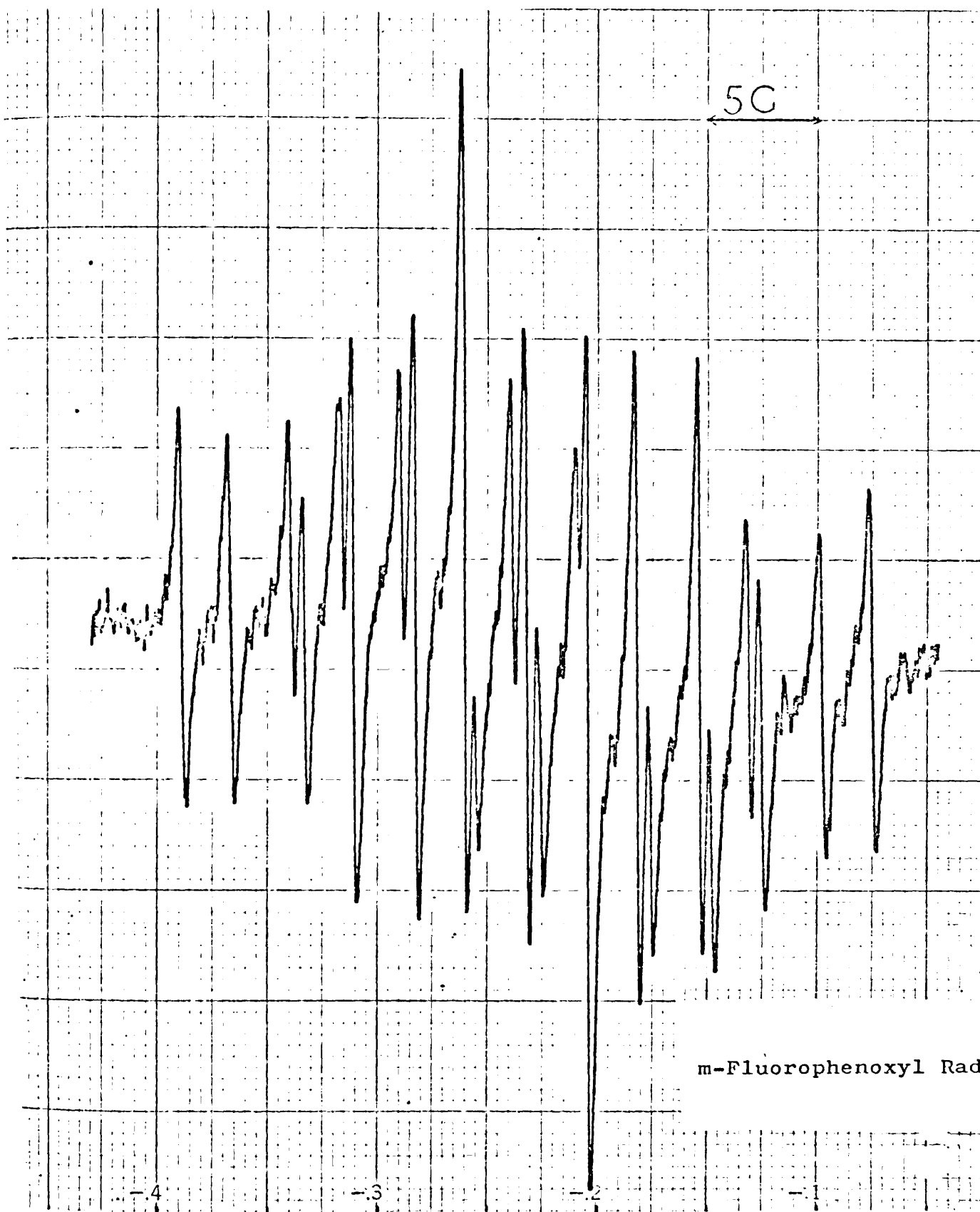


Radical from p-Cresol

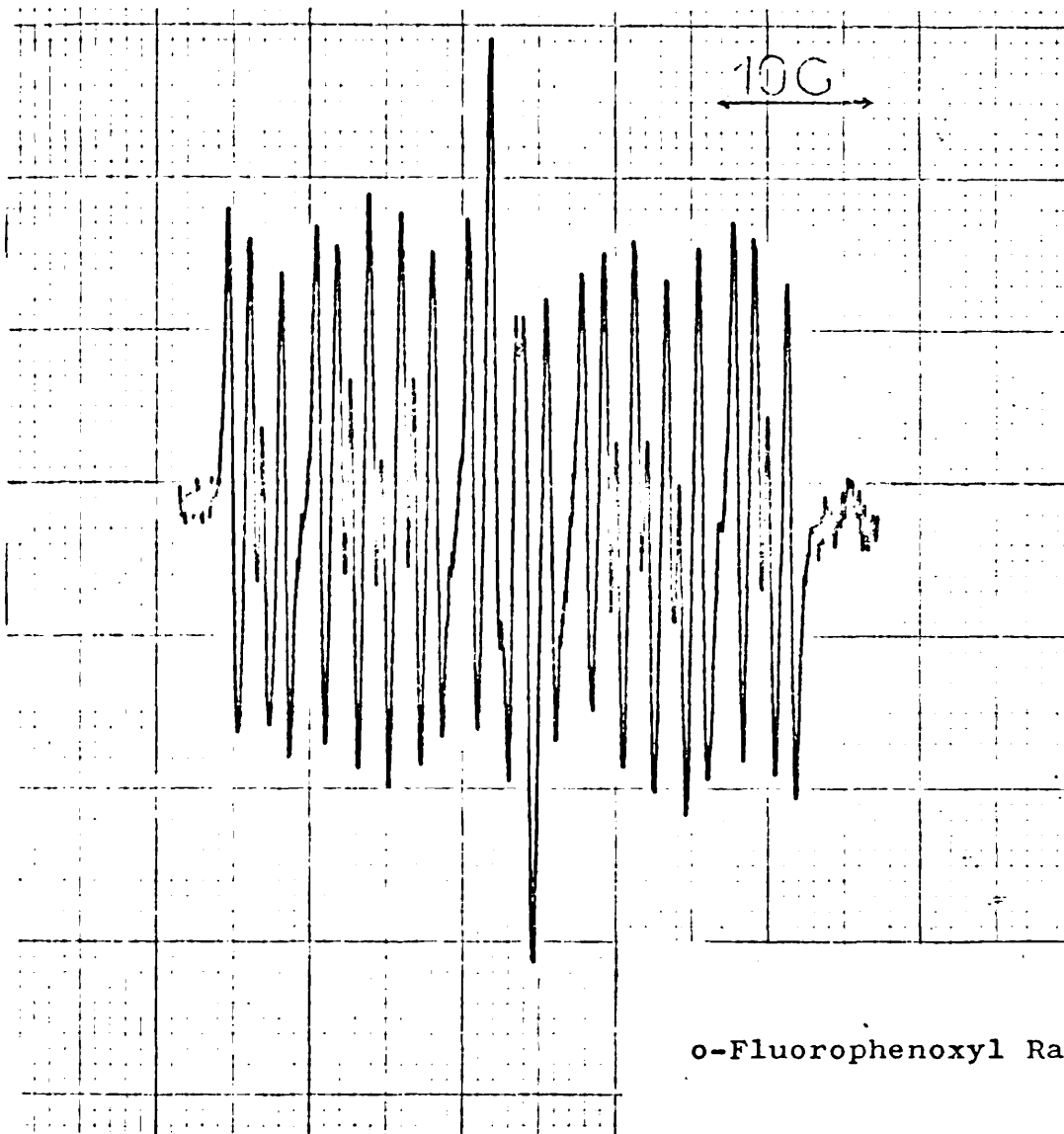
← 5 G →



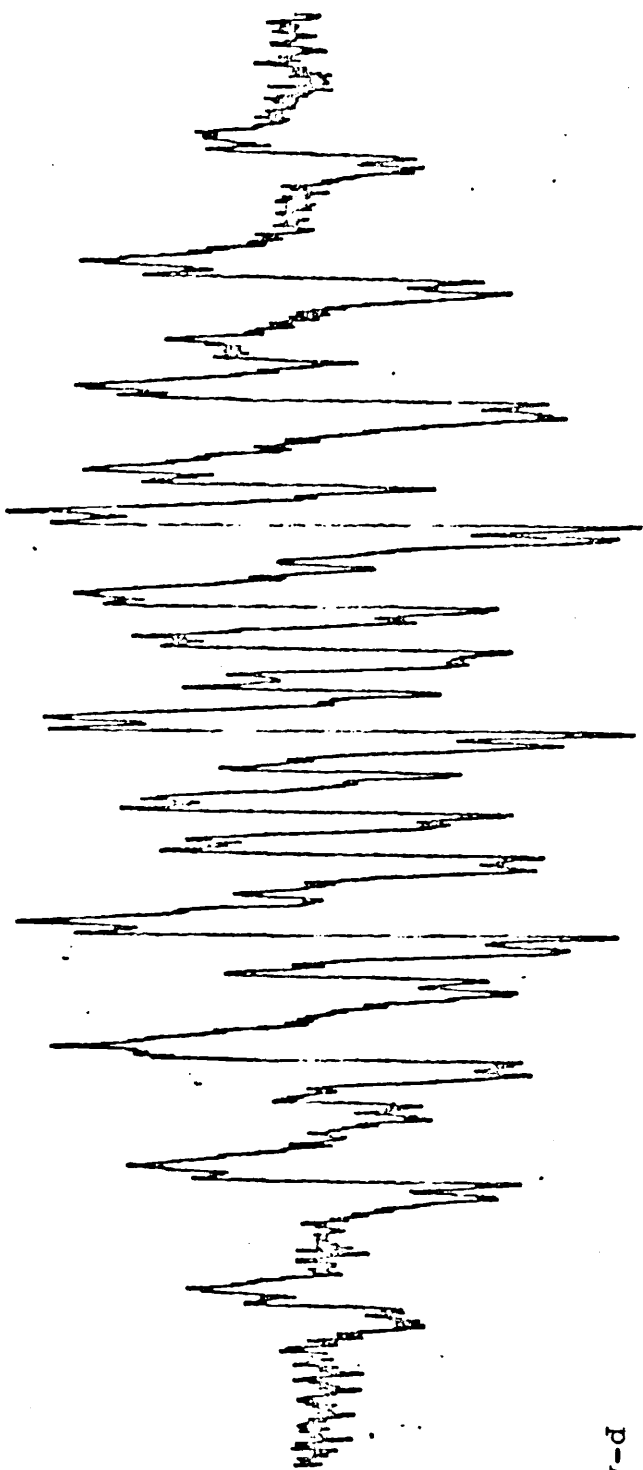
p-Fluorophenoxy Radical



m-Fluorophenoxy Radical

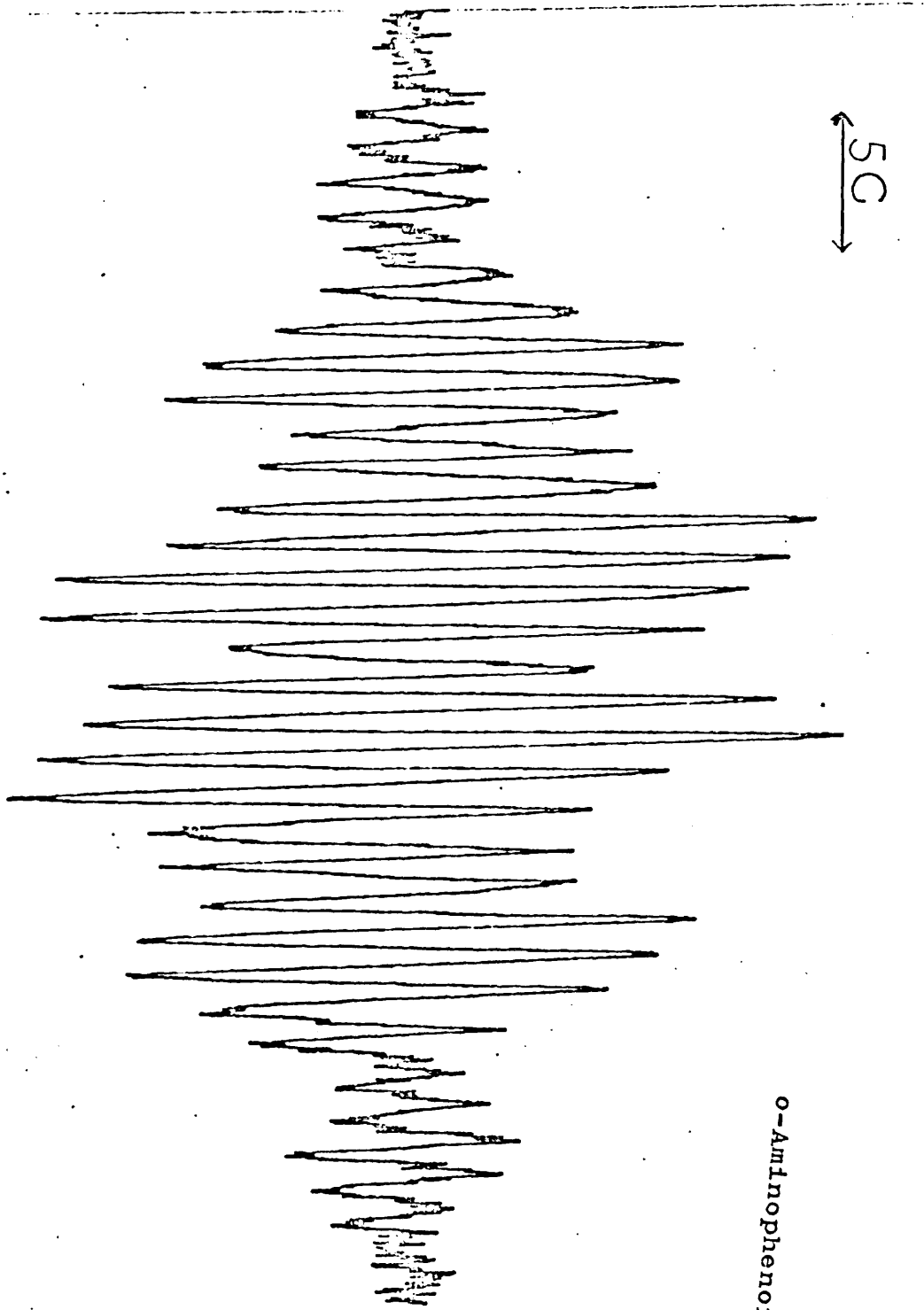


o-Fluorophenoxy Radical



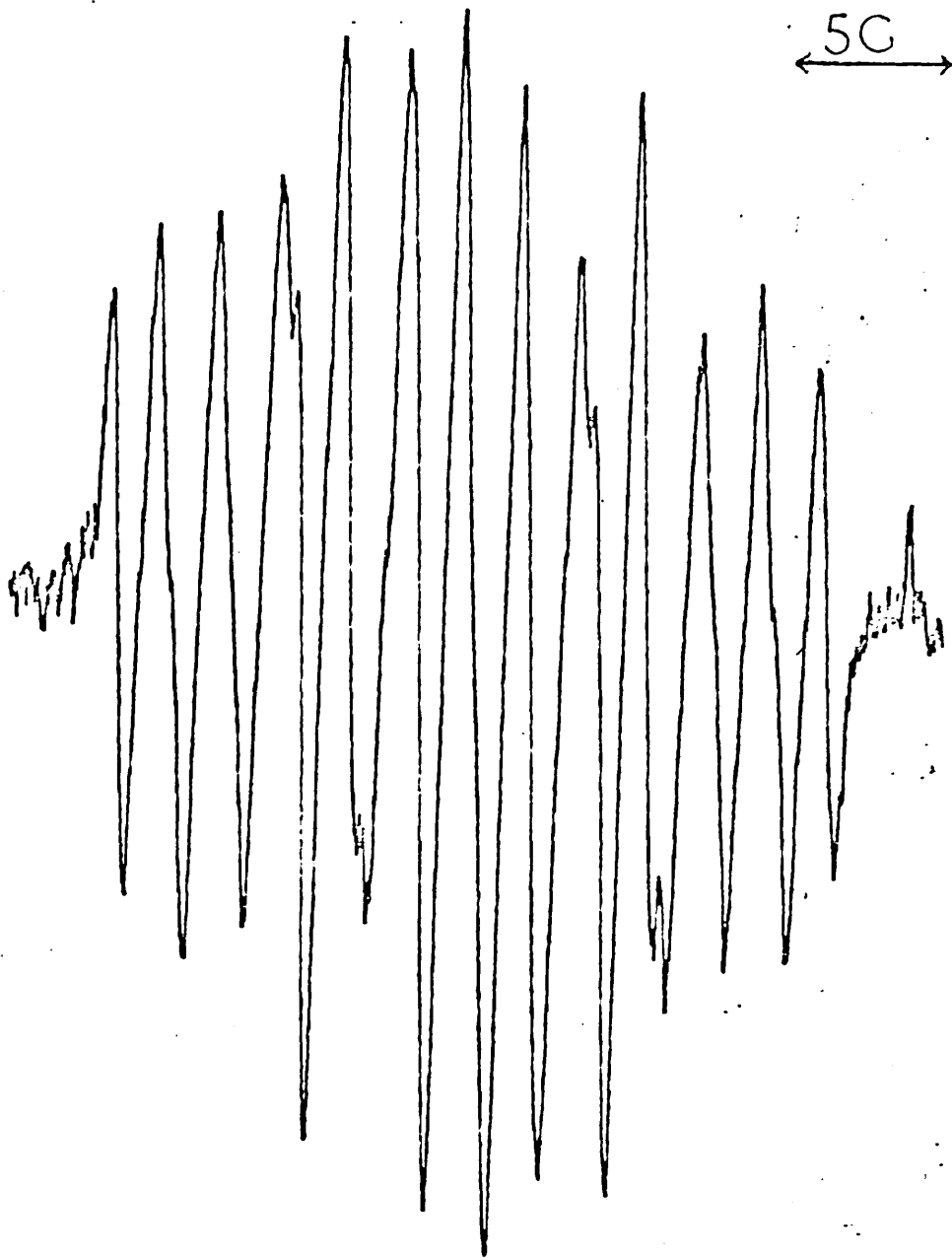
← 5G →

p-Aminophenoxy Radical

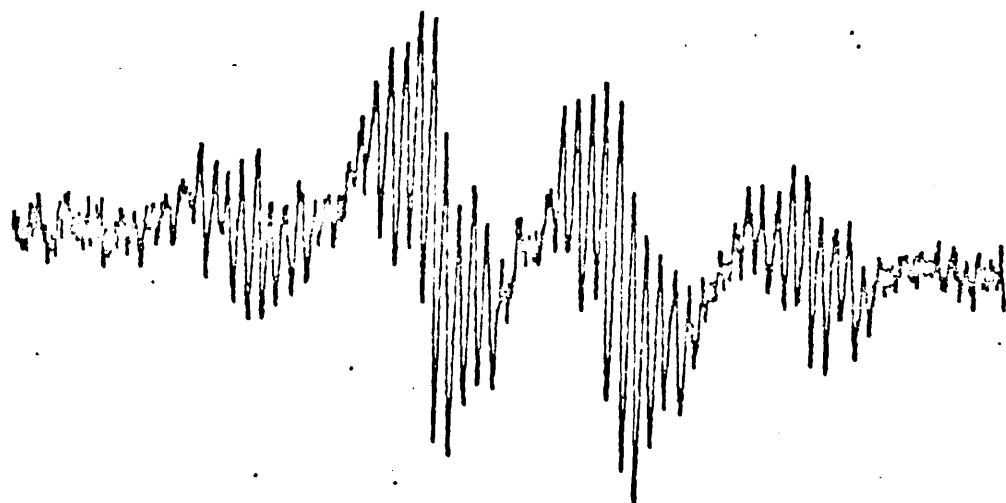


5G

o-Aminophenoxy I Radical



o-Isopropylphenoxy Radical



p-Isopropylphenoxy Radical

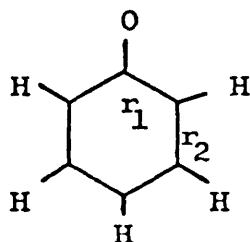
CHAPTER 3

Theory of hyperfine splittings

In previous chapter with our empirical method we arrived at the assignment and signs of hyperfine splittings. It is of intrinsic interest to explain theoretically the spin densities and also it would help to confirm the validity of our deductions.

Initially we approach this problem using the all-valence I.N.D.O. method of Pople and Beveridge,⁴⁵ which is a readily available method of calculation and which takes account of all electron repulsions. We tried out a number of these calculations for phenoxyl using the only variable parameters i.e. the geometry of the molecule. We found we could greatly affect the result by relatively small changes in bond length.

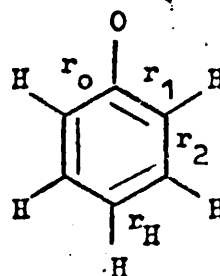
None of the variations of geometry which we tried gave results sufficiently close to the experimental ones, to give us much confidence in the method. At first we attempted to keep the regular hexagon, C-C bonds 1.40 Å, and we changed both C-O and C-H bond length; C-H was taken as 1.09 or 1.08 Å and C-O was changed from 1.22 to 1.35 Å.



At the second attempt we kept C-O and C-H bonds at 1.30 and 1.08 Å respectively and changed the shape of the hexagon from

Table 4

Results of INDO Calculations for



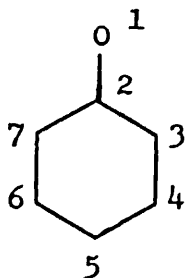
r_H	r_0	r_1	r_2	a_0	a_m	a_p
1.09	1.22	1.40	1.40	-6.31	3.62	-5.77
1.09	1.35	1.40	1.40	-4.36	2.36	-3.71
1.08	1.30	1.40	1.40	-4.97	2.81	-4.41
"	"	1.42	1.39	-5.13	2.95	-4.76
"	"	1.44	1.38	-5.55	3.40	-5.70
"	"	1.45	1.39	-5.83	3.67	-6.06
"	"	1.46	1.38	-5.94	3.84	-6.68
"	"	1.44	1.36	-5.50	3.38	-5.96
"	"	1.46	1.34	-5.81	3.77	-7.32

regular to a hexagon with two opposite short sides i.e. we elongated r_1 and shortened r_2 . The same kind of variation has been tried with some success by other workers^{46,47} i.e. in matching up theory with experiment. In all the cases, shown on the table 4, the predicted coupling constant at ortho position as a whole was in good agreement with the experiment. Whatever further geometrical changes might be tried it was clear that the negative spin density would always turn out much too big compared with the positive spin density.

From this point we looked for a much simpler type of calculation. Simple M.O. theory by itself could not possibly give very good predictions for phenoxyl because of appreciable negative spin densities occur in these radicals. However it is easy to modify simple M.O. theory by the method of McLachlan and we thought this a worthwhile procedure since this approach has frequently been used successfully. For example the spin densities of azulene anion radicals have been calculated by this method.^{48,49} Lott et al³² obtained satisfactory results for 1,2,4-trihydroxybenzene radical anion. However they had three parameters to explain three coupling constants.

In McLachlan's modification of simple M.O. theory the integrals connected with oxygen atom are variable parameters together with Q , the McConnell constant and also the perturbation parameter, which has to be of the order of unity (we took the original value given by McLachlan, 1.2). Q derives from McConnell relationship⁵⁰ and we took a rounded value of -30 G for it. The first object of our calculations was to

Table 5
Parameters for Phenoxy1



Heteroatom Model $Q = -30$

$\delta_0/\beta_{1,2}$	3	4	5
1.8/1.3	.214	-.060	.345
1.7/1.3	.218	-.063	.339
1.6/1.3	.223	-.066	.334
1.9/1.4	.225	-.064	.351
1.6/1.2	.207	-.509	.331
1.5/1.2	.211	-.062	.324
1.5/1.1	.194	-.055	.322

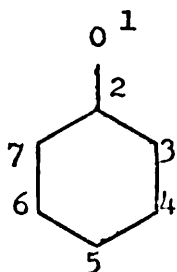
<u>Experimental</u>	3	4	5
	.221	.060	.336

Inductive Model $Q = -24$

0	3	4	5
-1.5	.273	-.077	.425

Table 6

Some of the parameters tried for phenoxy, poor result obtained.

Heteroatom Model

$\delta_0/\beta_{1,2}$	3	4	5
2.0/1.5	.235	-.068	.356
2.2/1.6	.240	-.069	.364
.5/.6	.102	-.037	.123
.5/.8	.147	-.053	.167
2.0/.6	.091	.003	.382
3.0/.4	.053	.029	.414
3.0/.6	.069	.018	.407
3.0/.8	.091	.005	.399

find parameters which reproduce theoretical results for phenoxy1. We write for the oxygen parameters $\alpha_0 = \alpha + h_0\beta$, $\beta_{CO} = k_{CO}\beta$. In itself this was trivial exercise, because we have three parameters for three coupling constants. However we then applied these parameters to calculations for other related radicals eg. semiquinones and substituted phenoxy1 radicals. Tables 5&6 show parameters which were tried many of which did not give results in good agreement with experiment. It is clear that the exact choice of parameters was of little consequence, because satisfactory results could be produced over a large range eg. 1.5/1.2, almost the same as 1.8/1.3.

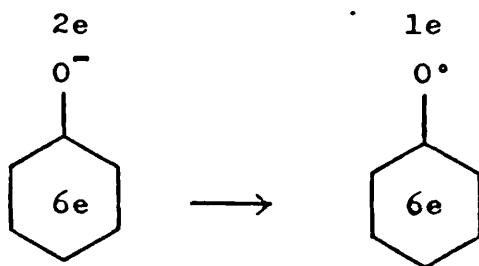
We shall show in detail the procedure which was adopted for McLachlan's S.C.F. calculation in the case of the phenoxy1 radical. Each step of the model is shown from the initial to the final Hückel calculation via the modification to the appropriate secular determinant. Two models are used for this purpose

- (1) 'Heteroatom' model
- (2) 'Inductive' model

'Heteroatom' model

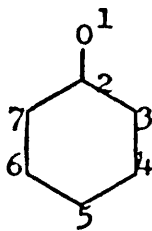
In this model each substituent is treated as a simple heteroatom X, so that two parameters have to be obtained i.e. α_X and β_{CX} of the heteroatom. In the case of phenoxy1 the substituent is just oxygen so that there is no difference between our model and the usual M.O. model. A quick way of

working out the number of electrons is to allow 5 electrons for the ring and two for each heteroatom. eg. for phenoxyl, total number of electrons = $5+2=7$ phenoxyl negative ion has $6+2=8$ electrons on oxidation one electron is lost and it will have 7 electrons



Now we go into detail calculation of spin densities by McLachlan's method.

Heteroatom model for phenoxyl If we use $\alpha_0 = 1.6$ and $\beta_{CO} = 1.3$ the overlap matrix before diagonalisation will become:-



1	2	3	4	5	6	7
1.6	1.3	0	0	0	0	0
1.3	0	1.0	0	0	0	1.0
0	1.0	0	1.0	0	0	0
0	0	1.0	0	1.0	0	0
0	0	0	1.0	0	1.0	0
0	0	0	0	1.0	0	1.0
0	1.0	0	0	0	1.0	0

The solution of this problem leads to the Energy levels which are :-

$$\alpha - E_1 = -2.619 \beta$$

$$\alpha - E_2 = -1.709 \beta$$

$$\alpha - E_3 = -1.0 \beta$$

$$\alpha - E_4 = -0.568 \beta$$

$$\alpha - E_5 = 1.0 \beta$$

$$\alpha - E_6 = 1.200 \beta$$

$$\alpha - E_7 = 2.096 \beta$$

The unpaired electron is in Energy level E_4 and the spin densities which are the square of coefficients, are:-

$$e_1 = .225$$

$$e_2 = .142$$

$$e_7 = e_3 = .173$$

$$e_6 = e_4 = .019$$

$$e_5 = .246$$

Using McConnell relation $a_1 = Qe_1$ for $Q = -30$, we get the coupling constants to be:-

$$a_7 = a_3 = 5.19 \text{ G}$$

$$a_6 = a_4 = .57 \text{ G}$$

$$a_5 = 7.38 \text{ G}$$

The modified matrix is:-

2.141	1.3	0	0	0	0	0
1.3	.341	1.0	0	0	0	1.0
0	1.0	.415	1.0	0	0	0
0	0	1.0	.047	1.0	0	0
0	0	0	1.0	.590	1.0	0
0	0	0	0	1.0	.047	1.0
0	1.0	0	0	0	1.0	.415

Spin density at a given position is given by McLachlan's relation:-

$$e = |\Psi_0|^2 + \sum \left\{ (\Psi_i)^2 - (\Psi_i')^2 \right\}$$

And the final results are as follows:-

$$e_1 = .230$$

$$e_2 = .121$$

$$e_3 = .223$$

$$e_4 = -.066$$

$$e_5 = .334$$

$$e_6 = -.066$$

$$e_7 = .223$$

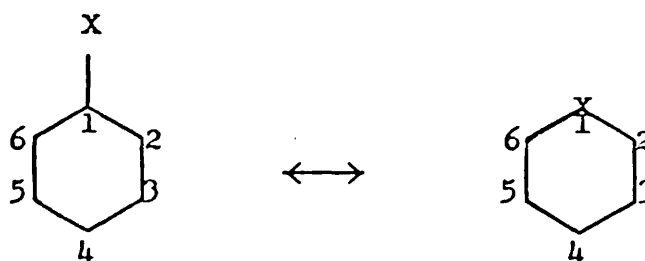
Coupling constant using McConnell relationship are:-

$$a_7 = a_3 = 6.69$$

$$a_6 = a_4 = -1.98$$

$$a_5 = 10.02$$

Inductive model In this model the groups attached to benzene skeleton are thought of only in terms of their influence on the neighbouring atom, and this is reflected in its coulomb integral. Each substituent has only one parameter associated with it i.e. the coulomb integral of its adjacent carbon atom.

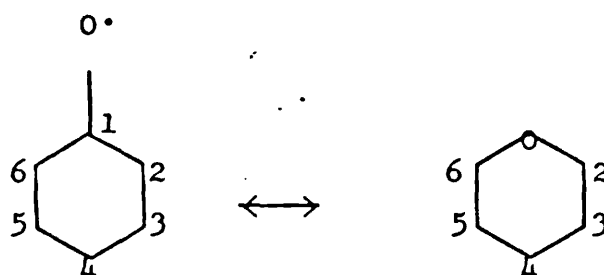


$$\alpha_1 = \alpha + h_X \beta$$

$$\alpha_2 = \alpha_3 = \alpha_4 = \alpha_5 = \alpha_6$$

and resonance integrals are the same as between carbon atoms i.e. $\beta_{12} = \beta_{23} = \beta_{34}$ etc. The molecule is regarded as a modified benzene positive ion so that two electrons are assigned to each substituent (atom) leaving 5 electrons on the ring. All problems are therefore reduced to one of 6 orbitals and 5 electrons. When $X = 'O^-'$ h_O is negative because in spite of oxygen's high electronegativity electrons have to be pushed into the ring. The details of calculations in this model for phenoxyl will be shown.

δ_0 has been taken -1.5 for phenoxyl and we took -24 G for Q value of McConnell relationship as discussed before. As we mentioned before, the appropriate matrix for phenoxyl in this model is reduced to 6×6 determinant.



-1.5	1	0	0	0	0	1
1	0	1	0	0	0	0
0	1	0	1	0	0	0
0	0	1	0	1	0	0
0	0	0	1	0	1	1
1	0	0	0	0	1	0

Energy levels are:-

$$\begin{aligned} \alpha \cdot E_1 &= -1.862 \beta \\ \alpha \cdot E_2 &= -1.00 \beta \\ \alpha \cdot E_3 &= -0.594 \beta \\ \alpha \cdot E_4 &= 1.00 \beta \\ \alpha \cdot E_5 &= 1.430 \beta \\ \alpha \cdot E_6 &= 2.525 \beta \end{aligned}$$

In this model we have chosen only 5 electrons for phenoxyl which are in E_1 , E_2 and E_3 energy levels, the unpaired electron is in E_3 and corresponding spin densities i.e. the square of

the coefficients of the odd electron orbitals are:-

$$c_1 = .196$$

$$c_2 = .215$$

$$c_3 = .028$$

$$c_4 = .317$$

$$c_5 = .028$$

$$c_6 = .215$$

The input matrix has been changed according to McLachlan's modification:-

-1.028	1.0	0	0	0	1.0
1.0	.516	1.0	0	0	0
0	1.0	.067	1.0	0	0
0	0	1.0	.761	1.0	0
0	0	0	1.0	.067	1.0
1.0	0	0	0	1.0	.516

Corresponding energy levels are:-

$$E_1 = -2.268$$

$$E_2 = -1.316$$

$$E_3 = -1.166$$

$$E_4 = .733$$

$$E_5 = 1.038$$

$$E_6 = 2.079$$

The resulting spin densities by using McLachlan's relations are:-

$$e_1 = .182$$

$$e_2 = .273$$

$$e_3 = -.077$$

$$e_4 = .425$$

$$e_5 = -.077$$

$$e_6 = .273$$

Theory of substituted phenoxyl radicals

(i) Hydroxylated radicals

In the previous sections we have found parameters for oxygen in phenoxyl, which lead to satisfactory agreement with our experiment. Now dealing with o-, m- and p- oxygenated phenoxyls i.e. semiquinones, we have found a range of parameters which give good results for phenoxyl and which also give reasonably satisfactory results for semiquinones and related radicals, see tables 7 & 8. As it is clear from the tables that our theoretical calculations, irrespective of the exact choice of oxygen parameters have reproduced the correct signs and the correct order of magnitude of the various hyperfine splittings, for example in the table for resorcinol negative spin densities are predicted for positions 3 and 7 as we deduced from the graphs previously.

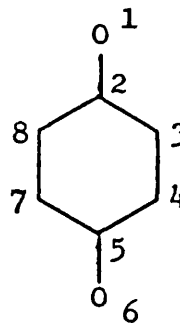
(ii) Substituted radicals

The same type of approach can be used to bring in the effect of substituents in these radicals. Thus in the hetero-

Table 7

Tabulation of oxygen parameterisation for dihydroxy phenoxylsHeteroatom Model

(i) Para-hydroxyphenoxyl

Experimental 0.08

 $\frac{\delta}{\beta}$ 3

2.2/1.5 .091

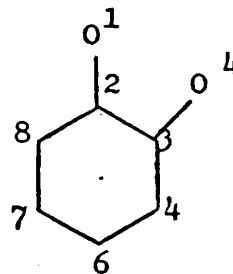
2.2/1.7 .103

2.2/1.6 .097

1.8/1.3 .083

1.9/1.4 .088

(ii) Ortho-hydroxyphenoxyl

Experimental 0.025 .125

 $\frac{\delta}{\beta}$ 5 6

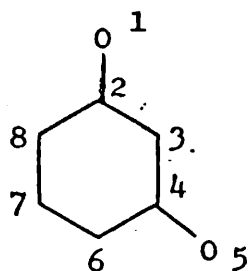
2.2/1.7 .045 .128

2.2/1.6 .029 .130

2.2/1.5 .014 .133

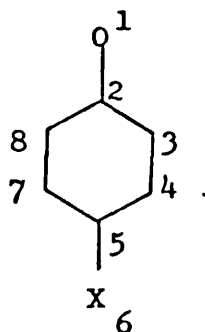
1.8/1.3 .007 .125

1.9/1.4 .016 .126

Table 83-Meta-substituted hydroxyphenoxyl

<u>Experimental</u>	<u>-0.023</u>	<u>0.375</u>	<u>-0.093</u>
$\frac{\delta}{\beta}$	3	6	7
2.2/1.7	-.024	.466	-.127
2.2/1.6	-.026	.455	-.123
1.9/1.4	-.029	.437	-.118
1.8/1.3	-.031	.425	-.114

Table 9

Parameters for substituents in phenoxy radicalHeteroatom Model

δ_X / β_{C-X}	3	4
.5/.2	.057	-.001
.5/.4	.055	.021
.5/.6	.043	.051
.5/.8	.030	.084
.5/1.0	.015	.120
.5/1.2	.001	.156
1.0/.1	.217	-.063
1.0/.2	.204	-.054
1.0/.3	.186	-.042
1.0/.4	.166	-.028
1.0/.6	.128	.004
1.0/1.2	.047	.114
1.5/.1	.221	-.064
1.5/.2	.216	-.061
1.5/.3	.208	-.055
1.5/.4	.198	-.047
1.5/.5	.186	-.037
1.5/.6	.172	-.024
1.5/.8	.144	.004
1.5/1.0	.115	.037
1.5/1.2	.089	.073
1.5/1.4	.065	.109

atom model, each substituent is to be assigned with two parameters and in the inductive model, each substituent has one parameter. We have fixed the oxygen parameters by one set of values for phenoxy radical i.e.

$$\alpha_0 = \alpha + 1.6\beta$$

$$\beta_{CO} = 1.3\beta$$

The assignment of the appropriate parameters were made by carrying out calculations using a spectrum of values Table 9 and choosing these for particular substituents by comparing the experimental splittings with the calculated ones.

Calculations were performed for o-, m- and p- substituted phenoxy radicals, given different values to the parameters. After some preliminary tests we decided that the range of coulomb integrals should be from $\alpha + .5\beta$ to $\alpha + 1.5\beta$ and we tested the range of 0.2β to 1.4β for resonance integral. For example inspection shows that in the heteroatom model, for $X \equiv -OMe$, two parameters i.e. coulomb integral and resonance integral which reproduce the empirical splittings satisfactorily are

$$\alpha_{OMe} = \alpha + 1.5\beta$$

$$\beta_{C-OMe} = 0.6\beta$$

Other pairs could also be chosen which could equally be assigned to $-OMe$, but for convenience we fixed the coulomb integral at $\alpha_X = \alpha + 1.5\beta$ and effectively varied only the resonance

integral $\beta_{CX} = k\beta$. For each substituent we then had to find only this resonance integral parameter 'k'. For $k = 0.3$, the two parameters would reproduce results corresponding to $-\text{CH}_3$ group and 0.8 for $-\text{NH}_2$ and 0.6 for $-\text{OMe}$ groups.

We tested these parameters at o-, m- and p- positions of the phenoxy, they are shown on Tables 10, 11, 12, in all cases the results are in good agreement with our experiment. The order of these parameters is connected to electron donating properties of the substituents i.e. $\text{O}^- > \text{NH}_2 > \text{OMe} > \text{CH}_3$.

Inductive model

A similar procedure as for heteroatom model was adopted here also. Now we only have one parameter namely a coulomb integral, which is changing.

Table 13 shows different coulomb integrals for phenoxy radical, all the resonance integrals are the same and we are changing h according to:- $\alpha_X = \alpha + h\beta$

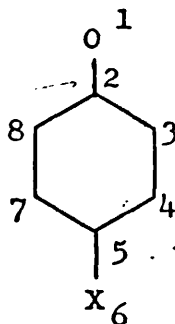
After some preliminary tests we decided that we will change h from -.2 to -1.5. The spin densities corresponding to the phenoxy radical are reproduced. Therefore we took $h = -1.5$ for oxygen value.

The same way as heteroatom model, we considered the o-, m- and p- substituted phenoxy radicals in this model. That is to say we fixed the coulomb integral of oxygen at -1.5 and gave different values to the coulomb integrals of the substituents, and compared the result with our experiment and the parameters

which corresponded to -OMe, -NH₂, -CH₃ and -COOH are as Tables 10,11,12. The para-substituted case, poor result is obtained in this model, and the greater the electron donating power of the substituents the worse the agreement, so that the worst case is p-semiquinone itself.

However whereas in heteroatom model we could find no parameters suitable for groups like NO₂ or COOH, this was possible in the framework of the inductive model. The calculations evidently confirm our empirical findings and one feels confident that the theory could give good predictions for other related systems.

Table 10

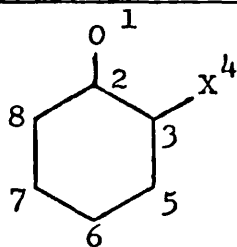
Para-substituted phenoxyHeteroatom Model

X	$\delta_X/\beta_{6,5}$	a_3	a_4	a_3 expt.	a_4 expt.
-OMe	1.5/ .6	5.16	-.72	4.9	0.0
-O ⁻	1.6/1.3	2.52	2.52	2.37	2.37
-CH ₃	1.5/.3	6.2	-1.6	6.1	-1.4
-NH ₂	1.5/.8	4.32	.12	4.0	0.5

Inductive Model

X	δ_X	a_3	a_4	a_3 expt.	a_4 expt.
-O ⁻	-1.5	3.2	3.2	2.37	2.37
-OMe	-.6	5.06	.02	4.9	0.0
-NH ₂	-.9	4.4	1.15	4.0	0.5
-COOH	.2	7.08	-2.28	6.75	-2.2
-CH ₃	-.2	6.02	-1.29	6.1	-1.4

Table 11

Ortho-substituted phenoxy1

$$\bar{\sigma}_0/\beta_{1,2} = 1.6/1.3$$

Heteroatom Model

Q = -30

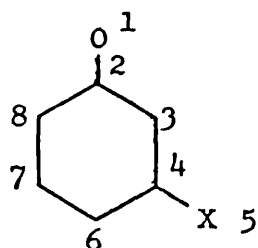
X	$\bar{\sigma}_X/\beta_{3,4}$	a_5	a_6	a_7	a_8
-OMe	1.5/.6	-2.6	8.07	-.27	3.99
	Expt.	-1.9	8.5	0.0	4.3
-NH ₂	1.5/.8	-2.16	6.57	.87	2.58
	Expt.	-.9	6.62	1.5	2.6
-O	1.6/1.3	.57	3.48	3.48	.57
	Expt.	0.75	3.75	3.75	0.75
-CH ₃	1.5/.3	-2.3	9.57	-1.56	5.91
	Expt.	-2.0	9.7	-1.5	6.0

Inductive Model

Q = -24

X	$\bar{\sigma}_X$	a_5	a_6	a_7	a_8
-O	-1.5	1.6	4.08	4.08	1.6
	Expt.	0.75	3.75	3.75	0.75
-OMe	-.6	-2.54	7.7	.86	3.12
	Expt.	-1.9	8.5	0.0	4.3
-NH ₂	-.9	-1.36	6.26	2.13	2.2
	Expt.	-.9	6.62	1.5	2.6
-COOH	.2	-.57	10.3	-2.42	7.8
	Expt.	-1.25	10.7	-2.1	7.15
-CH ₃	-.2	-2.64	9.6	-1.00	5.2
	Expt.	-2.0	9.7	-1.5	6.0

Table 12

Meta-substituted phenoxy1

$$\delta_0/\beta_{1,2} = 1.6/1.3$$

Heteroatom Model

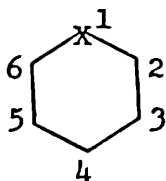
$$Q = -30$$

X	$\delta_X/\beta_{4,5}$	a_3	a_6	a_7	a_8
-OMe	1.5/.6	4.65	10.8	-2.37	8.01
	Expt.	3.5	11.4	-2.3	9.0
-NH ₂	1.5/.8	2.79	11.6	-2.7	9.2
	Expt.	3.1	10.9	-2.0	8.6
-O	1.6/1.3	-.84	12.8	-3.45	12.8
	Expt.	-.7	11.2	-2.8	11.2
-CH ₃	1.5/.3	6.2	10.2	-2.0	6.69
	Expt.	5.9	10.5	-1.9	7.1

Inductive Model

X	δ_X	a_3	a_6	a_7	a_8
-O	-1.5	-.52	12.16	-3.4	12.16
	Expt.	-.7	11.2	-2.8	11.2
-OMe	-.6	2.99	11.35	-2.6	8.8
	Expt.	3.5	11.4	-2.3	9.0
-NH ₂	-.9	1.12	11.88	-3.0	10.17
	Expt.	3.1	10.9	-2.0	8.6
-COOH	.2	7.4	9.8	-1.6	5.9
	Expt.	6.5	9.9	-1.9	7.25
-CH ₃	-.2	5.4	10.54	-2.08	8.80
	Expt.	5.9	10.5	-1.9	7.1

Table 13

Parameters for oxygen in phenoxyl radicalInductive Model

δX	2	3	4
-.2	.075	.016	.416
-.3	.093	.006	.415
-.4	.111	-.003	.415
-.6	.147	-.021	.416
-.8	.181	-.037	.418
-1.0	.211	-.050	.420
-1.5	.273	-.077	.425
-2.0	.315	-.095	.427

CHAPTER 4

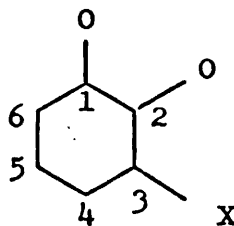
Di-substituted phenoxyl radicals

In Chapter 2 we assigned the coupling constants of mono-substituted phenoxyls by graphical method. The observation of regularities in the spin densities in these radicals enabled us to regard semiquinone not as totally different species but rather as phenoxyl radical with a particular substituent i.e. $X \equiv O^-$. Following the same procedure we are attempting in this chapter to obtain empirical assignments for di-substituted phenoxyl radicals, and to confirm them using the same theory as that developed above.

(a) Empirical Assignments

(i) 3-substituted o-semiquinones

The most distinct regularities were found in the graphs obtained by plotting the sum of the two splittings against the third.



For clarity in graph IX we use the final assignments. The plot of $a_4 + a_5$ against a_6 shown by curve AB, $a_5 + a_6$ against a_4 represented by curve AC, and $a_4 + a_6$ against a_5 represented by NM

Point A (4.55, -0.95) indicating pyrogallol which is the intersection of AB and AC, since a_4 and a_6 are the same in pyrogallol. Point Q (4.5, 3.75) indicating catechol (R=H) is the intersection of AC and MN, since in catechol $a_4 = a_5$. Experimental results are in Table 14.

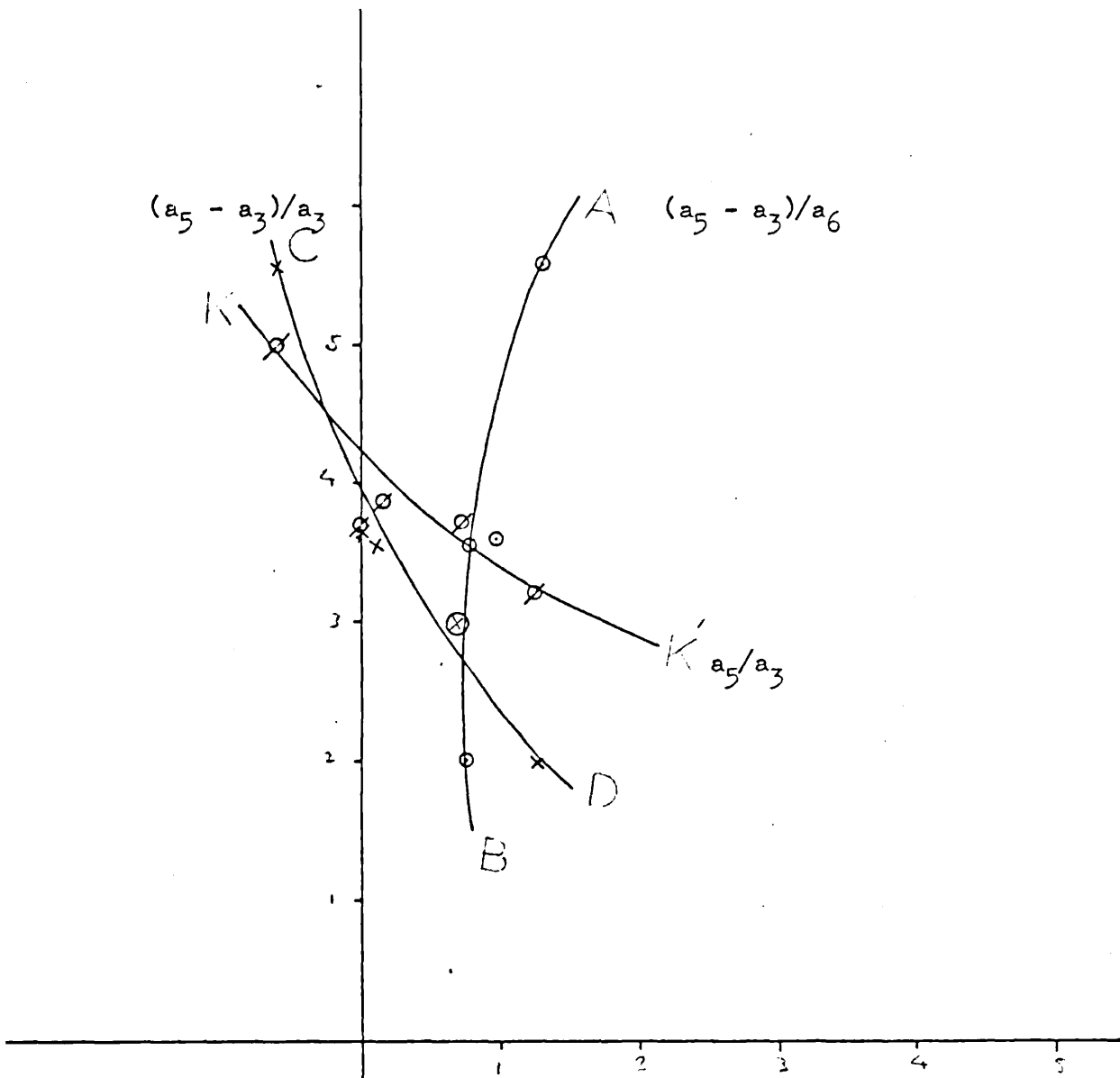
(ii) 4-substituted o-semiquinones

Once again combination of the two coupling constants is plotted against the third. It can be seen from graph VIII; we have taken the differences from the two coupling constants and plotted it against the other one.

Curve AB represents the plot of $a_5 - a_3$ against a_6 and curve CD is the plot of $a_5 - a_3$ against a_3 , and curve KK' is the variation of a_5 against a_3 . The smallest splitting in the semiquinone 1,2,4-trihydroxybenzene i.e. ($X \equiv O^-$) turns out to be negative, which is also confirmed by our calculations. Point A (5.58, 1.35) represents 1,2,4-trihydroxybenzene in which a_3 has a negative value. Point C and K also confirms this negative spin density. Experimental results are in Table 14.

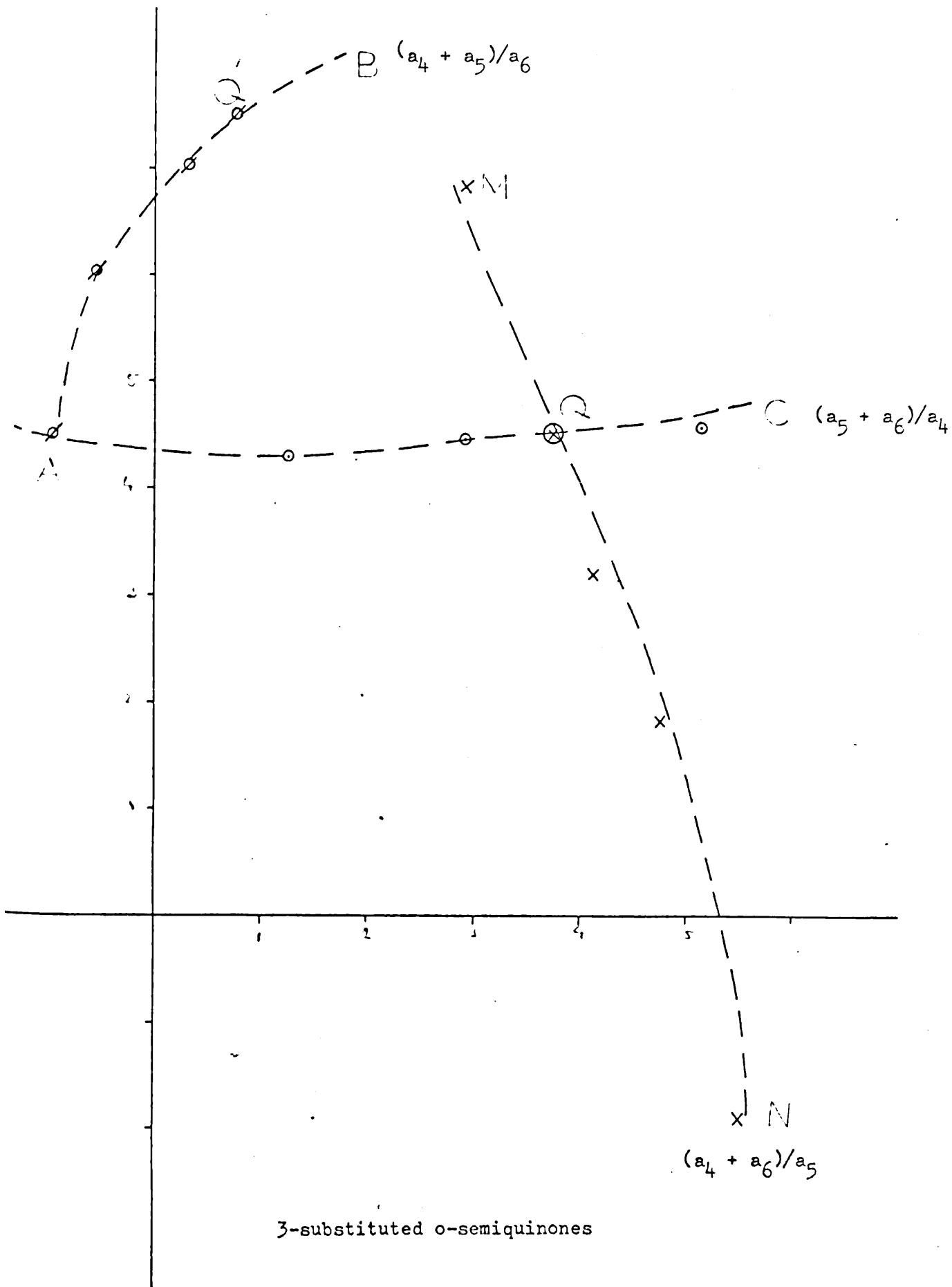
(iii) Substituted p-semiquinones

Effects of substituents on the overall spin distribution on these radicals are similar to those described before. We plotted graphs showing the regularities in the coupling constants. XY is the curve a_5 against a_3 . MN a_6 against a_3 and AB $a_5 - a_3$ against a_6 . When $X \equiv O^-$ i.e. 1,2,4-trihydroxybenzene, once again the negative sign of a_3 is confirmed.

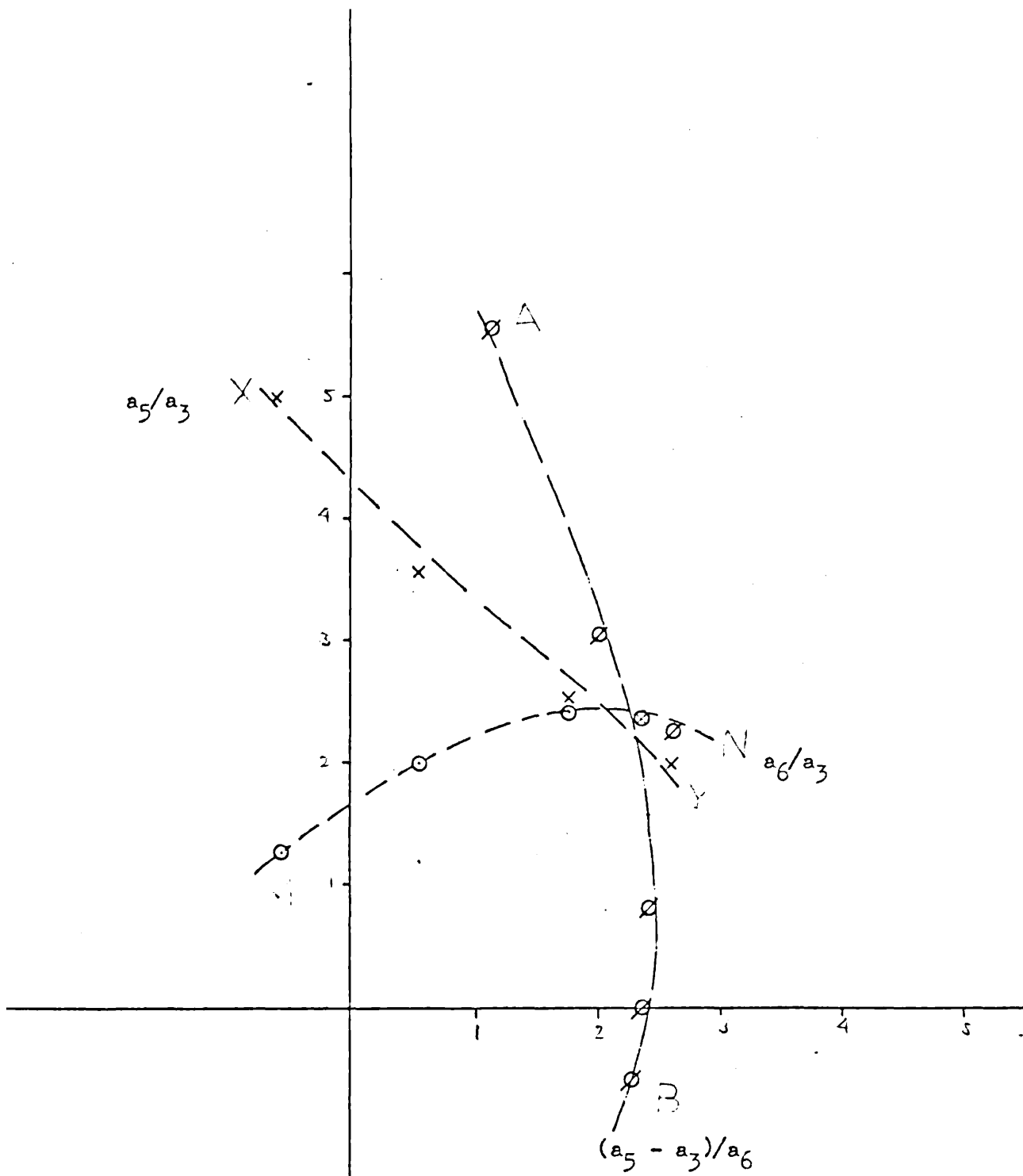


4-substituted o-semiquinone

GRAPH VIII



GRAPH IX



Substituted p-semiquinones

GRAPH X

Table 14
Comparison between Theory and Experiment for di-substituted
Phenoxy Radicals

		a_2	a_3	a_4	a_5	a_6
2 \bar{O} , 3Me	Expt	-	$a_{Me} = .65$	2.9	4.15	0.3
	Theory 1	-	-	3.06	3.6	.3
	Theory 2	-	-	2.8	4.6	.76
2 \bar{O} , 4Me	Expt	-	0.15	$a_{Me} = 4.85$	3.8	0.95
	Theory 1	-	.24	-	3.63	.66
	Theory 2	-	.62	-	4.6	1.9
2 \bar{O} , 3OMe	Expt	-	$a_{OMe} = 0.65$	1.3	4.75	-0.55
	Theory 1	-	-	1.8	4.02	-.42
	Theory 2	-	-	.288	5.5	-.74
2 \bar{O} , 4OMe	Expt	-	0.0	$a_{OMe} = 1.1$	3.7	0.75
	Theory 1	-	-.57	-	4.07	.84
	Theory 2	-	-.69	-	5.7	2.4
2 \bar{O} , 3CO ₂ H	Expt	-	-	5.15	2.9	1.7
	Theory 2	-	-	5.2	3.5	2.4
2 \bar{O} , 4CO ₂ H	Expt	-	1.25	-	3.25	0.75
	Theory 2	-	2.8	-	3.6	1.27
2 \bar{O} , 3 \bar{O}	Expt	-	-	-0.95	5.5	-0.95
	Theory 1	-	-	-1.59	4.29	-1.59
	Theory 2	-	-	-1.82	5.5	-1.82
2 \bar{O} , 4 \bar{O}	Expt	-	-.6	-	4.98	1.35
	Theory 1	-	-1.41	-	6.1	.96
	Theory 2	-	-1.27	-	8.2	3.09

Table 14 cont.

		a_2	a_3	a_4	a_5	a_6
4 \bar{O} , 2Me	Expt	-	1.75	-	2.6	2.4
	Theory 1	-	2.07	-	2.76	2.43
	Theory 2	-	1.92	-	4.08	3.28
4 \bar{O} , 2OMe	Expt	-	.57	-	3.66	2.01
	Theory 1	-	.87	-	3.45	2.16
	Theory 2	-	-.168	-	5.59	3.21
4 \bar{O} , 2CO ₂ H	Expt	-	2.6	-	2.0	2.25
	Theory 2	-	4.8	-	2.54	3.28

Theory 1: heteroatom model

Theory 2; inductive model

(b) Theoretical Calculations

We followed the same procedures as in Chapter III, for calculation of spin density in these radicals. The parameters used for the different groups were the same as before:-

(i) Heteroatom model

$$\begin{aligned} \text{For oxygen} \quad \alpha_{\text{O}} &= \alpha + 1.6\beta \\ \beta_{\text{CO}} &= 1.3\beta \end{aligned}$$

$$\begin{aligned} \text{For methyl} \quad \alpha_{\text{CH}_3} &= \alpha + 1.5\beta \\ \beta_{\text{C-CH}_3} &= 0.3\beta \end{aligned}$$

$$\begin{aligned} \text{For methoxy} \quad \alpha_{\text{OMe}} &= \alpha + 1.5\beta \\ \beta_{\text{C-OMe}} &= 0.6\beta \end{aligned}$$

(ii) Inductive model

$$\text{For oxygen} \quad \alpha_{\text{O}} = \alpha - 1.5\beta$$

$$\text{For methyl} \quad \alpha_{\text{CH}_3} = \alpha - 0.2\beta$$

$$\text{For methoxy} \quad \alpha_{\text{OMe}} = \alpha - 0.6\beta$$

$$\text{For carboxy} \quad \alpha_{\text{COOH}} = \alpha + 0.2\beta$$

From the tables it is clear that both models give fair agreement with experiment. (Table 14)

From these radicals we came across with the deficiency in

our heteroatom model, which cannot deal with electron attracting groups such as $-\text{COOH}$, for this group we were not able to find a set of parameters which will reproduce a reasonable answer with comparing with experiment.

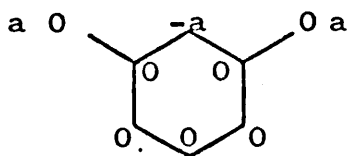
Inductive model was not so good when we had two electron donating groups para with respect to each other, but on the other hand give reasonably good results for electron attracting group eg. $-\text{COOH}$.

1,2,4-trihydroxybenzene was calculated by Lott, Short and Waters³² in which a_3 has a negative value for different sets of parameters. Our two models of calculations have confirmed this negative spin density.

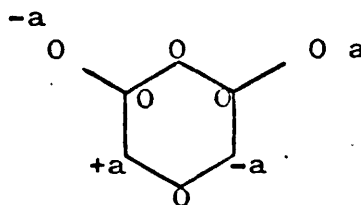
Substituted Resorcinols

The coupling constants of resorcinol can be estimated from simple Hückel theory.

We have two possibilities, symmetrical and antisymmetrical orbitals. Looking at the model systems in which differences between coulomb integrals are neglected, there are two non-bonding orbitals of opposite symmetries.

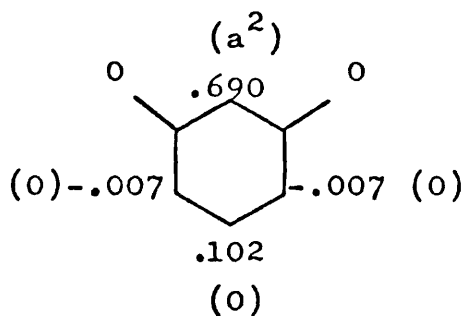


Symmetrical

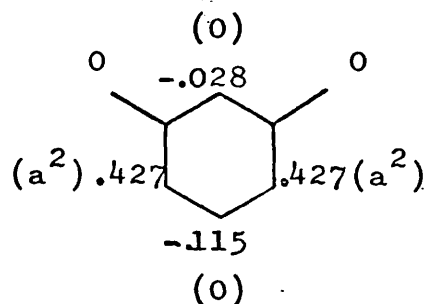


Antisymmetrical

McLachlan type calculations of the spin densities with 7 or 9 electrons, effectively show the influences of these two types of orbitals which may be said to contain the odd electron in the two cases.



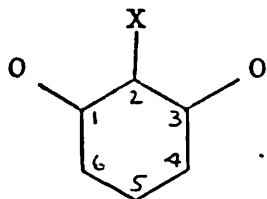
(7 electrons)



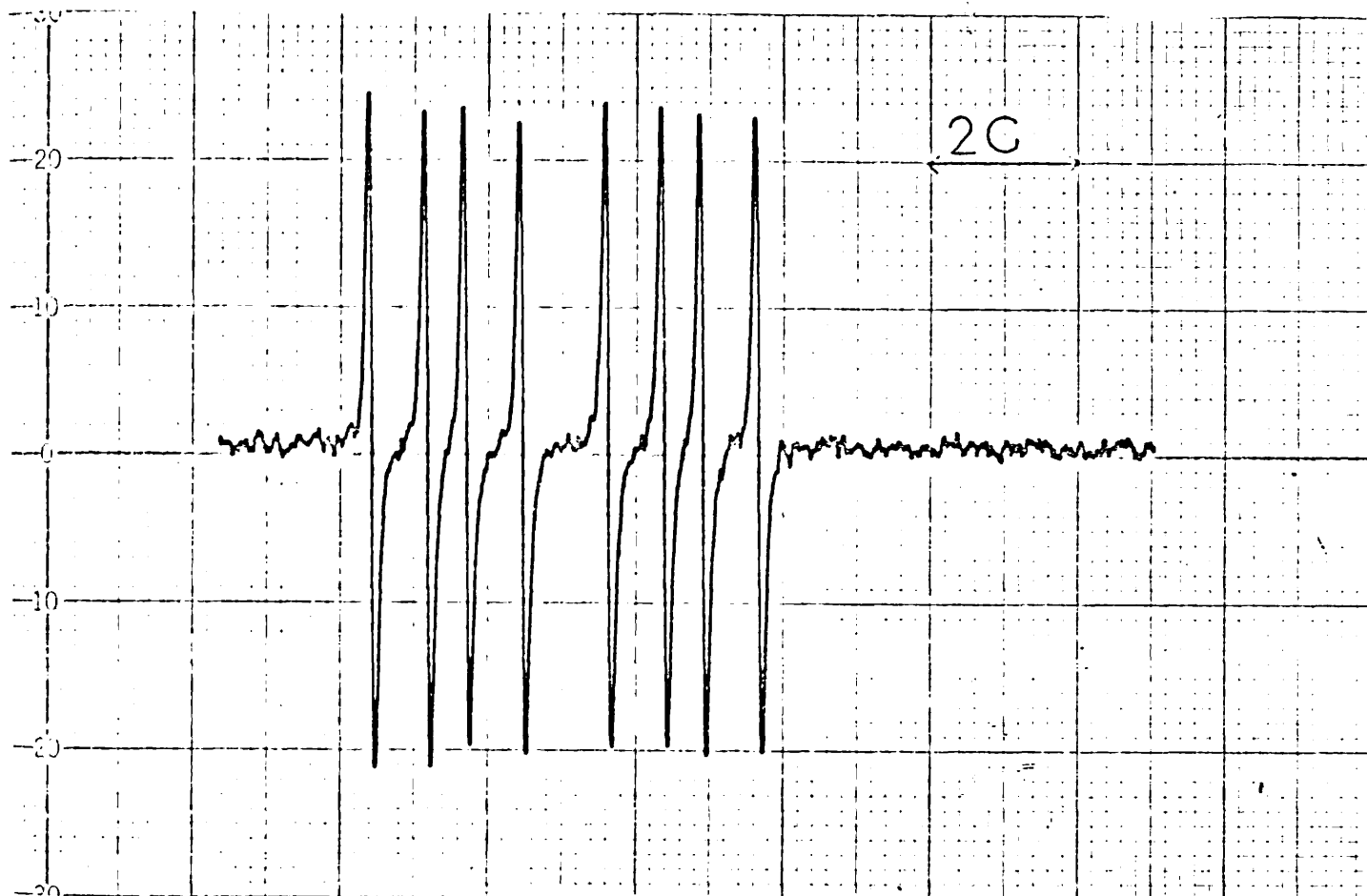
(9 electrons)

Hückel densities in parenthesis

The substituent effect on the coupling constants of the resorcinol is small when the substituents are on the plane of symmetry i.e. position 2. This can be seen from table that substituents such as CH_3 , NO_2 , COOH , COCH_3 at position 2 do not make a remarkable change on the coupling constants of the ring protons. (Table 15)

Table 15Experimental results for 2-substituted resorcinol

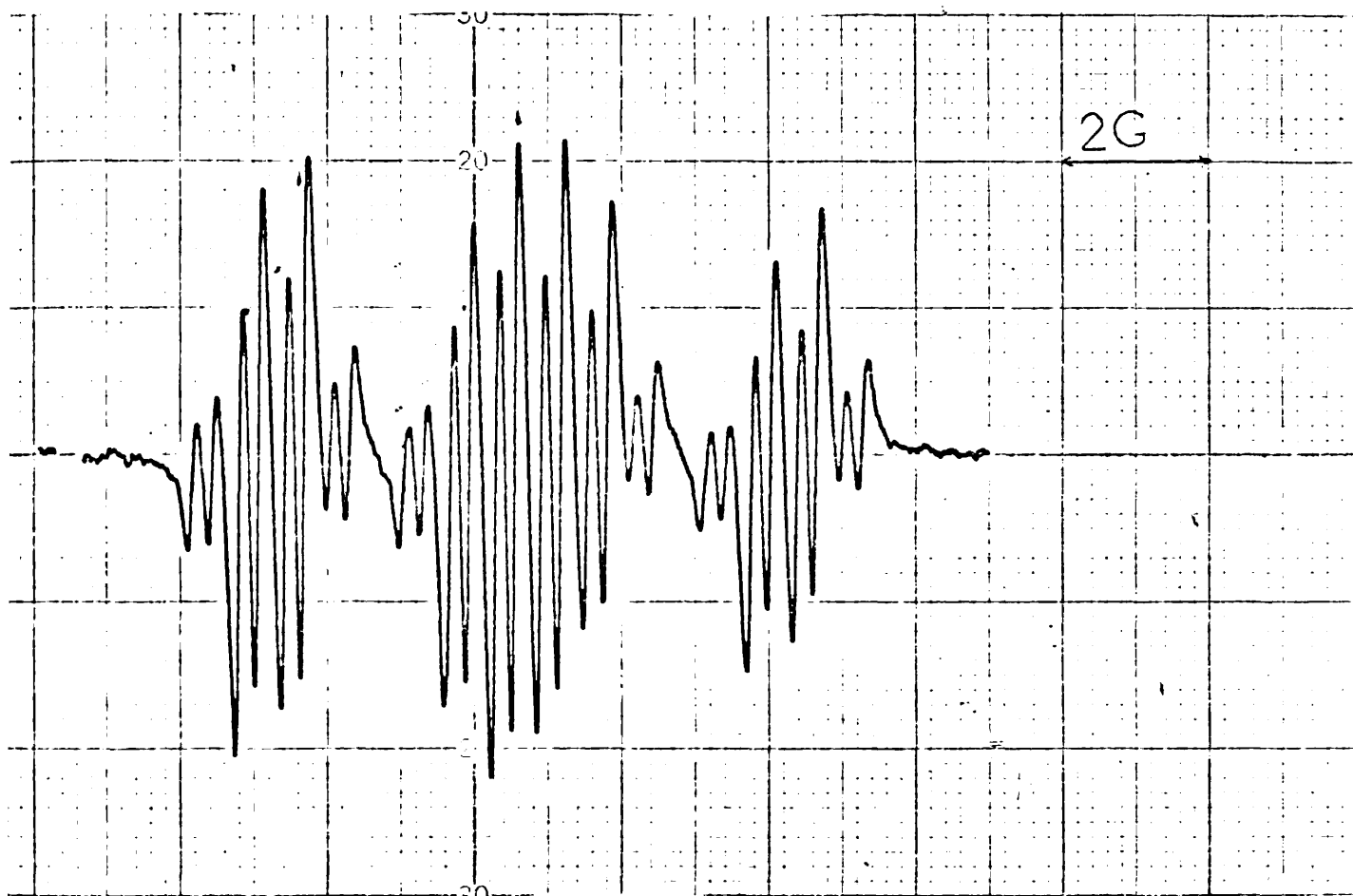
X	4	5
H	10.0	2.3
CH ₃	9.1	1.9
NO ₂	10.75	2.5
COOH	11.25	2.5
COCH ₃	10.4	2.6



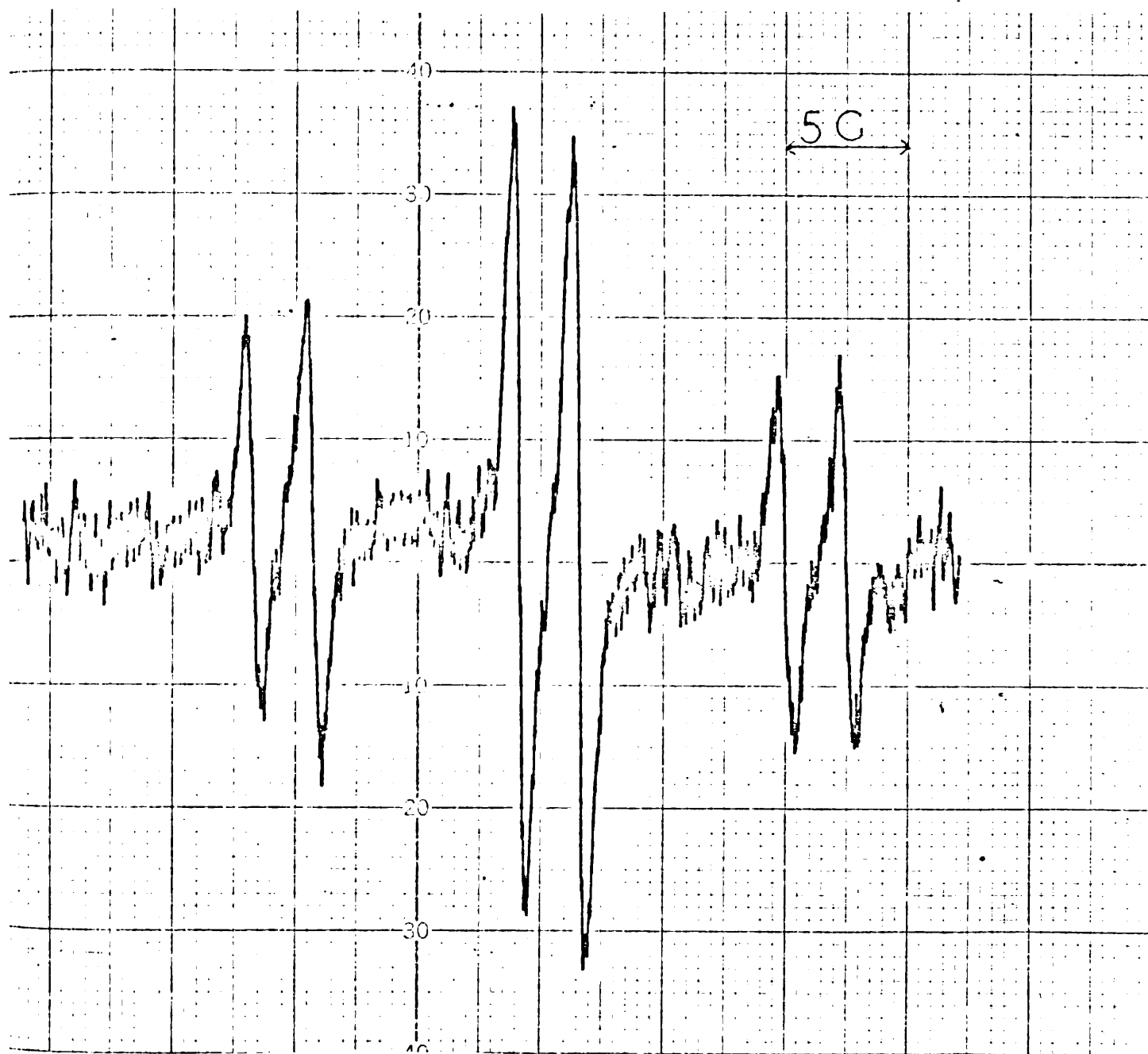
Radical from 4-Carboxycatechol



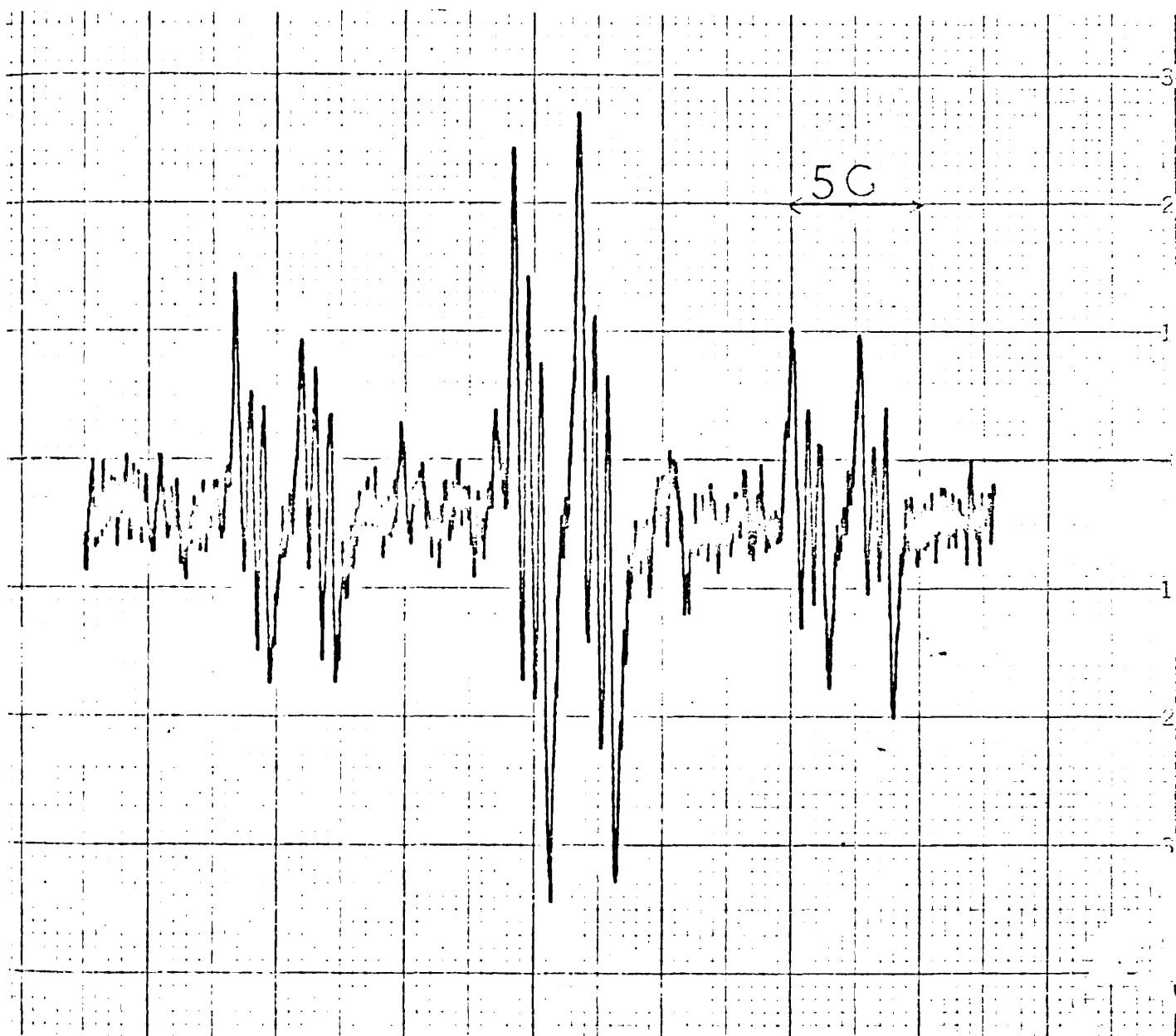
Radical from
4-Methylcatechol



Radical from
3-Methylcatechol

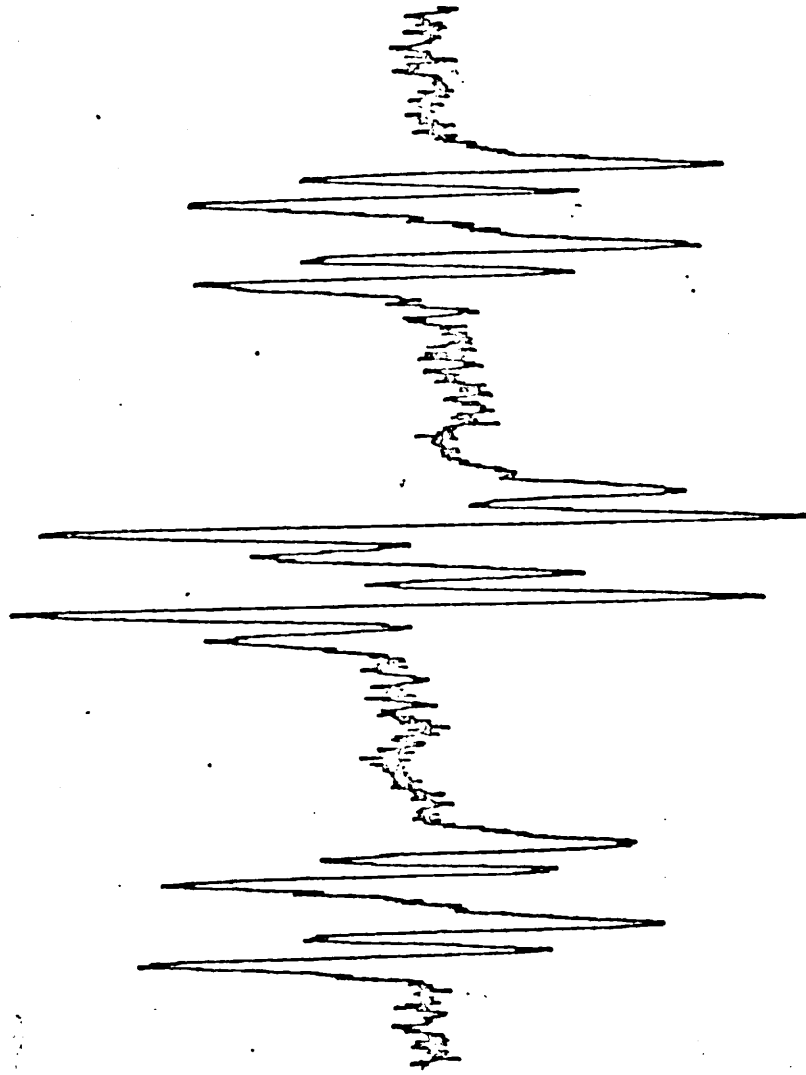


Radical from 2,6-Dihydroxybenzoic Acid

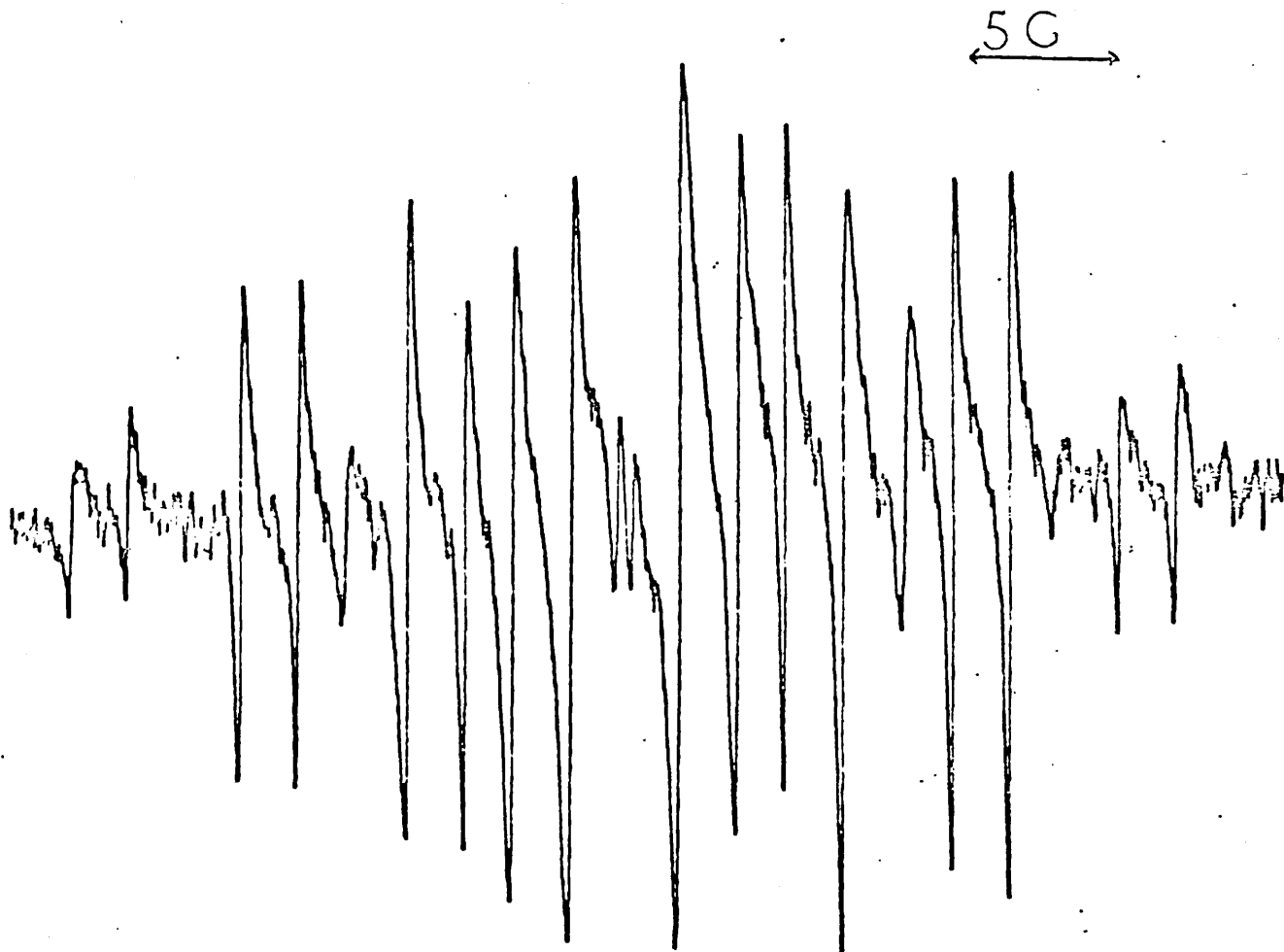


Radical from
2-Nitroresorcinol

5G

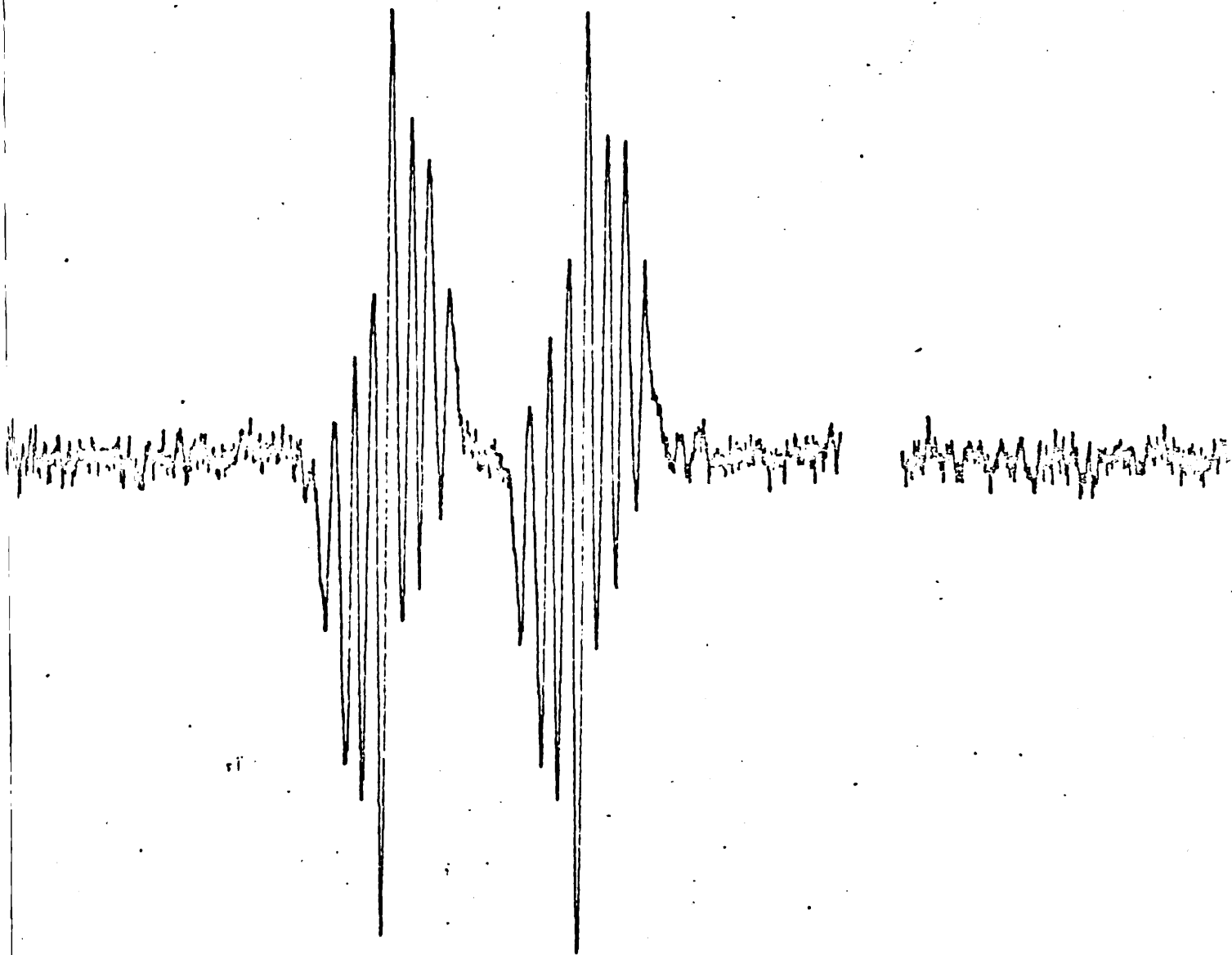


Radical from 2,6-Dihydroxyacetophenone Radical



Radical from
2-Methylresorcinol

5G



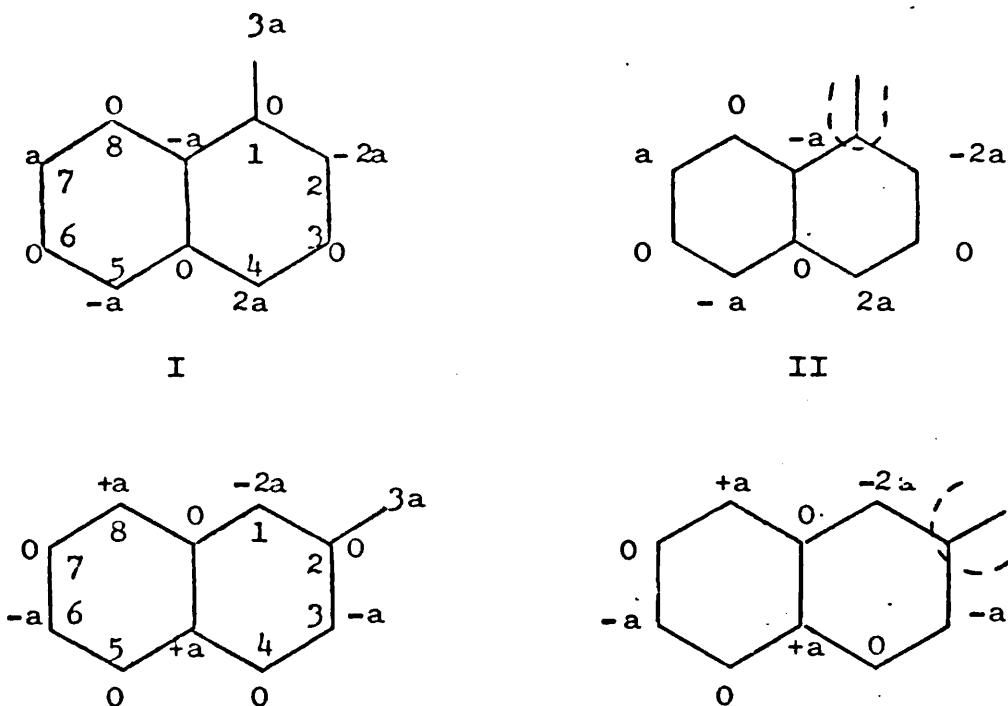
Radical from Pyrogallol

CHAPTER 5

Naphthoxyl Radicals

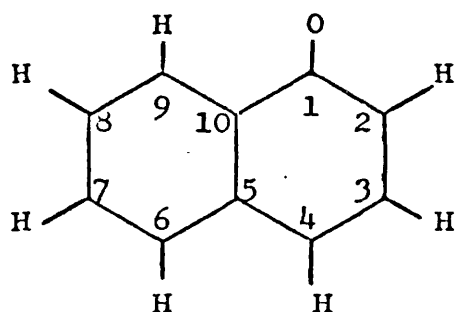
The e.s.r. spectra of both α and β naphthoxyl radicals were first obtained by Stone and Waters. But the signal-to-noise ratio was unfavourable and analysis was not possible. Dixon, Foster and Murphy⁵¹ obtained the e.s.r. spectra of these radicals by oxidation of naphthols by ceric ions and have been able to analyse them.

The assignments of these coupling constants are ambiguous without obtaining a set of data of substituted naphthoxyls. We were interested to see how far our theories, developed above, could be used to verify the assignments for these fused ring systems. In the first instance it is instructive to look at the simple Hückel theory for the corresponding benzyl type radical, (I), or even the π -electron radical formed by eliminating C_1 (II)

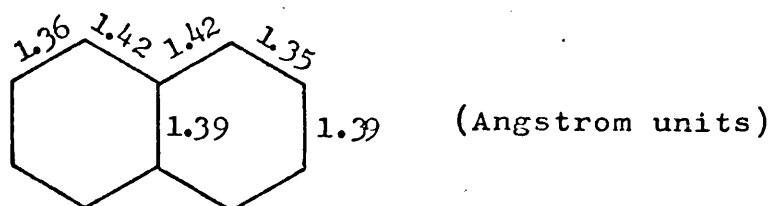


In either case the predicted odd electron densities have the same pattern. It is reasonable to expect negative spin densities when Hückel theory leads to prediction of zero. The main pattern obviously fits the experiments, for large splittings appear only where there are non-zero coefficients in the Hückel model above. However the exact distribution is not reproduced by the theory even allowing for negative spin densities especially in the case of a_3 in β -naphthoxyl which is in fact very small.

The presence of many observable negative spin densities means that we cannot expect very good results from Hückel theory, so now we should describe the result of some I.N.D.O. calculations. In the I.N.D.O. calculations on α and β naphthoxyl we varied the geometry by changing C-O and C-C bond lengths. The C-H bond length was kept at 1.08 \AA which is the same as we took for phenoxy. C-O was given the values 1.21 \AA and 1.30 \AA .

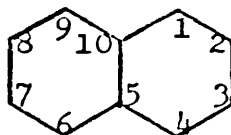


C_1-C_2 and C_2-C_3 bonds were also changed. Crystallographic data⁵² on naphthalene shows that the geometry of the molecule is not two regular hexagons, but that the geometry is as follows



This is why we chose the type of variations given in Table below.

I.N.D.O. calculation for naphthoxyl radical and some naphtho-
semiquinones



Naphthoxyl	r_H	r_O	$r_{1,2}$	$r_{2,3}$	$r_{9,10}$
α -	1.08	1.21	1.45	1.4	1.45
α -	1.08	1.21	1.45	1.39	1.39
α -	1.08	1.30	1.4	1.4	1.4
β -	1.08	1.30	1.4	1.4	1.4
1,2-semiquinone	1.08	1.30	1.4	1.4	1.4
1,4-semiquinone	1.08	1.30	1.4	1.4	1.4
2,7-semiquinone	1.08	1.30	1.4	1.4	1.4

Table continued over

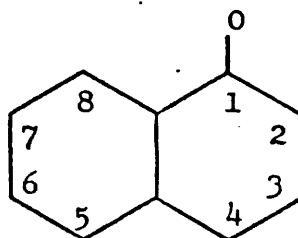
Naphthoxyl	a_1	a_2	a_3	a_4	a_6	a_7	a_8	a_9
α -		-9.11	5.7	-10.36	-5.2	3.66	-4.2	4.4
α -		-8.9	5.5	-10.5	-3.7	2.6	-3.3	3.0
α -		-6.9	3.8	-6.31	-2.95	2.28	-2.63	2.75
β -	-7.1		-4.3	3.52	2.61	-2.71	2.21	-3.08
1,2- semiquinone*			-2.24	.34	.116	.029	-.55	.79
1,4- semiquinone		-1.3	-1.3		.47	-.16	-.16	.47
2,7- semiquinone	-1.9		-1.92	1.17	-1.90		-1.90	1.17

* See Table 21 for experimental details.

Comparison of these calculated values with experimental values shows that, as with phenoxyl, they are not in good agreement.

Calculations for some of the semiquinone radicals are also in the table these coupling constants are not very close to those observed experimentally. The poor agreement again implies deficiencies in the general I.N.D.O. approach which is not reliable enough for what we wish to do i.e. to be able to predict hyperfine splittings in these class of compounds with reasonable confidence.

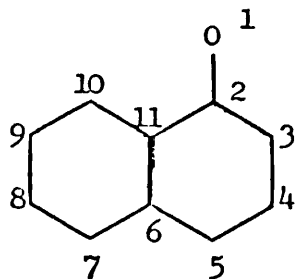
Next we decided to apply McLachlan's S.C.F. method to these radicals because it was so successful for phenoxyls.



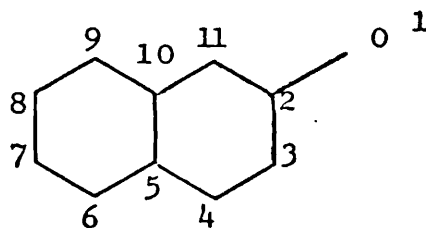
McLachlan's S.C.F. Method

Table 16

Different Parameters for α and β Naphthoxyl

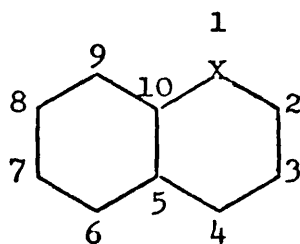


$\delta_0/\beta_{1,2}$	a_3	a_4	a_5	a_7	a_8	a_9	a_{10}
1.0/1.8	.362	-.101	.390	.118	-.036	.097	-.019
1.2/1.4	.294	-.072	.361	.127	-.026	.088	.012
1.2/1.6	.326	-.085	.378	.125	-.031	.093	0.0
1.9/1.3	.229	-.040	.345	.154	-.010	.081	.066

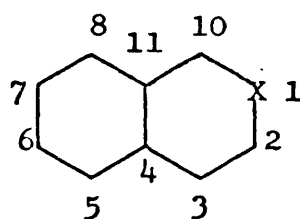


$\delta_0/\beta_{1,2}$	a_3	a_4	a_6	a_7	a_8	a_9	a_{11}
1.0/1.8	.086	-.038	-.038	.137	-.055	.156	.501
1.2/1.4	.021	.009	-.005	.135	-.050	.171	.446
1.8/1.3	-.039	.100	.066	.133	-.037	.214	.408
1.5/1.1	-.041	.105	.072	.126	-.034	.210	.387

Table 17

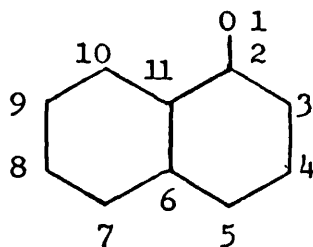
Parameters for α , β NaphthoxylInductive Models

δ_X	a_2	a_3	a_4	a_6	a_7	a_8	a_9
-1.5	.286	-.059	.400	.165	-.018	.097	.054
-1.2	.249	-.043	.380	.172	-.011	.090	.076
-1.8	.317	-.073	.414	.159	-.024	.101	.037



δ_X	a_2	a_3	a_5	a_6	a_7	a_8	a_{10}
-1.5	-.036	.093	.053	.156	-.047	.231	.470
-1.8	-.017	.065	.028	.163	-.053	.224	.510
-1.2	-.050	.125	.085	.144	-.037	.238	.431

Table 18

Heteroatom Model

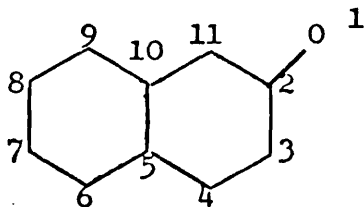
$\beta_{2,3}$	$\beta_{4,5}$	$\beta_{7,8}$	$\beta_{9,10}$	a_3	a_4	a_5	a_7	a_8	a_9	a_{10}
1	1	1	1	.244	-.048	.349	.147	-.015	.083	.052
1.3	1.3	1.3	1.3	.282	-.025	.260	.077	-.004	.064	.038
1.2	1.2	1.2	1.2	.207	-.052	.410	.154	.002	.047	.092
1.4	1.4	1.4	1.4	.290	-.020	.236	.061	-.002	.057	.032
1	1	1.2	1.2	.247	-.051	.357	.094	-.011	.079	.028
1	1	1.4	1.4	.248	-.054	.361	.059	-.009	.070	.012

<u>Experimental</u>	a_3	a_4	a_5	a_7	a_8	a_9	a_{10}
	.275	.058	.358	.083	.021	.083	0.0

Inductive Model

$\beta_{2,3}$	$\beta_{4,5}$	$\beta_{7,8}$	$\beta_{9,10}$	a_3	a_4	a_5	a_7	a_8	a_9	a_{10}
1	1	1	1	.286	-.059	.400	.165	-.018	.097	.054
1.2	1.2	1.2	1.2	.315	-.035	.341	.118	-.004	.085	.059
1.4	1.4	1.4	1.4	.334	-.014	.299	.089	.003	.075	.057
1	1	1.2	1.2	.292	-.062	.417	.109	-.013	.094	.031
1	1	1.4	1.4	.295	-.065	.428	.070	-.010	.084	.015
1.2	1.2	1	1	.300	-.031	.317	.177	-.008	.086	.094
1.4	1.4	1	1	.284	-.005	.242	.206	.001	.079	.146

Table 19



$$\delta_0/\beta_{1,2} = 1.6/1.3$$

Heteroatom Model

$\beta_{2,11}$	$\beta_{3,4}$	$\beta_{6,7}$	$\beta_{8,9}$	a_3	a_4	a_6	a_7	a_8	a_9	a_{11}
1	1	1	1	-.029	.076	.045	.135	-.042	.203	.418
1.2	1.2	1.2	1.2	.005	.033	.001	.148	-.042	.121	.353
1.3	1.3	1.3	1.3	.019	.017	-.010	.143	-.036	.085	.296
1.4	1.4	1.4	1.4	.039	.001	-.022	.140	-.029	.059	.266
1	1	1.2	1.2	.001	.051	.006	.133	-.039	.123	.412
1	1	1.4	1.4	.040	.024	-.012	.117	-.033	.071	.388

Experimental

a_3	a_4	a_6	a_7	a_8	a_9	a_{11}
.048	0.0	.048	.180	.040	.143	.358

Inductive Model

$\beta_{2,11}$	$\beta_{3,4}$	$\beta_{7,6}$	$\beta_{8,9}$	a_3	a_4	a_6	a_7	a_8	a_9	a_{11}
1	1	1	1	-.036	.093	.053	.156	-.047	.231	.470
1.2	1.2	1.2	1.2	-.003	.057	.011	.183	-.051	.153	.416
1.4	1.4	1.4	1.4	.040	.014	-.024	.189	-.037	.077	.310
1	1	1.2	1.2	-.004	.072	.011	.159	-.045	.145	.479
1	1	1.4	1.4	.039	.044	-.011	.144	-.039	.088	.464
1.2	1.2	1	1	-.030	.077	.065	.176	-.055	.250	.408
1.4	1.4	1	1	-.025	.061	.082	.200	-.063	.269	.336

Using the same resonance integral for all the C-C bonds did not produce expected result.

Variations of coulomb and resonance integral of oxygen for both α and β naphthoxyl radicals are shown in Table 16. Satisfactory features are emerged, and although we were not completely happy with the result it can be seen that they all give negative spin densities at positions 3 and 6 for α -naphthoxyl and in some cases at position 8 too, (eg. when $\delta_0 = 1.0$ and $\beta_{CO} = 1.8$), but for β -naphthoxyl the patterns of negative spin densities is different for different parameterization.

We came to conclusion that a change in the geometry of the molecule should be investigated, so we again fixed the O parameters at $\delta_0 = 1.6$ and $\beta_{CO} = 1.3$. The bond lengths between C₁-C₂, C₃-C₄, C₅-C₆ and C₇-C₈ for both α and β - naphthoxyl were effectively varied by changing the resonance integrals between these carbon atoms. These changes were carried out in both the heteroatom and the inductive model.

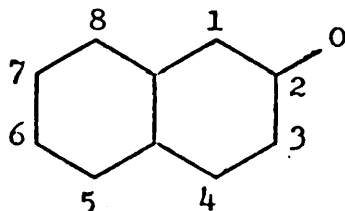


The experimental coupling constants shown in Tables 18 and 19.

In α -naphthoxyl radical gives most of the spin densities at the first ring i.e. giving a high value in p-position and smaller at ortho position to oxygen, as expected the meta

position (3) is small and further more, the proton couplings in the second ring are all small, our theoretical calculations, show the same trend over the two rings thus giving high spin density at p-position and second highest at ortho position in the first ring in both models. There seems to be no particular advantage in changing the geometrical model.

In β -naphthoxyl the high spin densities are at 1, 6 and 8 positions according to experiment.



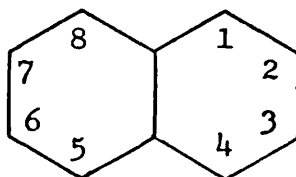
In all cases the calculated large spin densities appear on the positions 1, 6 and 8 too. However the agreement between the relative magnitudes of the coupling constants observed and those calculated are not very convincing so that we could not expect any of the models tried to give really reliable results for other naphthalene compounds.

For inductive models in our calculations we chose -1.5 for oxygen value i.e. the same as for phenoxyl. Other values viz. -1.8 and -1.2 were examined, they all produce similar patterns for spin density. (Table 17)

We have also calculated the spin distributions in the semiquinones using both heteroatom and inductive models,

the results are shown in Tables 20 and 21. For fused ring systems our calculations do not seem to reproduce results in good agreement with experiment.

Table 20

Calculated spin densities for naphthosemiquinone radicals

$$d_0 = 1.6$$

$$\beta_{CO} = 1.3$$

Heteroatom Model

	1	2	3	4	5	6	7	8
1,2			-.049	.192	.047	.033	.021	.059
1,4		.125	.125		.047	.025	.025	.047
2,6	.221		-.027	.094	.221		.027	.094

Inductive Model

	1	2	3	4	5	6	7	8
1,2			-.012	.266	.052	.039	.039	.051
1,4		.214	.214		.041	.031	.031	.041
2,6	.279		-.021	.103	.279		-.021	.103

Table 21Experimental spin densities in naphthosemiquinone radicals

	1	2	3	4	5	6	7	8
1,2 [*]			.014	.148	.009	.047	.004	.043
1,4 [†]		.108	.108		.021	.019	.019	.021
2,6 [‡]	.140		.023	.043	.140		.023	.043

* See Ref. 18

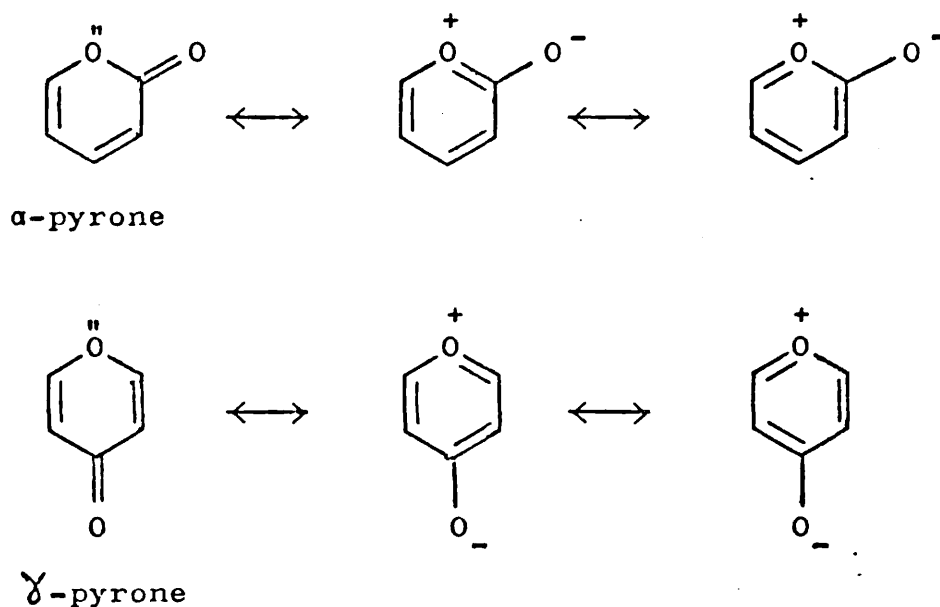
† See Ref. 65

‡ See Ref. 66

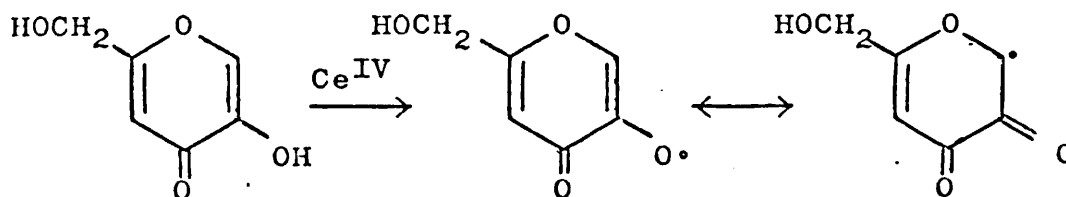
CHAPTER 6

Radicals from naturally occurring hydroxypyrones

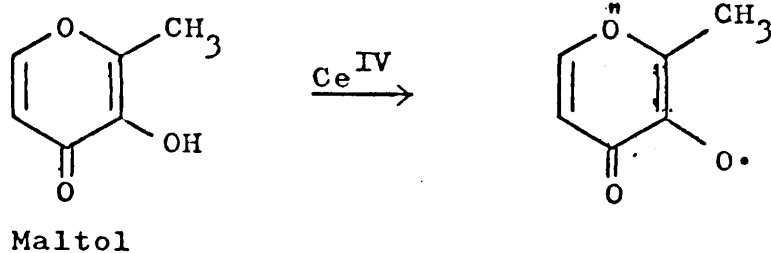
During the course of investigation of substituted phenoxy radicals discussed in Chapter 2 and the theories which were described in Chapter 3 we were able to rationalise the coupling constants observed in their e.s.r. spectra. This understanding lead us to predict spin densities in other types of oxygenated radicals such as those derived from hydroxylated pyrones.



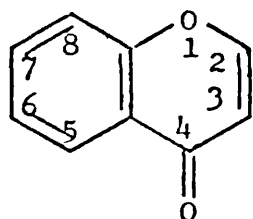
These compounds occur widely in nature, the monocyclic derivatives such as kojic acid and maltol being found in certain fungal metabolites (1).



Kojic acid

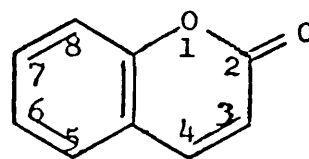


Benzopyrones such as chromones, coumarins and flavones are distributed throughout the plant kingdom.²



γ -chromone

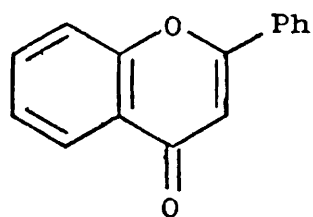
γ -benzopyrone



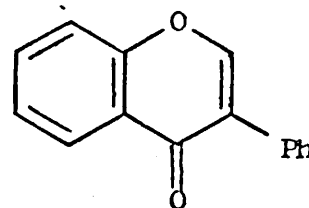
α -benzopyrone

α -chromone

(coumarin)



α -flavone



isoflavone

Kojic acid exhibits a number of phenolic properties¹ for it is strongly acidic and gives a characteristic colour with ferric

chloride. It was not surprising, therefore, that these oxygen hetrocyclic compounds could also be oxidised by cerium IV, or by hydroxyl radicals generated in the Ti^{3+}/H_2O_2 system⁶ to give radicals analogous to phenoxyl.

Assignment of coupling constants

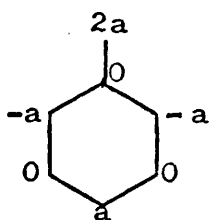
Some of the coupling constants are easily assigned because of the siting of the substituents in our chosen examples. However, in order to make a more complete assignment it is necessary to turn to theory as a guide, we have previously been able to account for the hyperfine splittings in a variety of phenoxy radicals by McLachlan's S.C.F. theory, using as oxygen parameters $a_O = a_C + 1.6\beta_{CC}$ and $\beta_{C-O} = 1.3\beta_{CC}$. The theoretical results given in Table ?? were calculated using this method, and the agreement with experiment is encouraging, considering the restricted class of compounds for which this semi-empirical theory was developed.

The general pattern of spin densities in radicals related to phenoxyl can often be predicted from two very simple M.O. models, both involving an odd electron in a non-bonding orbital.^{62,63}

In the first model 'A', the extranuclear oxygen atoms are treated effectively as carbon atoms, and in the second 'B', we consider the fragment left after removing these oxygen atoms and the adjacent carbons,⁶⁴ the model systems for phenoxyl, the NBO coefficients are:-

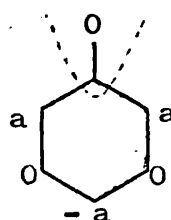


Phenoxyl



Model A

$$a = \frac{1}{\sqrt{7}} \quad (\text{benzyl})$$



Model B

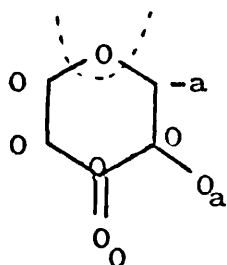
$$a = \frac{1}{\sqrt{3}}$$

(pentadienyl)

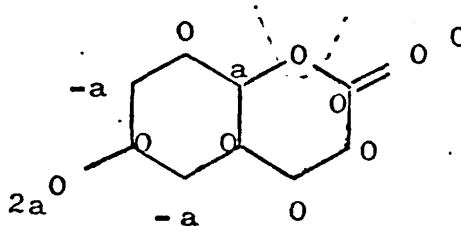
Both models give the same pattern of N.B.O. coefficients and it is assumed where zero's occur near to large spin densities in the theory, appropriate (smaller) negative spin densities will result in practice.

Application of this crude theory often gives better, as well as more rapid, predictions than much more sophisticated calculations. There have, of course, been other similarly successful applications of simple M.O. theories.³³

It is an illustration of the usefulness of these models that we did correctly forecast the number and positions of relatively high spin density in most of the radicals in Table 2.2 the best match with experiment was obtained when the models were modified by excluding the nuclear oxygen.



$$a = 1/\sqrt{2}$$



$$a = 1/\sqrt{7}$$

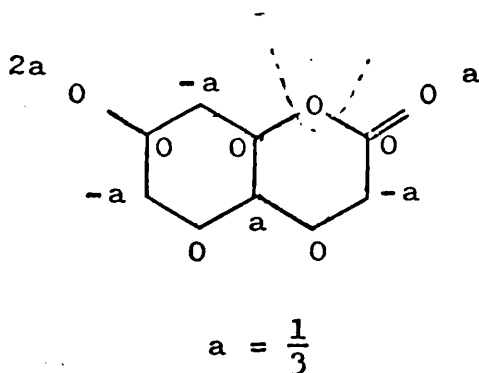
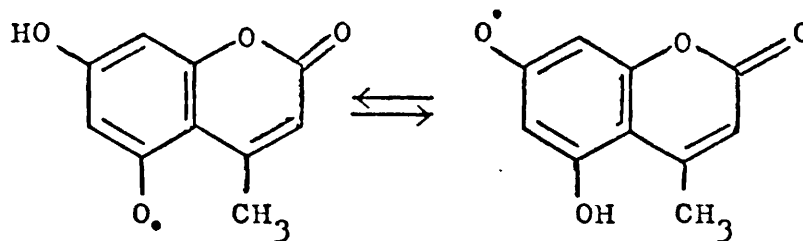


Table 22 shows experimental and calculated values of hyperfine coupling constants, calculated values are in square brackets. Two sets of calculations were carried out for 5,7-dihydroxyflavone (chrysin) and 5,7-dihydroxy-4'-methoxyisoflavone (biochanin A). The oxygen parameters used at C_5 and C_7 were (a) $\alpha_0 = \alpha + 1.6\beta$, $\beta_{CO} = 1.3\beta$ (i.e. oxygens at C_5 and C_7 , both not protonated) and (b) at C_5 $\alpha_0 = \alpha + 1.6\beta$, $\beta_{CO} = 1.3\beta$ at C_7 $\alpha_{OH} = \alpha + 1.5\beta$, $\beta_{C-OH} = 0.6\beta$. (i.e. C_7 oxygen protonated).

5,7-Dihydroxy-4-methyl coumarin, the calculated values in the table are from equilibrium between radicals protonated at 5- or 7- oxygens.

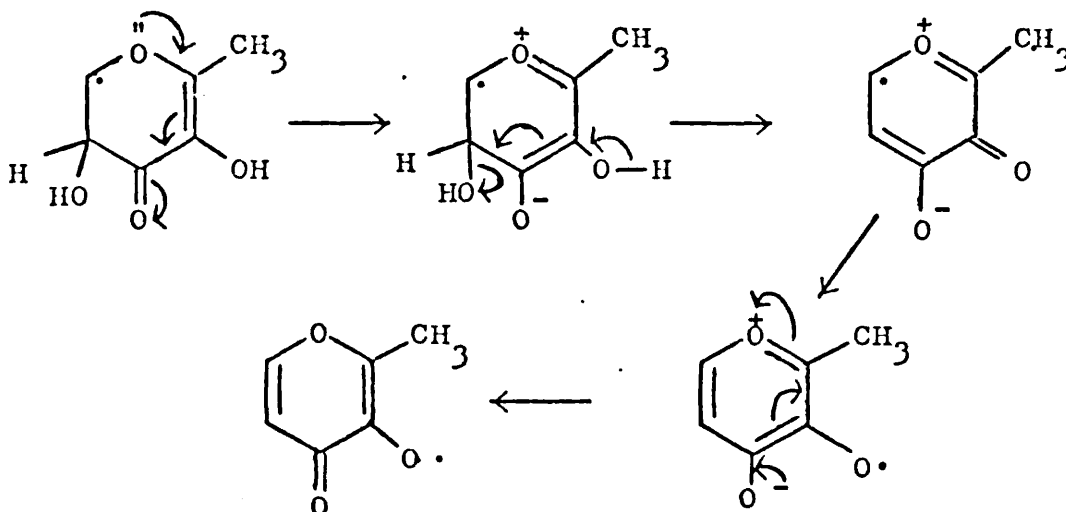


Results from the hydroxy-flavone derivatives were unexpected in the sense that two large coupling constants were observed where by analogy with the radicals from resorcinol, one would have expected only one. However, comparison with the result from hesperidin suggests that under the strong acidic solutions, the oxygen attached to C_7 must be preferentially protonated. This was confirmed by calculation, using parameters found previously to be suitable for phenoxy group. i.e.

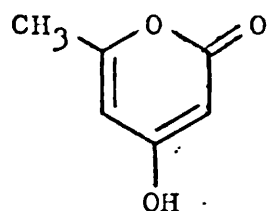
$$\alpha_{OH} = \alpha_C + 1.5\beta_{C-OH}, \quad \beta_{C-OH} = 0.6\beta_{C-C}.$$

Reactions using hydroxyl radical

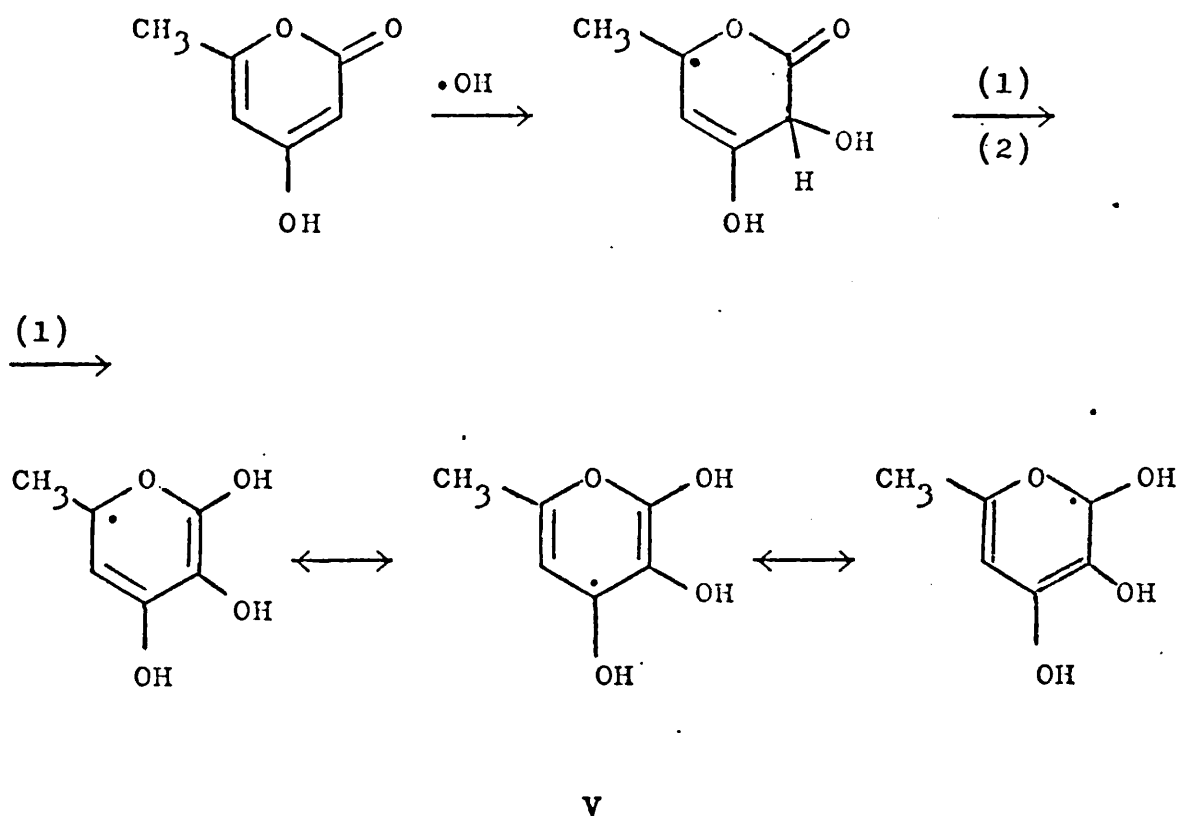
A largely unanalysable mixture of radicals was obtained when kojic acid was present during the Ti^{3+}/H_2O_2 reaction. In contrast to this, a pure spectrum was obtained when maltol was substrate, for in this case the most reactive position is blocked and $\cdot OH$ will add to the ring followed by water elimination giving:-

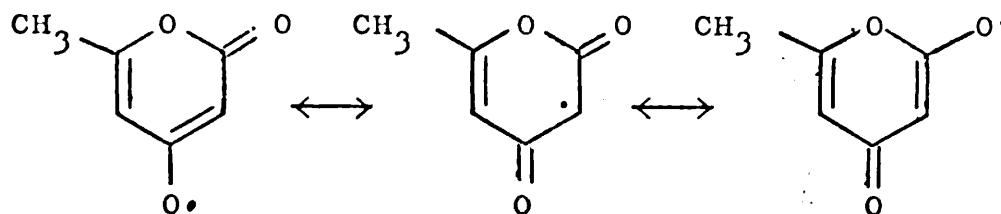


Similarly there was a remarkably intense spectrum when the substrate was 4-hydroxy-6-methyl pyran-2-one.



The coupling constants observed were 0.075 mT (doublet) and 0.645 mT (quartet) and we ascribed the spectrum to the novel radical (V). We suggest that it arises from initial addition of $\cdot\text{OH}$ followed by rapid enolisation in preference to acid-catalysed loss of water.⁶⁰



(2)
→

VI

The McLachlan-type calculations, using the parameters already given for $\cdot\text{OH}$ and O and neglecting the effects of the methyl group, are given in Table 23 and it is clear that whereas the predicted values for V are almost exactly the same as those observed, those for VI do not resemble the experimental splitting at all.

Table 22.

Coupling constants in radicals by one electron oxidation of pyrone derivatives

Starting material	Coupling constants ($10^{-4}T$)							
	a_2	a_3	a_4	a_5	a_6	a_7	a_8	
5-Hydroxy-2(hydroxymethyl)-4H-pyran-4-one (kojic acid)	$a_{CH_2} = 1.38$ (-2.0)	0.35 (0.63)			13.2 (-7.4)			
3-Hydroxy-2-methyl-4H-pyran-4-one	$a_{CH_3} = 11.75$ (-7.4)			0.25 (0.63)	1.38 (-2.0)			
7-Hydroxy-coumarin (umbelliferone)		5.6 (-8.0)	1.9 (1.9)	2.1 (0.63)	5.6 (-3.3)		6.8 (-6.8)	
7-Hydroxy-4-methyl coumarin		5.6 (-8.0)	$a_{CH_3} = 1.9$ (1.9)	1.9 (0.63)	5.6 (-3.3)		6.3 (-6.8)	
6-Hydroxy-4-methyl coumarin		0.4 (0.4)	$a_{CH_3} = 0$ (-0.66)	5.2 (-7.8)		7.3 (-2.0)	1.1 (-1.2)	
5,7-Dihydroxy-flavone (chrysin)		1.0 (2.4)			8.2 (-5.2)		11.25 (-15.1)	
		(-2.0)*			(-8.7)*		(-13.0)*	

Table 22 cont.

Starting material	Coupling constants (10^{-4}T)							
	a_2	a_3	a_4	a_5	a_6	a_7	a_8	
3',5,7-Trihydroxy-4'-methoxyflavone 7-rhaminosido glucoside (hesperidin)		1.5 (-2.0)		9.0 (-8.7)			11.5 (-13.0)	
5,7-Dihydroxy-4'-methoxy isoflavone (biochanin A)	0.0 (0.2) (-0.3)*			7.8 (-5.52) (-8.7)*			10.75 (-15.1) (-13.0)*	
7,8-Dihydroxy-4-methyl coumarin (4-methyl daphnetin)		0.0 (-0.8)	$a_{\text{CH}_3} = 0.0$ (0.06)	6.6 (-5.16)	1.3 (1.4)			
6,7-Dihydroxy-4-methyl coumarin (4-methyl-aesculetin)		2.4 (-2.22)	$a_{\text{CH}_3} = 0.8$ (0.24)	2.4 (-2.9)			0.0 (0.8)	
6,7-Dihydroxy-coumarin (aesculetin)		2.62 (-2.22)	1.0 (0.24)	2.62 (-2.9)			0.25 (0.8)	
5,7-Dihydroxy-4-methyl coumarin		5.45 (-6.0)**	$a_{\text{CH}_3} = 1.30$ (1.2)**	4.25 (-3.5)**			10.5 (-11.2)**	

Table 22 cont.

Calculated values are in square brackets.

'Q' value for methyl protons is taken to be the same as that for aromatic protons but is of opposite sign ($Q_H = -30$).

* Values calculated for the radical with the 7-oxygen protonated.

** Values calculated for equilibrium between radicals protonated at 5- or 7-oxygens.

Table 23

Comparison of calculations with results of oxidation
of 4-hydroxy-6-methyl pyran-2-one

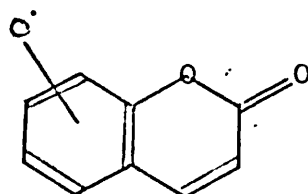
	<u>Coupling constants ($10^{-4}\tau$)</u>		
	<u>a_3</u>	<u>a_5</u>	<u>$a^{\text{I}}_{\text{CH}_3}$</u>
Experimental	0*	0.75*	6.55
Calculation for V		1.7	7.2
Calculation for VI	17.6	3.3	3.5

* These are of course ambiguous

I $Q_{\text{CH}_3} = -Q_{\text{H}}$ in the calculations

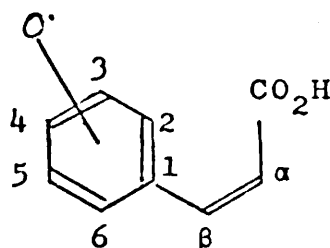
Radicals derived from hydroxycinnamic acid

In our studies of the e.s.r. spectra of radicals (I) from hydroxycoumarins we were able to account for the spin distribution by considering the radicals



I

as if there were no connection between the annular oxygen and the benzenoid ring. From the theoretical viewpoint, then, it was as if the heterocyclic opened and we were dealing with radicals from hydroxycinnamic acids (II).



II

However, in (I) we would expect the two rings to be planar whereas in cinnamic acid itself we would expect, e.g. from crystallographic data,⁶⁸ that there would be a small angle of twist (Ca 20°) about the C₁-C_β bond. We decided to investigate this possibility, both for its intrinsic interest and in order to confirm that we had indeed previously observed radicals

of type I. Provided that certain technical difficulties can be overcome e.s.r. is an ideal tool to use in this type of problem, for in the actual radicals of type II, the delocalisation of spin into the side chain will be very sensitive to the dihedral angle θ , i.e. the angle between the nodal plane of the benzenoid ring and that of the double bond.

Experimental results are in Table 24.

McLachlan-type calculations

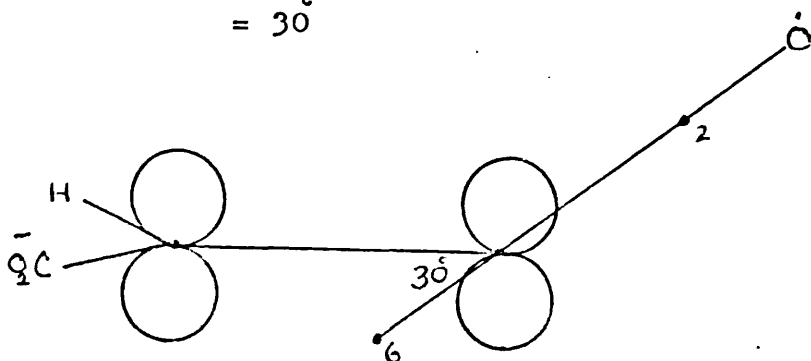
As we have previously found that a straight forward application of McLachlan's simplified S.C.F. theory accounted well for the coupling constants in a wide variety of phenoxy radicals if we used as oxygen parameters $\alpha_O = \alpha_C + 1.6\beta$, $\beta_{CO} = 1.3\beta$. This theory also gave good results for oxygen heterocyclic systems discussed in Chapter 6 so we expect that it could be applied successfully to these radicals too.

Since the double bond is significantly shorter than the bond length in benzene we took a resonance integral of 1.2β and the π -resonance integral for the C_1-C_β bond was varied, which is, in effect equivalent to varying the angle of twist. Table 25 gives the results for one radical, and similar calculations were carried out for all other radicals. No account was taken of the carboxyl group. The best overall fit was obtained with a value of 0.5β for the variable integral. No significant changes in the results came from including the

effects of hyperconjugation with the vinyl α -bond system. Taking Q values of 30 i.e. $Q_H = -30G$ and $Q_{CH_3} = +30G$. The calculations also gave an angle of about 30° . i.e. for ortho isomer

$$a_\alpha = 0.027 + 0.693 \times 2\sin^2 = 0.38$$

$$= 30^\circ$$



The theory was used for assignments of the hyperfine splittings in the radicals considered. However we feel that it is not fine enough for us to be able to calculate small differences in the dihedral angle with any degree of confidence. As far as we can tell the dihedral angle is not significantly affected by an adjacent oxygen atom. However a methyl group attached to the β -carbon atom, does have a very large effect and we deduce that there must be a dihedral angle of about 60° in these cases.

Table 24.

E.S.R. parameters for radicals obtained from hydroxycinnamic acids

Substituents	a ₂	a ₃	a ₄	a ₅	a ₆	a _α	a _β
2-OH	(a) 5.4 (5.5)	5.4 (5.5)	1.6 (-1.4)	9.1 (9.1)	2.1 (-2.3)	2.6 (2.0)	3.8 (-3.6)
3-OH	(a) 6.4 (6.1)		7.4 (7.0)	2.0 (-2.0)	10.4 (10.4)	0.6 (0.0)	0.85 (0.80)
4-OH	(a) 1.7 (-1.5)	5.4 (5.85)		5.4 (5.85)	1.7 (-1.5)	3.1 (2.6)	6.4 (-4.7)
3,4-(OH) ₂	(a) 1.75			3.5	0.15	2.45	4.8
	(c) 0.15 (0.30)			1.35 (0.63)	2.75 (3.6)	1.2 (0.8)	2.45 (-1.9)
3-OH-4-OCH ₃	(a) 3.2 (3.3)		a _{OCH₃} = 1.9	1.9 (2.6)	8.0 (8.3)	0.0 (0.3)	0.0 (0.0)
2,4-(OH) ₂	(b)*	3.5 (3.7)		9.0 (8.5)	2.0 (-2.3)	3.25 (2.6)	4.75 (-4.8)
2,3,4-(OH) ₃ -β-CH ₃	(c)			0.8	5.4	0.0	a _{CH₃} = 0.0
2,4,5-(OH) ₃	(c)	0.45 (-1.35)			1.35 (0.8)	1.9 (1.1)	2.9 (-3.4)

* Average values, assuming rapid proton exchange.

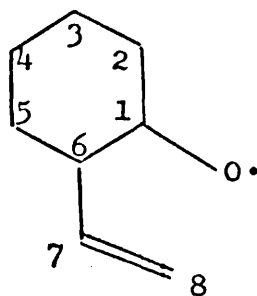
Negative of the calculated values in parenthesis.

(a) Oxidation by Ce^{IV} in acid solution. (b) Oxidation by Fe^{III} in alkaline solution. (c) Autoxidation in H_2O

aqueous alkali.

Table 25

Theoretical results for the radical from 2-hydroxycinnamic acid

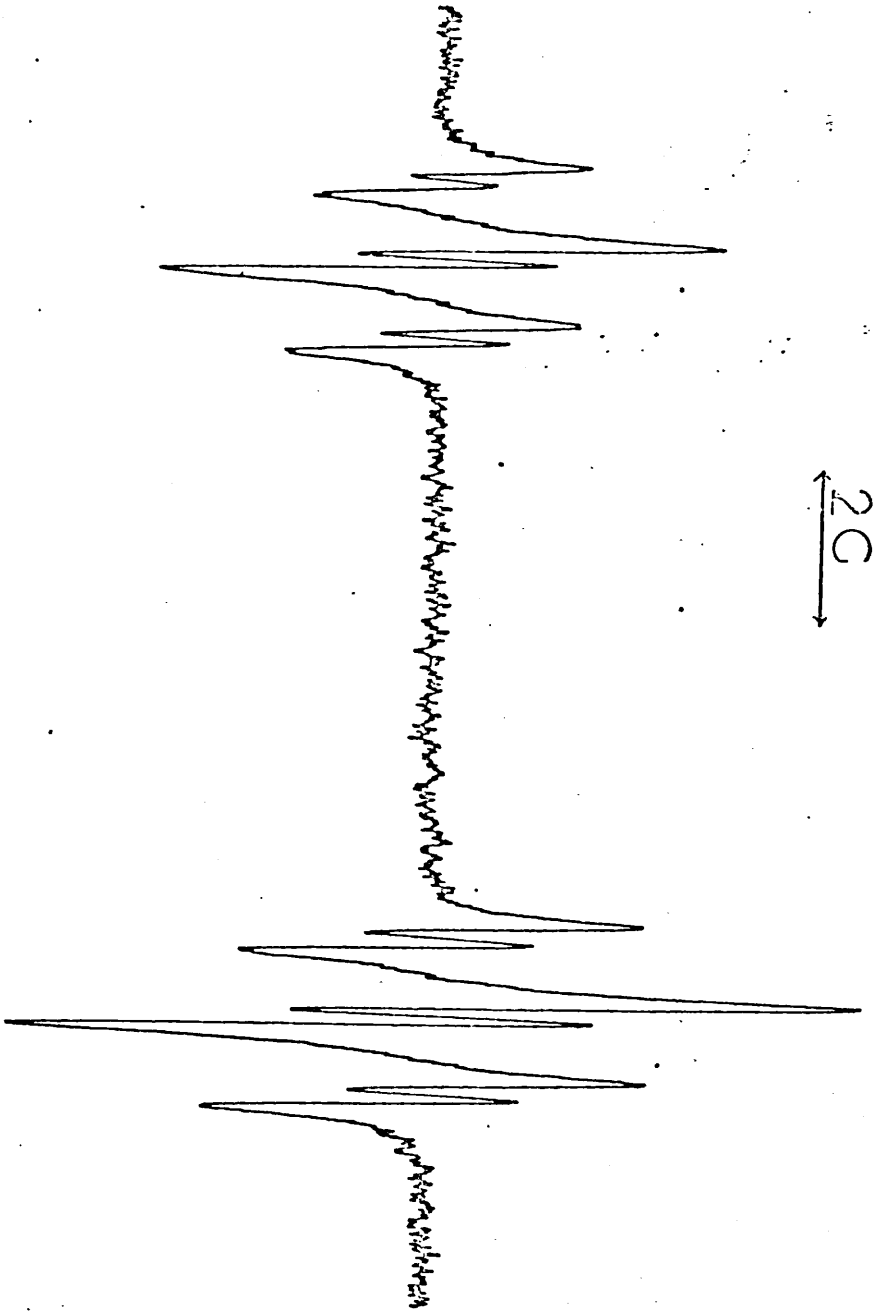


$\beta_{67/\beta}$	a_2	a_3	a_4	a_5	a_7^*	a_8
0.3	6.2	-1.7	9.7	-2.1	-3.3	0.72
0.5	5.5	-1.4	9.1	-2.3	-3.7	2.0
0.7	4.6	-0.9	8.2	-2.4	-4.0	4.0
Expt.	5.4	(-)1.6	9.1	(-)2.1	(-)3.8	2.6

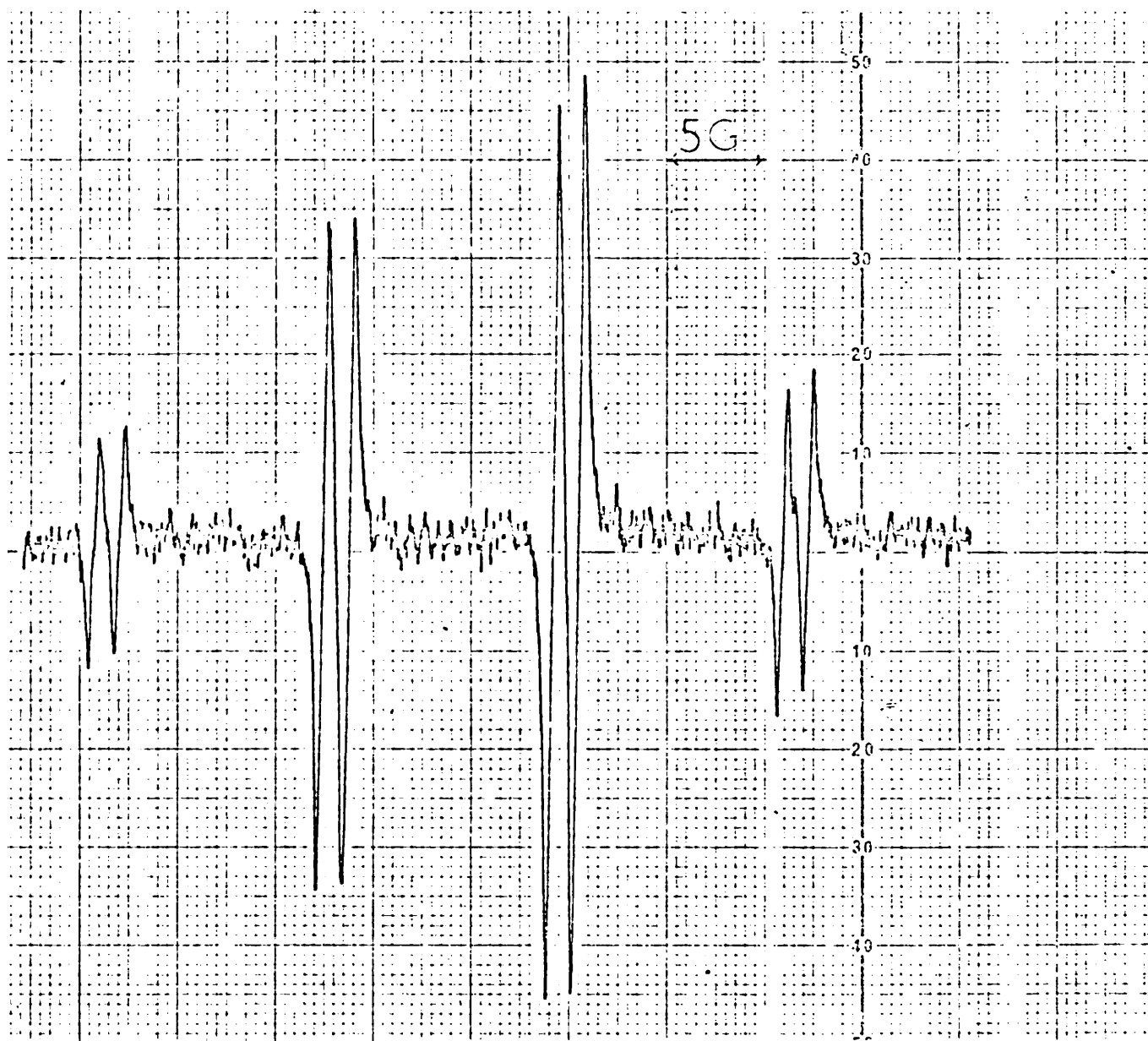
* calculated in each case for dihedral angle of 30°

using $Q_{CH_3} = 3.0$ $\beta_{78} = 1.2\beta$

2G

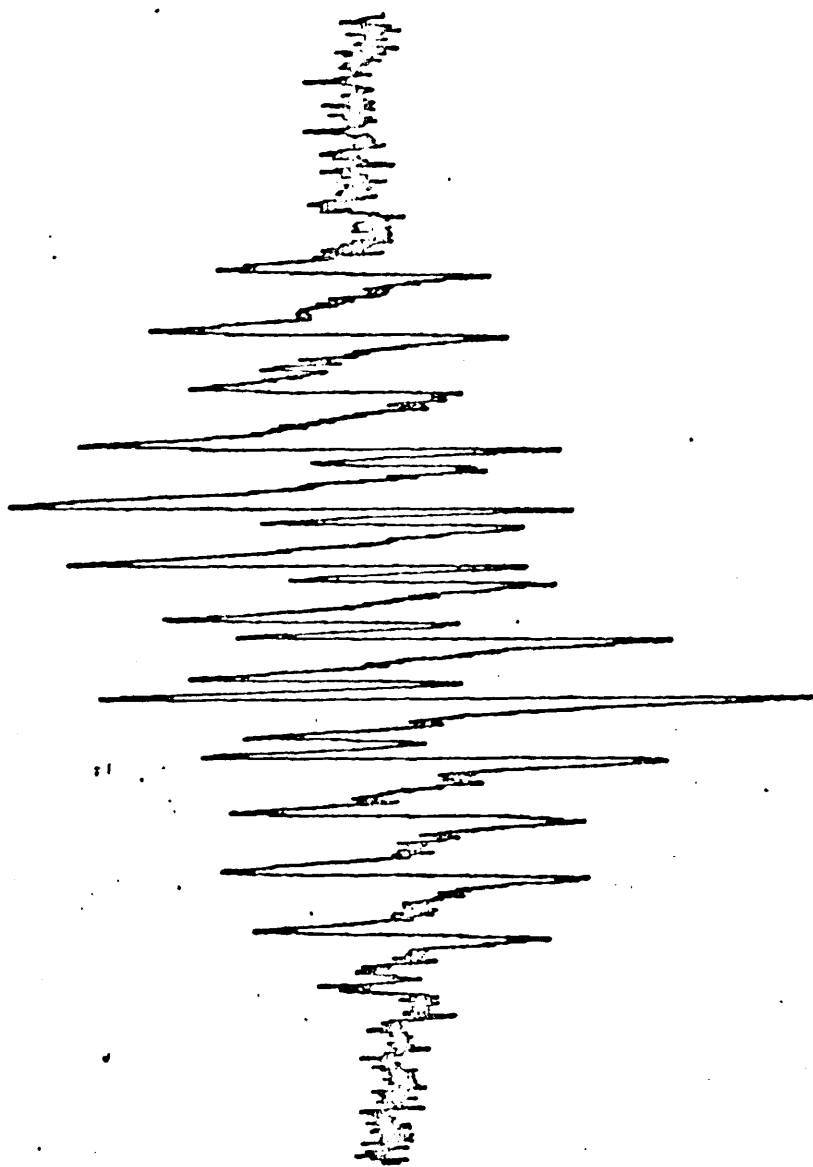


radical from kojic acid



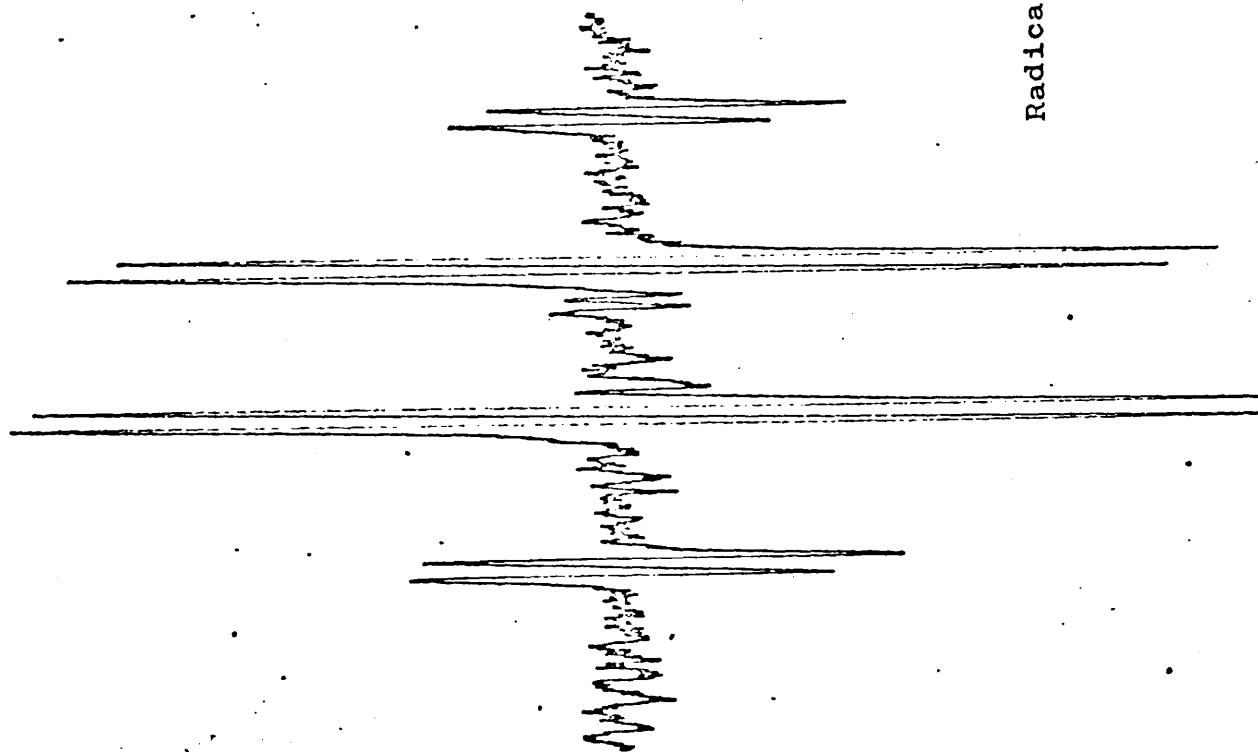
Radical from Maltol

5C



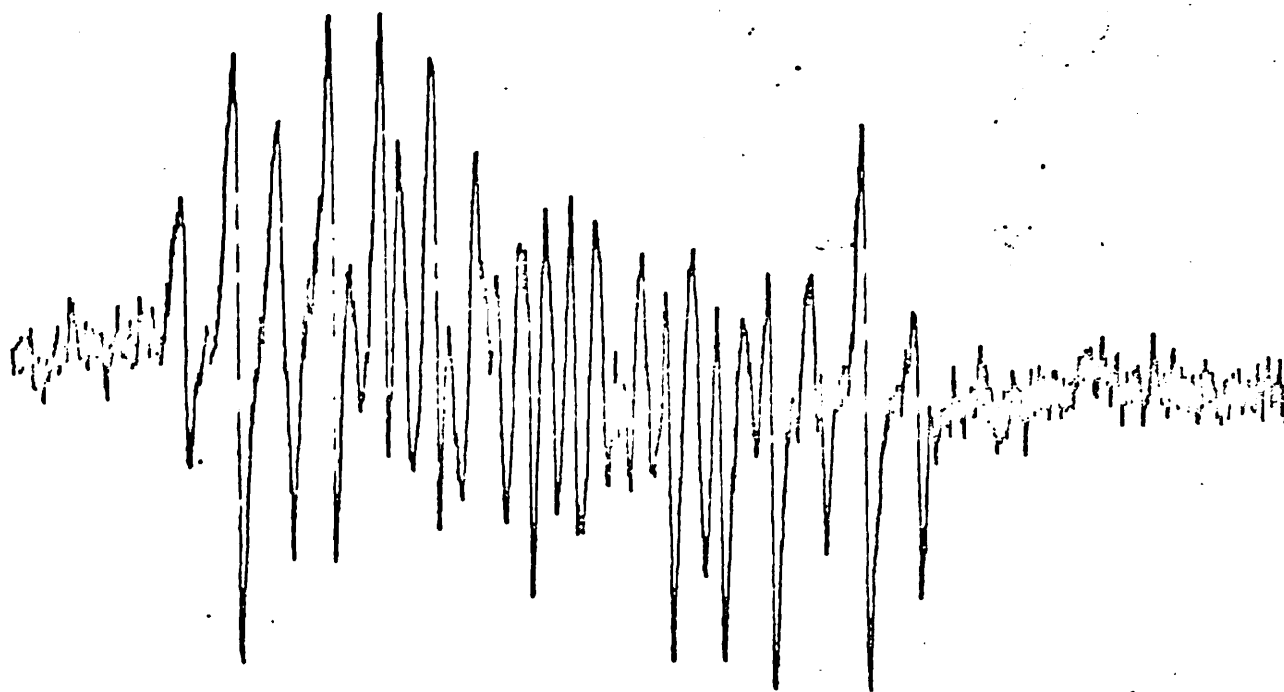
Radical from 7-Hydroxy-4-methylcoumarin

5G



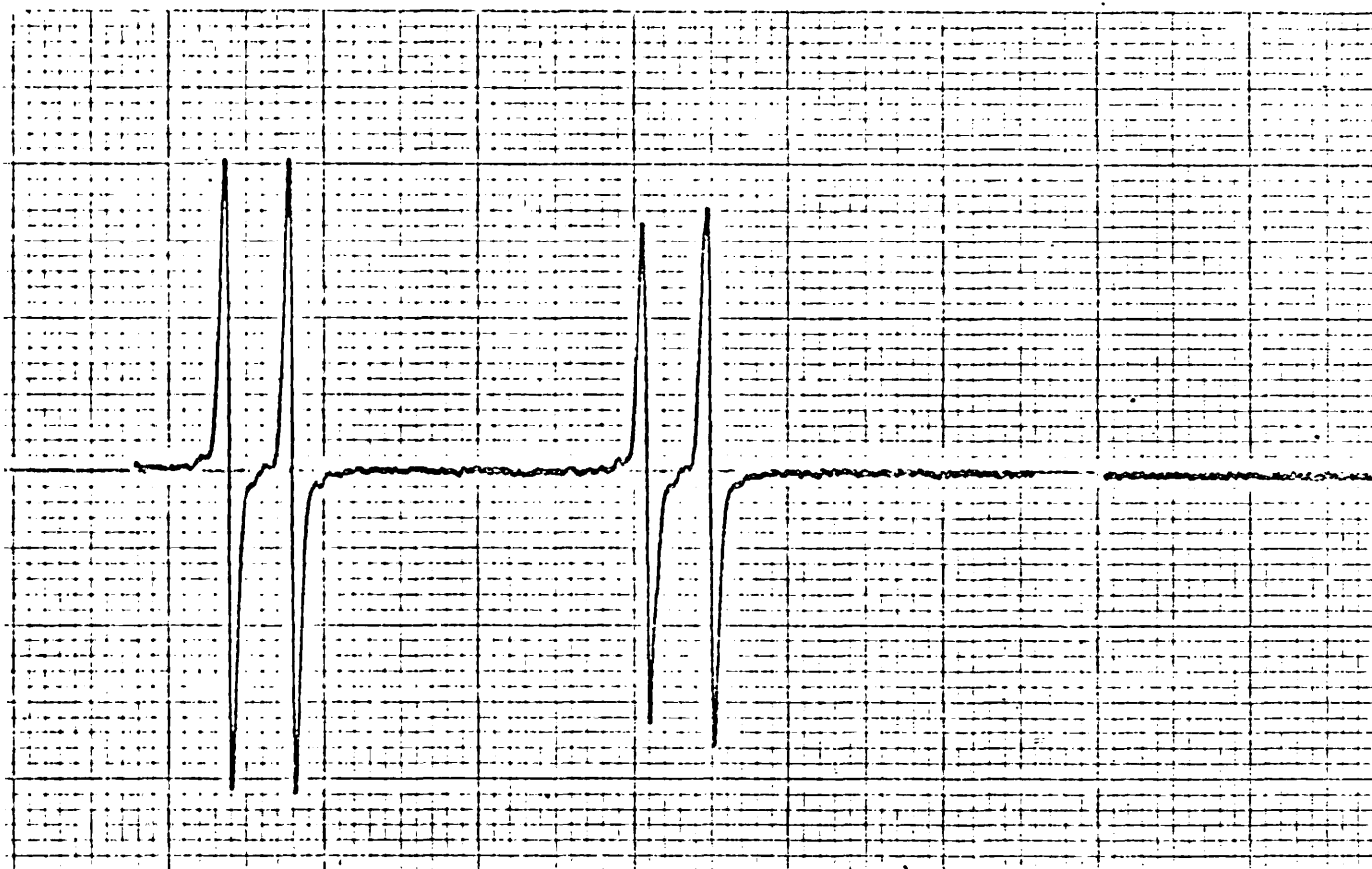
Radical from 4-Hydroxy-6-methyl-2-pyrone

5G



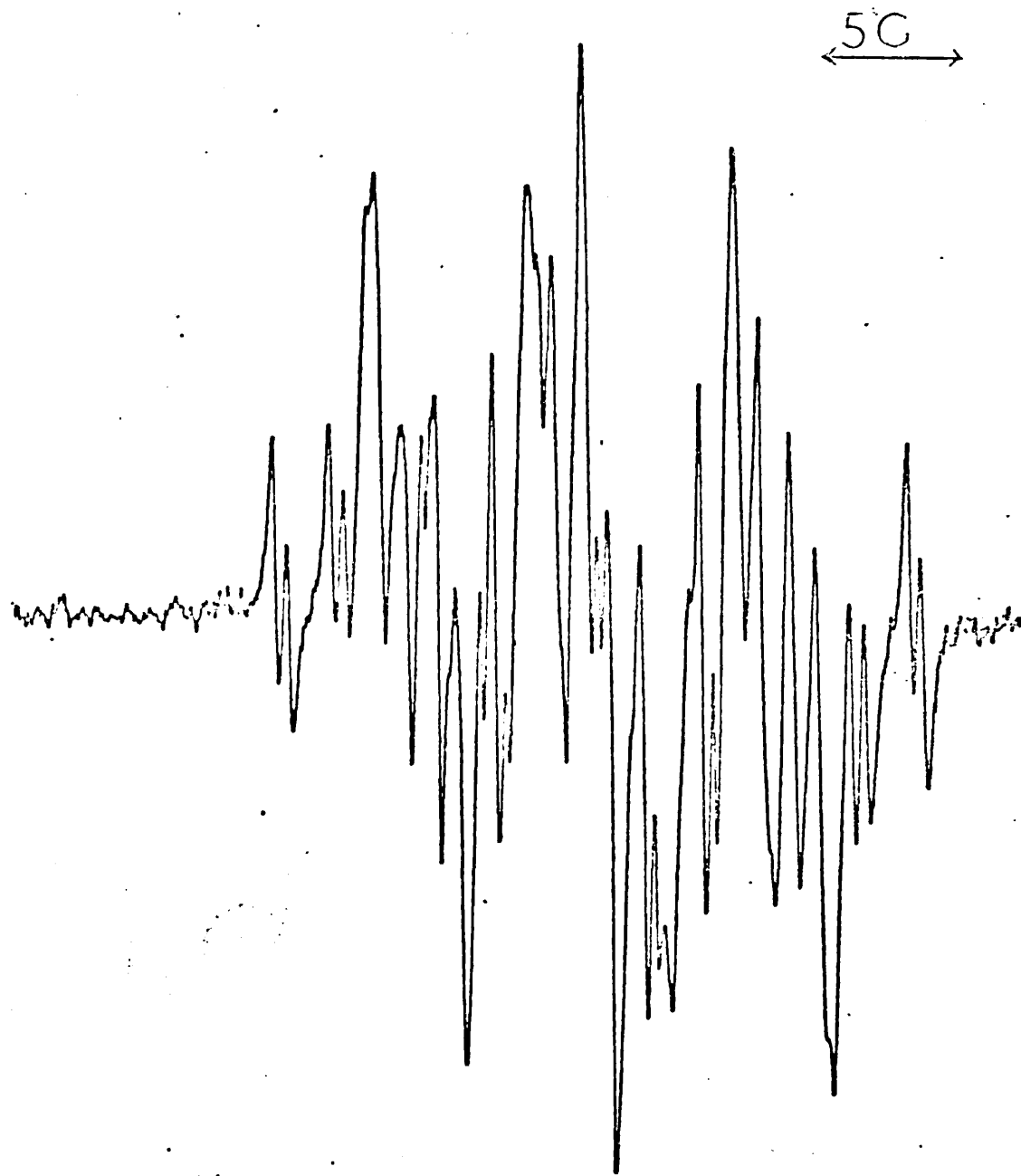
Radical from 4-Hydroxycinnamic Acid

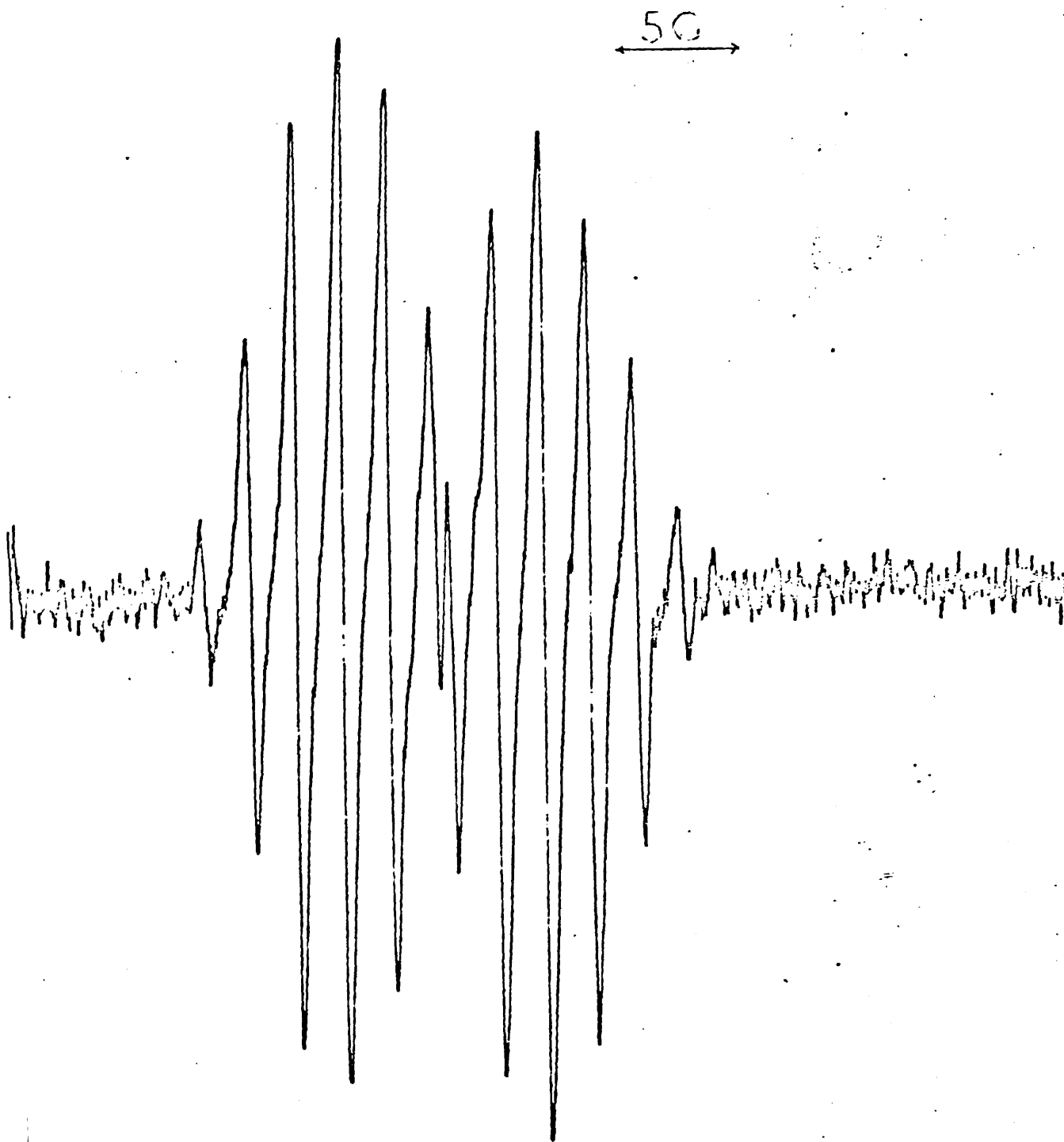
← 2G →



Radical from 2,3,4-Trihydroxy- β -methylcinnamic Acid

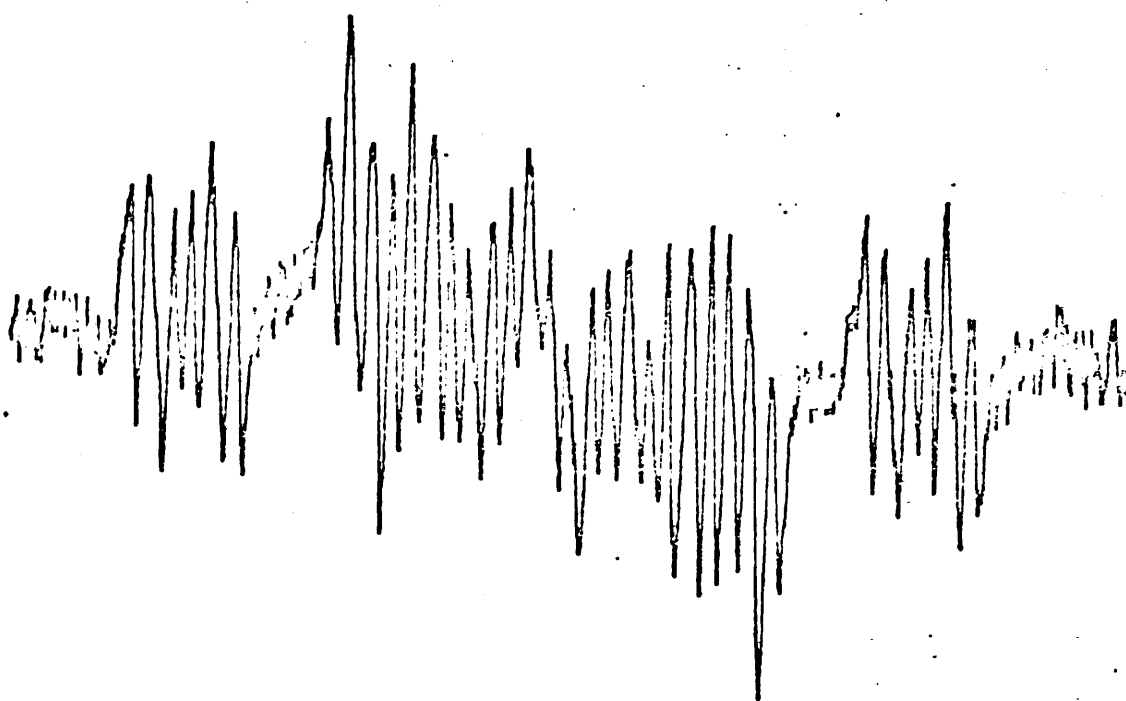
Radical from 2,4-Dihydroxycinnamic Acid





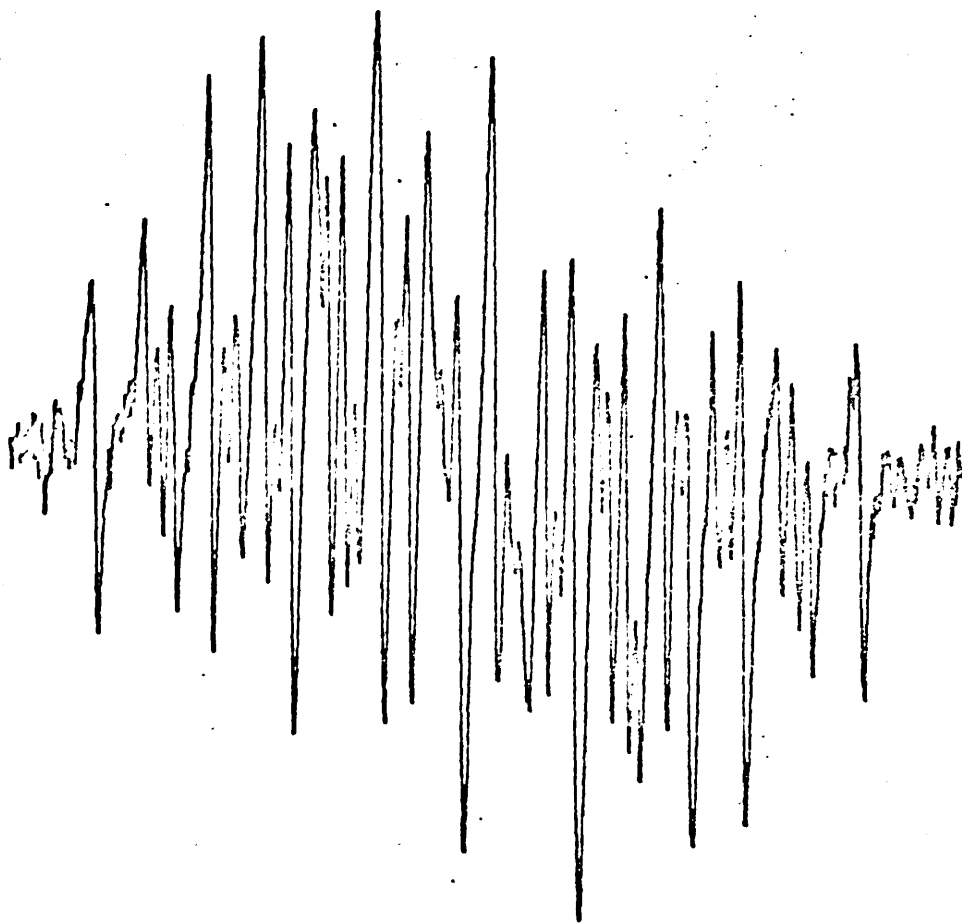
Radical from 3-Hydroxy-4-methoxycinnamic Acid

5G



Radical from 3-Hydroxycinnamic Acid

5C



Radical from 2-Hydroxycinnamic Acid

PROGRAMME FOR MCLACHLAN S.C.F. CALCULATIONS

UNIVERSITY OF MINNESOTA 6600 FORTRAN COMPILER SCOPE 3.4 PSR10 20/09/74
 (C,E=4,B=PRUG,R=0)

```

1* PROGRAM LAMDA (INPUT,OUTPUT)
2* DIMENSION A(25,25), B(25,25), AA(25,25), C(25,25), E(25,25)
3* DIMENSION SUM(2,25), CC(25), DIFF(25), ANS(25)
4* INTEGER ELECTRN,MM,ELECT1

C ***** READ IN MATRIX SIZE, AND ELECTRON NUMBER IN 214 FORMAT
5* READ 110,MM,ELECTRN
6* PRINT 111,MM,ELECTRN
7* 111 FORMAT (1P1,'**** MATRIX SIZE IS ',I4,' ****'//1X,
1'**** ODD ELECTRON LEVEL IS ',I4,' ****'//)
8* 110 FORMAT(2I4)
9* IF (MM.LE. 25 .AND. ELECTRN.LE. MM ) GO TO 57
10* PRINT 56      E      STOP
12* 56 FORMAT('*****ERROR IN DATA : FIRST CARD-MATRIX SIZE OR
1 UNPAIRED ELECTRON LEVEL OUT OF RANGE')

13* 57 CALL MU(MM,ELECTRN,A,B,AA,C,E,SUM,CC,DIFF,ANS)
14* END

15* SUBROUTINE MU(MMM,ELECTRN,A,B,AA,C,E,SUM,CC,DIFF,ANS)
C * * * * *
C THIS SUBROUTINE CALL IS NOT REALLY A SUBROUTINE CALL AT ALL, BUT THE
C START OF AN INNER 'BLOCK' SO THAT THE ARRAYS CAN BE DIMENSIONED
C PROPERLY
C * * * * *
16* DIMENSION A(MMM,MMM),B(MMM,MMM),AA(MMM,MMM),C(MMM,MMM),E(MMM,MMM)
17* DIMENSION SUM(2,MMM),CC(MMM),DIFF(MMM),ANS(MMM)
18* INTEGER ELECTRN,ELECT1,MM

C***** LOCAL COPY OF SUBROUTINE PARAMETER IS MORE EFFICIENT
19* MM=MMM
20* ELECT1=ELECTRN-1
21* XLAM=1,2

C***** ICOUNT=1 WHILE PROCESSING INPUT MATRIX,=2 FOR MATRIX 1
22* ICOUNT=1
23* PRINT 127
24* 127 FORMAT (1X,'**** INPUT MATRIX ****'/)

C***** READ IN FIRST MATRIX TO A
25* DO 1 I=1,MM
26* 1 READ 100, (A(I,J),J=1,MM)
C***** COPY TO E
27* DO 22 I=1,MM
28* DO 22 J=1,MM
29* 22 E(I,J)=A(I,J)

```

```

C ***** DO MATRIX MANIPULATIONS
30* 10 DO 7 I=1,MM
31* 7 PRINT 102,(A(I,J),J=1,MM)
32* CALL MSTR (A,AA,MM,0,1)
33* CALL EIGEN (AA,B,MM,0)
34* CALL MSTR(AA,C,MM,1,0)
35* PRINT 103
36* DO 2 I=1,MM
37* C(I,I)=-C(I,I)
38* 2 PRINT 101,C(I,I)
39* PRINT 104
40* 104 FORMAT(/////1X,'***** COEFFICIENTS *****'/)
41* DO 4 I=1,MM
42* 4 PRINT 102,(B(I,J),J=1,MM)
43* PRINT 105
44* DO 5 I=1,MM
45* 5 PRINT 102,(((B(I,J))**2),J=1,MM)

46* DO 12 J=1,MM
47* SUM(ICOUNT,J)=0
48* DO 13 I=1,ELECT1
49* 13 SUM(ICOUNT,J)=SUM(ICOUNT,J)+B(J,I)*B(J,I)
50* 12 CONTINUE

51* IF (ICOUNT.EQ.2) GO TO 15
C***** MODIFY INPUT MATRIX, TO REPROCESS
52* DO 9 I=1,MM
53* 9 A(I,I)=B(I,ELECTRN)*B(I,ELECTRN)*(2.0*XLAM)+A(I,I)

54* PRINT 201

```

```

55* 201  FORMAT(1H1,'**** MATRIX B ****!/')
56*      ICCOUNT=ICOUNT+1
57*      GO TO 10

C ***** SECOND TIME (MATRIX B) COMPUTE SPIN DENSITIES
58* 15  DO 17 I=1,MM
59* 17  CC(I)=B(I,ELECTRN)*B(I,ELECTRN)

60*      DO 14 I=1,MM
61*      DIFF(I)=SUM(2,I)-SUM(1,I)
62* 14  ANS(I)=CC(I)+DIFF(I)
63*      PRINT 108, (ANS(I),I=1,MM)
64* 108  FORMAT(///5X,'SPIN DENSITY=',(/8X,10F12.5))

C***** READ IN ELEMENT TO CHANGE INPUT MATRIX
65*      READ 102, E(5,8), E(8,5)
66*      IF(E(5,8).EQ.999.0) STOP
67*      DO 23 I=1,MM
68*      DO 23 J=1,MM
69* 23  A(I,J)=E(I,J)

70*      PRINT 202
71* 202  FORMAT(1H1,'**** MODIFIED INPUT MATRIX ****!/')
72*      ICCOUNT=1
C***** GO BACK AND DO IT AGAIN
73*      GO TO 10

74* 100  FORMAT (8F10.0)
75* 101  FORMAT(6X,F10.5)
76* 102  FORMAT(1X,13F10.5)
77* 103  FORMAT(///1X,'**** ENERGY LEVELS ****!/')
78* 105  FORMAT(///1X,'**** SQUARES ****!/')
79*      END

```

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