

AN E.S.R. STUDY OF SOME NITROGEN
SUBSTITUTED FREE RADICALS

by

John D. R. Clay

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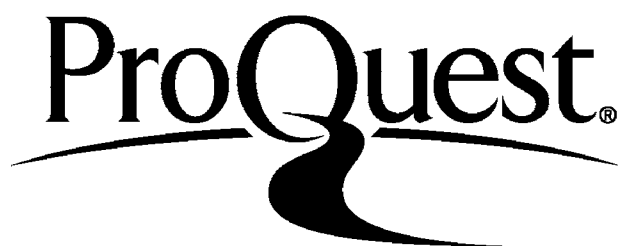
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ABSTRACT

E.s.r. spectra were obtained of as many amino-1,4- and amino-1,2-semiquinones as possible. This was achieved by means of catalytic hydrogenation of their respective nitro-1,4- and nitro-1,2-dihydroxybenzene precursors in ethanolic solution and subsequent radical generation under standard autoxidative conditions.

Assignment of coupling constants in the symmetrical species is obvious. The assignments in the mono-aminosemiquinones are made by a simple graphical procedure and in the asymmetric diamino- and triaminosemiquinones assignments are made by comparison with the corresponding dimethoxy- and trimethoxysemiquinones.

It is observed that the amino-proton coupling constants are substantially smaller than those of the attached nitrogens and this is interpreted in terms of out-of-plane movement by the amino-group.

E.s.r. spectra of a wide variety of nitrogen-containing heterocyclic semiquinones were also obtained. Assignments of coupling constants are made by comparison with similar systems and this simple approach is justified by a molecular orbital approach and on grounds of symmetry. It is also found that nitrogen has little effect on the spin density distribution in these heterocycles in comparison to their non-heterocyclic analogues.

McLachlan S.C.F. calculations were performed for all the radicals in this investigation and calculated coupling constants were, in general, in reasonable agreement with experimental.

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Chapter I

INTRODUCTION

I.1. Starting Point

E.s.r. spectra of aromatic radicals in which nitrogen occurs as either an amino-group substituent¹⁻⁵ or as a ring heteroatom⁶⁻⁹ are well characterised. Generally, nitrogen splittings are explained in terms of a π - σ exchange polarisation mechanism,^{6-8,10-13} and for amino-substituents and protonated heterocycles, the relationship $a_N \approx a_{NH}^H$ has been demonstrated.^{2,3}

Recently, however, spectra from several amino-semiquinones have been reported¹⁴ and in these radicals the $-NH_2$ proton splittings are, generally, much smaller than the nitrogen splitting. The work in this thesis started from an attempt to undertake a much more systematic investigation of these aminosemiquinones.

Three main areas of interest were identified. Firstly, it was hoped that the accumulation of a complete set of hyperfine coupling constants for aminosemiquinones would lead to a rationalisation of the spin density distribution, particularly in the amino-group, in terms of simple molecular orbital theory.

It has been observed in the literature that an interesting feature of some heterocyclic semiquinones in which the second rings contain nitrogen, is that there seems to be little effect on the spin density, which remains mainly on the semiquinone part.⁹ Since, in many cases, the spin distribution in the heterocyclic radical is virtually identical with that in the related aminosemiquinone, a second aim of this work was to obtain a wide variety of nitrogen heterocyclic semiquinones in order to see whether this relationship is of use in explaining the observed splitting patterns.

Thirdly, using the amino- and heterocyclic semiquinones as models, it was hoped to extend e.s.r. studies to a number of relatively accessible naturally occurring compounds.

I.2. Theory of Electron Spin Resonance

The fundamental requirement for the generation of an e.s.r. spectrum by a molecule is that it should possess one or more electrons with unpaired spin and is based on the fact that such an electron has a magnetic moment. The total magnetic moment includes its orbital moment and its spin moment. The motion of the electron in its orbit results in the appearance of the orbital magnetic moment, while its rotation around its own axis generates the spin magnetic moment. Since magnetic moments of the electron are produced by its displacements to which correspond definite momenta, there is a direct relationship between the magnetic moments and the angular momenta of the electron. It is the interaction of the magnetic dipole associated with the unpaired electron with an applied external magnetic field that forms the basis of e.s.r. studies.

The electron can have two spins, as represented by the spin quantum number, $M_s = +\frac{1}{2}, -\frac{1}{2}$. Thus, from quantum mechanical considerations, there are two possible orientations with respect to the applied field, each of which represents an energy level. The separation of these two energy levels increases linearly with the applied magnetic field as governed by the relationship:

$$\Delta E = g\beta H \quad (1)$$

where H is the magnetic field strength, g is a constant (close to 2 for most systems), and β is the Bohr magneton¹⁵ which is a constant converting electron angular momentum to magnetic moment.

Resonance between the two levels can be achieved by supplying the appropriate energy, $h\nu$, to satisfy the resonance condition, where ν is the frequency of radiation and h is Planck's constant. The resulting transition can then be detected as an energy absorption.

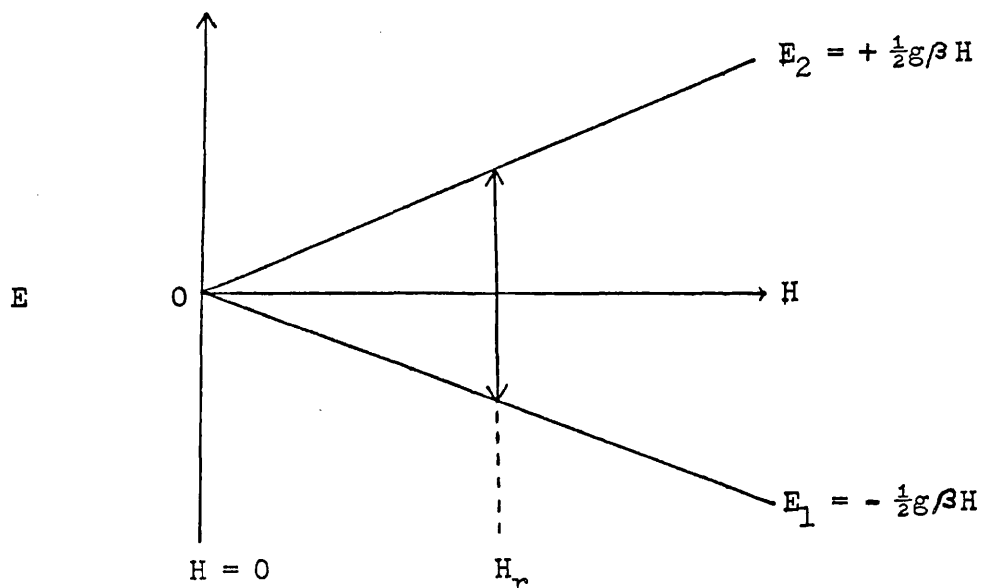


Fig. 1. Energy level scheme showing e.s.r. transition for $M_s = \pm \frac{1}{2}$.

Thus a spectrum may be generated either by keeping H constant and varying the frequency of incident radiation until resonance occurs or by maintaining a constant frequency and varying the field strength. Usually it is the external magnetic field which is varied.

I.2.1. Nuclear Hyperfine Interaction

If the only observable interaction were that of the unpaired electron with the external magnetic field then an e.s.r. spectrum would consist of only a single line. However, the interactions which make e.s.r. so useful are those of the electron's magnetic dipole with other magnetic nuclei in the molecule. For this interaction to occur such nuclei must possess intrinsic spin with a resultant nuclear magnetic moment. For a nucleus of spin I, there are $(2I + 1)$ possible spin states where I can be $1/2, 1, 3/2, 2, \dots$ etc.. For example, the hydrogen atom has nuclear spin $I = \frac{1}{2}$ so the electron will experience two local fields corresponding to

$M_I = +\frac{1}{2}, -\frac{1}{2}$. These nuclear spins may be aligned either parallel or antiparallel with the spin states of the electron making a total of four levels which have different energies in the presence of a magnetic field. The allowed e.s.r. transitions are governed by the selection rule, $\Delta M_S = \pm 1$, $\Delta M_I = 0$, so that the spectrum of the hydrogen atom consists of two absorption lines, corresponding to the allowed transitions as shown in Fig. 2.

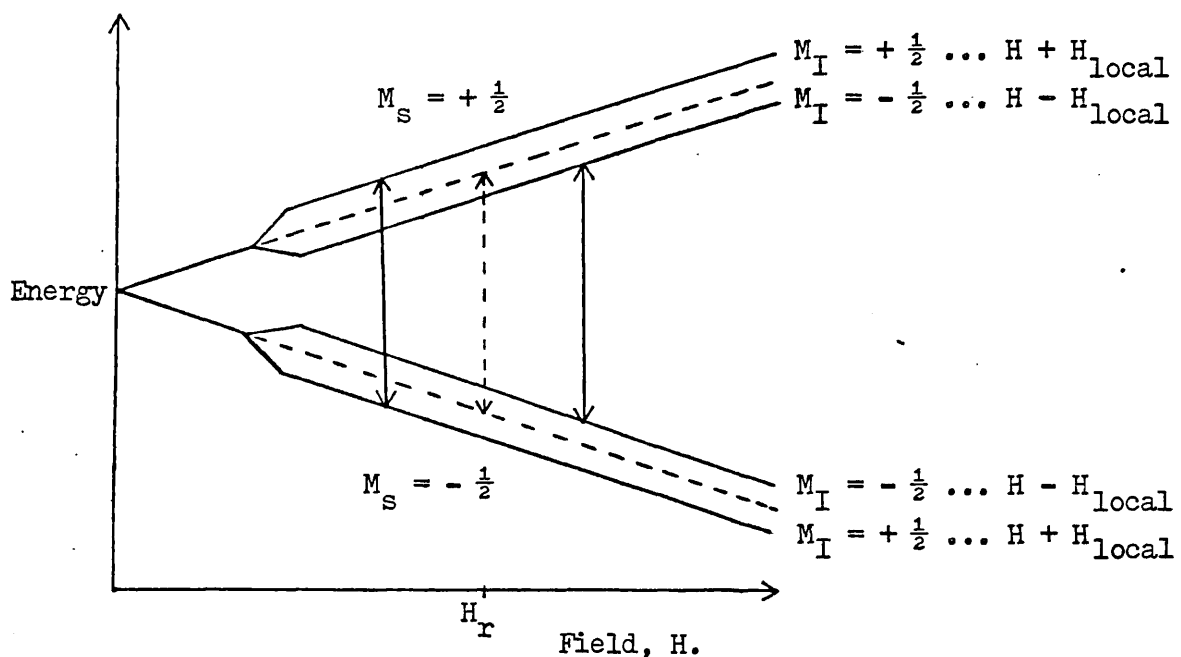


Fig. 2. Energy level scheme showing allowed transitions resulting from interaction of an unpaired electron with a proton in an applied magnetic field.

↔ Observed transition

⋯ Transition which would occur in the absence of proton.

The magnetic field strength, H , in eqn. (2) represents the field experienced by the unpaired electron. Any local magnetic field, H_{local} , will add vectorially to the external magnetic field, H , to give an effective

field, H_{eff} . Thus:

$$H_{\text{eff}} = H + H_{\text{local}} \quad (2)$$

and the resonance equation becomes:

$$\Delta E = h\nu = g\beta(H + H_{\text{local}}) \quad (3)$$

The two absorption lines in Fig. 2. are of equal intensity because the energy differences between the levels with the same M_S value but different M_I are so small that their populations at room temperature are approximately equal. The distance between the two lines is called the hyperfine coupling constant and is dependent on the separation of the nuclear energy levels. The number of splittings from a single magnetic nucleus depends upon the nuclear spin value, I , and is given by $(2I + 1)$.

The relative intensities of the lines of a spectrum are dependent on the degeneracies of the energy levels. A doubly degenerate level will give rise to a line of double intensity. For a magnetic nucleus of spin $\frac{1}{2}$, such as hydrogen, the degeneracies of the lines of a spectrum from a set of n equivalent nuclei are given by the binomial expansion $(a + b)^n$ and are shown in Pascal's triangle.

<u>n</u>	<u>Relative amplitude of lines</u>						
0				1			
1			1	1			
2		1	2	1			
3		1	3	3	1		
4		1	4	6	4	1	
5		1	5	10	10	5	1

Fig. 3. Relative line intensities from a set of n equivalent nuclei of spin $\frac{1}{2}$.

For a nucleus of spin $I = 1$, such as nitrogen, the relative line intensities are given by the expansion $(a + b + c)^n$.

<u>n</u>	<u>Relative amplitude of lines</u>								
1		1	1	1					
2		1	2	3	2	1			
3		1	3	6	7	6	3	1	
4	1	4	10	16	19	16	10	4	1

Fig. 4. Relative line intensities from a set of n equivalent nuclei of spin $I = 1$.

In systems where there are non-equivalent nuclei interacting with the unpaired electron, intensity patterns are often not obvious in the spectrum. Each non-equivalent nucleus will interact differently and there will often be accidental overlap of spectral lines. When spectral lines are coincident, the intensity of the resultant line is the sum of the intensities of the two coincident lines.

The hyperfine splitting constants are usually measured in gauss and are the same for equivalent nuclei.

I.2.2. Mechanism of Hyperfine Interaction¹⁶

In organic free radicals there are two mechanisms by which the unpaired electron can interact with magnetic nuclei to produce hyperfine splitting. The first of these, anisotropy, is a dipole-dipole interaction between the magnetic moments of the electron and the nuclei. The magnitude of this interaction is proportional to the cube of the distance between the two interacting centres and is also dependent on the relative orientation

of the two spins. In the liquid phase, however, the orientation of the radical relative to the external magnetic field changes rapidly due to Brownian motion and the dipole-dipole interactions average to zero.^{16,17} Thus anisotropic interaction is measured only in the solid phase.

The second mechanism, isotropy (or Fermi¹⁸ contact), does not average to zero when the molecule is moving randomly and is dependent on there being finite unpaired-electron density at the nucleus concerned. Theoretically, therefore, there should be no interaction involving electrons in p, d, or f orbitals which have no electron density at the nucleus. An explanation has therefore to be found for the hyperfine interaction arising from π -radicals which have the unpaired electron situated in a carbon $2p_z$ orbital. The answer to this apparent paradox was found by McConnell.¹⁹ He found that in planar conjugated radicals the proton hyperfine splittings are proportional to the unpaired π -electron density on the carbon atom adjacent to the proton as represented by the relationship:

$$a_{\text{CH}}^{\text{H}} = Q_{\text{CH}}^{\text{H}} \rho_{\text{C}}^{\pi} \quad (4)$$

where a_{CH}^{H} is the proton hyperfine coupling constant, ρ_{C}^{π} is the unpaired π -electron density on the carbon atom, and Q_{CH}^{H} is the proportionality constant which usually has a value between 22.5 and 30 gauss.

The π -electron density on the carbon atom is explained by an interaction between the unpaired electron in the carbon $2p_z$ orbital and the electrons in the carbon-hydrogen σ -bonding orbital.²⁰ The interaction is best demonstrated by considering a $>\text{CH}$ fragment of the conjugated system in isolation. A C-H σ -bonding orbital is formed by the overlap of the carbon sp^2 hybrid orbital with the hydrogen $1s$ orbital and is occupied by two electrons. The unpaired electron occupies a carbon $2p_z$ orbital whose axis is perpendicular to the trigonal plane.

There are thus two possible arrangements of the electrons, both equally likely if there were not an unpaired electron in the carbon $2p_z$ orbital.

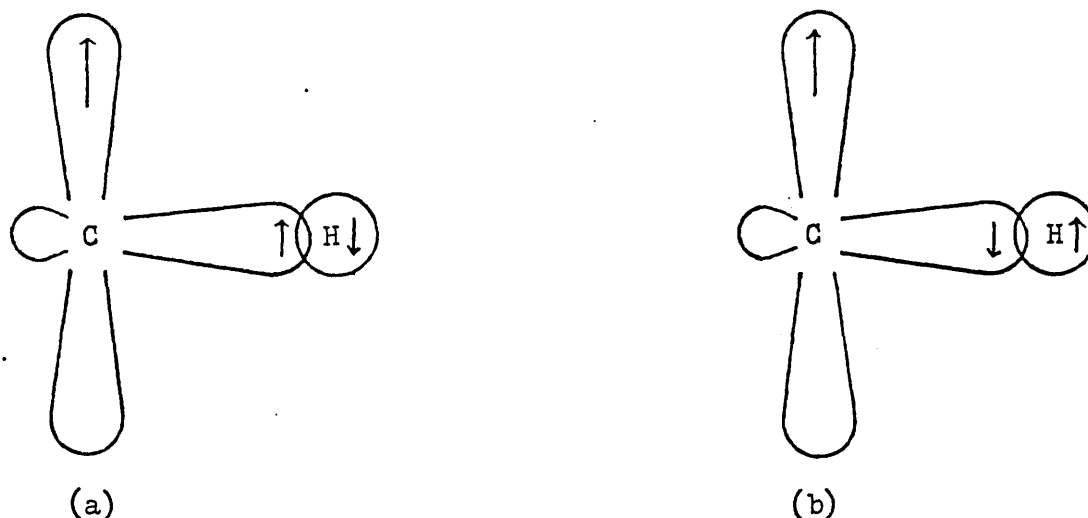


Fig. 5. - Diagram showing the two possible electron orientations in the C-H σ -bonding orbital of a $>CH$ fragment in a conjugated system.

If there were no electron in the carbon $2p_z$ orbital then the configurations (a) and (b) would be equally probable and the unpaired electron spin density in the nodal plane would be zero. However, there is a tendency for the carbon sp^2 electron to orient its spin parallel to that of the unpaired electron in the $2p_z$ orbital thus making (a) the slightly preferred configuration. This results in there being a small amount of unpaired electron spin density at the proton which gives rise to the isotropic hyperfine interaction.

The spin density induced at the proton is opposite in sign to that of the unpaired electron so that Q_{CH}^H should be negative¹⁹ and this has indeed been confirmed experimentally.²¹ By the same token there will be a positive spin density at the carbon nucleus. This polarisation effect is rather small and corresponds to an approximate 4% spin polarisation

induced coupling when comparing the proton hyperfine splitting of a proton attached to a carbon atom with that of the hydrogen atom.

I.3. Molecular Orbital Theory

The simplest approach to molecular orbital theory is to treat a molecular orbital as a linear combination of atomic orbitals (LCAO).²² An expression can then be written for the wave function, ψ , of the molecular orbital in terms of the wave functions of the constituent atomic orbitals:

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n \quad (5)$$

where ϕ represents the wave function of the individual atomic orbitals and c is an associated coefficient. Equation (5) can be more concisely expressed as

$$\psi = \sum_{r=1}^n c_r \phi_r \quad (6)$$

where r is the index of the different atoms, and n is the number of atoms which comprise the conjugated system.

The next step is the determination of the combinatorial coefficients, c_r , and for this the Variation method²³ is used. By this method the coefficients, c_r , are chosen so that the energy of the molecular orbital is a minimum.

This energy value can be obtained from a solution of the Schrödinger Equation which is written in the form

$$\hat{H}\psi = E\psi \quad (7)$$

ψ is the wave function of a single electron, E is its energy, and \hat{H}

is a differential operator known as the Hamiltonian. This procedure has the consequence that equation (7) is solved for just one set of coordinates dealing with each electron separately rather than solving it with a multi-electron Hamiltonian involving an impracticably large number of terms.

The condition of minimum energy is given by the expression

$$E = \frac{\int \psi \mathcal{H} \psi d\tau}{\int \psi^2 d\tau} \geq E_0 \quad (8)$$

Substitution of the LCAO (eqn. (6)) into equation (8) gives

$$E = \frac{\int \left(\sum_r c_r \phi_r \right) \mathcal{H} \left(\sum_s c_s \phi_s \right) d\tau}{\int \left(\sum_r c_r \phi_r \right) \left(\sum_s c_s \phi_s \right) d\tau} \quad (9)$$

$$= \frac{\sum_r \sum_s c_r c_s \int \phi_r \mathcal{H} \phi_s d\tau}{\sum_r \sum_s c_r c_s \int \phi_r \phi_s d\tau} \quad (10)$$

In order to simplify eqn. (10), it is convenient to introduce the notation

$$H_{rs} \equiv \int \phi_r \mathcal{H} \phi_s d\tau \quad (11)$$

$$H_{rr} \equiv \int \phi_r \mathcal{H} \phi_r d\tau \quad (12)$$

$$S_{rs} \equiv \int \phi_r \phi_s d\tau \quad (13)$$

$$S_{rr} \equiv \int \phi_r \phi_r d\tau \quad (14)$$

not the case (S_{12} for π -bonded carbon atoms has a value of about 0.25), this assumption does not seem to affect calculations very significantly.

Using these assumptions greatly simplifies the secular equations (16), which now become -

$$\begin{aligned}
 c_1(\alpha - E) + c_2 \beta_{12} + \dots + c_n \beta_{1n} &= 0 \\
 c_1 \beta_{21} + c_2(\alpha - E) + \dots + c_n \beta_{2n} &= 0 \\
 &\dots\dots\dots \\
 c_1 \beta_{n1} + c_2 \beta_{n2} + \dots + c_n(\alpha - E) &= 0
 \end{aligned}
 \tag{18}$$

and the secular determinant becomes -

$$\begin{vmatrix}
 \alpha - E & \beta_{12} & \beta_{13} & \dots & \beta_{1n} \\
 \beta_{21} & \alpha - E & \beta_{23} & \dots & \beta_{2n} \\
 \beta_{n1} & \beta_{n2} & \beta_{n3} & \dots & \alpha - E
 \end{vmatrix} = 0 \tag{19}$$

I.3.2. McLachlan S.C.F. Theory²⁶

One serious limitation of the HMO method is that it fails to account for the occurrence of negative spin densities which have been found in certain aromatic free radicals.^{27,28} This arises from the fact that HMO theory does not take into account the difference between electron spins (α or β). If, for example, the unpaired electron is of spin α then it will affect the motions of electrons of α and β spins differently. Electrons of like spin attract one another so there

would be an exchange polarisation effect between the unpaired electron (conventionally of spin α) and paired electrons of like spin.

The occurrence of negative spin densities can be explained by assuming that electrons of α and β spin occupy independent sets of orbitals²⁹ $\phi_0, \phi_1 \dots \phi_n$ and $\phi'_1 \dots \phi'_n$ where the odd electron (of spin α) occupies ϕ_0 . Thus a self consistent wave function is obtained:

$$\Psi = \left\| \phi_1^\alpha \phi_1'^\beta \dots \phi_n^\alpha \phi_n'^\beta \phi_0^\alpha \right\| \quad (20)$$

From this self consistent wave function the spin density, ρ , becomes

$$\rho = |\phi_0|^\alpha + \sum_1^n \left\{ |\phi_i|^\alpha - |\phi_i'|^\beta \right\} \quad (21)$$

and a negative spin density arises when $|\phi_i'|^\beta$ exceeds $|\phi_i|^\alpha$ at a node of ϕ_0 .

McLachlan²⁶ used the concept of self consistent orbitals in order to modify the Hückel calculations of spin density. Having assumed the unpaired electron to be of spin α he assumed that β electrons are in unperturbed orbitals and that α electrons are in perturbed orbitals due to exchange polarisation with the unpaired electron. The spin densities of the perturbed orbitals are obtained by modifying the Hückel Coulomb integral for that orbital.

Thus

$$\alpha_{(\text{modified})} = \alpha_{\mathbf{r}} + 2\lambda\rho\beta \quad (22)$$

where α_r is the Hückel Coulomb integral, λ is a constant of about 1.2, ρ is the Hückel unpaired electron density and β refers to an electron of β spin, since $\alpha_{(\text{modified})}$ is for an electron of α spin in terms of that of one of β spin.

I.4. Heteroatoms and Parameterisation

When heteroatoms are introduced into the conjugated system it is necessary to make an adjustment for this in both the Coulomb integral, α , and the resonance integral, β . This is achieved by treating heteroatoms as pseudo-carbon atoms and expressing the adjusted values of α and β in terms of the original values pertaining to a carbon-conjugated system. Thus, by introducing two new parameters, h and k , associated with the Coulomb and resonance integrals respectively, new definitions can be written -

$$\alpha_x = \alpha_0 + h_x \beta_0 \quad (23)$$

$$\beta_{cx} = k_{cx} \beta_0 \quad (24)$$

where α_0 and β_0 are the original integrals for a carbon-conjugated system.

Specific values of h and k therefore have to be found for the various heteroatoms. Ideally, they should be derived from first principles starting with a correlation between some experimental property and a calculated quantity established for hydrocarbon systems. This would be followed with an application of this correlation to a number of compounds containing heteroatoms with a systematic variation of h_x and k_{cx} . In practice, however, they are normally found empirically on the basis of best fit with some measurable experimental property. There are no unique values of h and k for any given heteroatom and the extent of the difficulty in trying to obtain them is reflected by the great profusion in the literature of different sets of parameters.³⁰

Part of the problem is that there are several variations of MO theory and each will require different parameters. There are also many different criteria on which these parameters are based. One such criterion is electronegativity and it has been suggested that α_x be proportional to empirical electronegativities³¹ and h_x be proportional to electronegativity differences.^{32,33} Other criteria used as a basis for parameterisation include bond energies,³³ resonance energies³⁴ and dipole moments.³⁵

Recent studies on systems similar to those encountered in this investigation, using the McLachlan S.C.F. procedure for calculation, have developed a set of parameters found empirically on the basis of the best fit to experimental coupling constants.^{14,28} This set of parameters gave calculated values which, broadly, were in good agreement with experimental values in a wide range of examples and these successful parameters have formed the basis for the calculations performed in this investigation (see Chapter III., Section 1.).

I.5.1. ^{14}N Hyperfine Coupling

The relationship between ^{14}N hyperfine coupling and spin density at the nitrogen atom has been studied in a number of free radicals, both where nitrogen forms part of the conjugated aromatic system,^{10-13,36} and where it is part of an attached substituent.¹⁻⁵ The interpretation of this relationship has led to much argument, the point of contention being whether ^{14}N splittings depend significantly on the spin density at adjacent atoms or not.

It has already been demonstrated (Section I.2.2) that σ - π interaction accounts for the occurrence of unpaired spin density at the nucleus of aromatic protons, and is dependent upon the spin density at the contiguous carbon atom. This theory of interaction can be extended to include intracyclic nuclei such as ^{14}N and ^{13}C by taking into account contributions from nearest-neighbour atoms as well as from the π -orbital

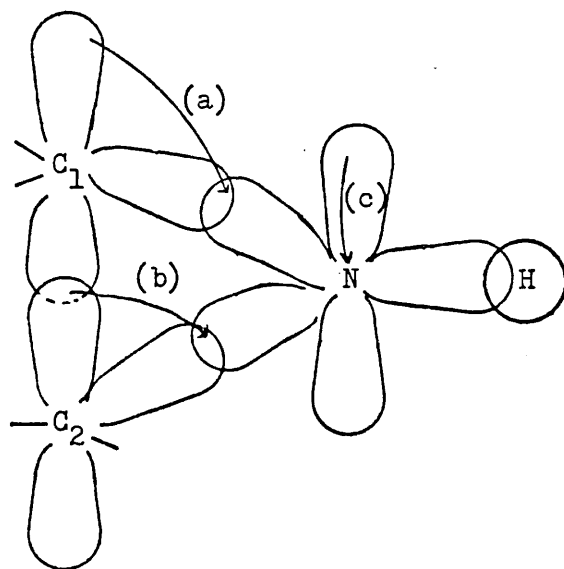


Fig. 6. - Diagram showing spin polarization contributions to the ^{14}N splittings in a $\text{C}_1\text{N-H}$ fragment.

The interactions are (a) $Q_{\text{C}_1\text{N}}^{\text{N}}$ (b) $Q_{\text{C}_2\text{N}}^{\text{N}}$ (c) Q_{NN}^{N}

spin density on the nucleus under consideration.³⁷⁻⁴¹ Contributions from nearest-neighbour atoms would be by means of a $\pi - \sigma$ electronic exchange interaction transmitting unpaired spin polarisation into the connecting bond, while exchange polarisation produces a large unpaired spin density at the nucleus that is proportional to the π -orbital spin density on the atom containing the nucleus.

Thus equation (25) can be written, expressing the nitrogen splitting in terms of the three contributions.⁴¹

$$a_N = Q_{NN}^N \rho_N^\pi + Q_{CN}^N (\rho_{C_1}^\pi + \rho_{C_2}^\pi) \quad (25)$$

However, although there is undoubtedly a contribution to a_N from nearest-neighbour atoms (as shown in equation (25)), the proportionality constant, Q_{CN}^N , for this relationship has been found to be small.^{6,8,11,36,41-45} This does not, therefore, conflict greatly with the argument that this contribution is insignificant and that ^{14}N splittings can adequately be interpreted by assuming that they are proportional to the π -electron spin density on the nitrogen atom itself.^{13,43} Thus many workers have chosen to use the much simpler relationship -

$$a_N = Q_{NN}^N \rho_N^\pi \quad (26)$$

The parameter Q_{NN}^N is positive and has been found to be of the order of 25G.^{8,11,13}

I.5.2. Amino-group Spin Density

The proton hyperfine splitting, a_{CH}^{H} for a hydrogen atom bonded to a carbon atom in an aromatic system is related to the π -electron

spin density, ρ_C^π , on the carbon atom by McConnell's well-known relationship:-

$$a_{CH}^H = Q_{CH}^H \rho_C^\pi \quad (\text{see eqn. (4), Section I.2.2}) .$$

The sign of Q_{CH}^H has been calculated as being negative¹⁹ and this has been confirmed experimentally.²¹

On theoretical grounds, a similar relationship would be expected to exist between the proton splitting, a_{NH}^H , from a hydrogen atom bonded to a nitrogen atom and the π -electron spin density, ρ_N^π on the nitrogen atom. It is therefore possible to write an equation similar to eqn. (4), (Section I.2.2).

$$a_{NH}^H = Q_{NH}^H \rho_N^\pi \quad (27)$$

Q_{NH}^H would similarly be expected to have a negative value and linewidth studies of the dihydropyrazine cation have confirmed this.¹¹ Studies by various workers have found the parameter Q_{NH}^H to be in the range -25 to -35 G.^{2,8,11,26,46}

Equation (4) is of the same form as equation (27) relating a_N to the π -electron spin density on the nitrogen atom, differing only by the numerical value of Q . Since the parameters Q_{NN}^N and Q_{NH}^H have been found to be of roughly the same numerical magnitude (though of opposite sign) it would be expected that the two splittings a_N and a_{NH}^H should be approximately equivalent. Thus

$$| a_N | \approx | a_{NH}^H | \quad (28)$$

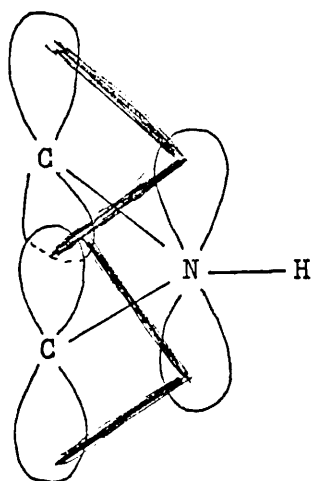
and this approximate relationship has been found to apply in a large number of compounds, both where nitrogen is a member of a heterocyclic

ring and where it is part of an attached substituent.^{2,3,11}

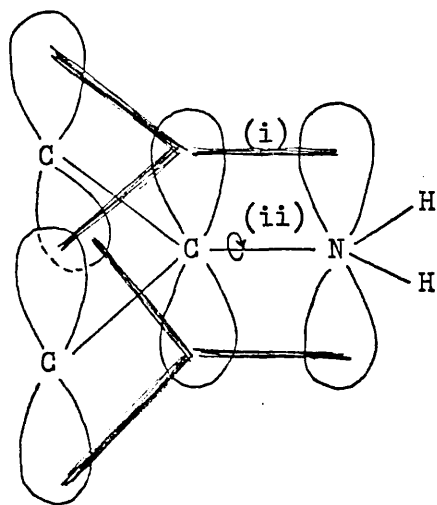
However, more recent studies have shown that in the cases of two aminobenzosemiquinones the approximate relationship $|a_N| \approx |a_{NH}^H|$ no longer holds.¹⁴ Since the contribution from spin polarisation to both a_N and a_{NH}^H is dependent on the same function, ρ_N^π , the implication is that hyperconjugation must be contributing to the unpaired spin density on the protons (see Section 2., Chapter IV.).

In the case of a proton attached to a heterocyclic nitrogen, the nitrogen $2p_z$ orbital forms part of the conjugated system and the nitrogen atom is held firmly in the molecular plane. Consequently, the N - H bond is also held in the molecular plane (apart from very small deviations due to wagging). Therefore, the only mechanism which can significantly contribute to the unpaired spin density on the proton is spin polarisation. This situation is analogous to that of aromatic protons attached to a carbon atom and as long as Q_{NN}^N and Q_{NH}^H are numerically roughly equivalent, the relationship $a_N \approx a_{NH}^H$ should always hold where the nitrogen atom in question forms part of the ring system.

In the situations where nitrogen forms part of an attached substituent, although in a great many cases it aligns itself so that the $2p_z$ orbital overlaps with the ring p^π -system,^{2,3,5,46} there is the possibility of rotation about the C - N bond which moves the N - H protons out of the molecular plane. When the N - H protons move out of the molecular plane, positive spin density may be transferred onto the proton by means of a hyperconjugative mechanism and, as a result, equation (27) would no longer apply.



(a)



(b)

(i) When nitrogen $2p_z$ orbital overlaps with ring p^π -system protons are also held in molecular plane.

(ii) Rotation may occur about the C-N bond which moves attached protons out of molecular plane.

Fig. 7. - Showing (a) heterocyclic nitrogen where attached proton is held in the molecular plane and (b) substituent nitrogen where rotation about the C-N bond may move the attached protons out of the molecular plane.

I.6. Hyperconjugation⁴⁷

The concept of hyperconjugation as a means of explaining the occurrence of unpaired electron spin density on the protons attached to substituent groups in aromatic free radicals is most commonly related to methyl groups.⁴⁸ In the case of a substituent methyl group, the occurrence of hyperfine splittings due to the methyl protons cannot be explained purely in terms of exchange interactions and so a hyperconjugation model has been developed.⁴⁹⁻⁵¹

In this model, the three hydrogen 1s orbitals (a,b,c) are combined to form three new group orbitals^{52,53} (see Fig. 8.) which are -

$$\Psi_1 = \frac{1}{\sqrt{3}} (a + b + c) \quad (29)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} (b - c) \quad (30)$$

$$\Psi_3 = \frac{1}{\sqrt{6}} (2a - b - c) \quad (31)$$

Ψ_1 has σ -symmetry about the C-C bond while Ψ_2 and Ψ_3 have nodal planes in the axis of the C-C bond and have elements of π -symmetry perpendicular to the C-C bond axis.

The three methyl protons are treated as a single $-H_3$ group attached to the methyl carbon atom by bonding through Ψ_1 , leaving the two group orbitals with π -symmetry, Ψ_2 and Ψ_3 , to overlap with the p_y and p_z orbitals of the carbon atom respectively. Having an orbital, Ψ_3 , with p_z character, the $-H_3$ group can now be considered as part of the overall conjugated π -system through which the unpaired electron may

be delocalised.

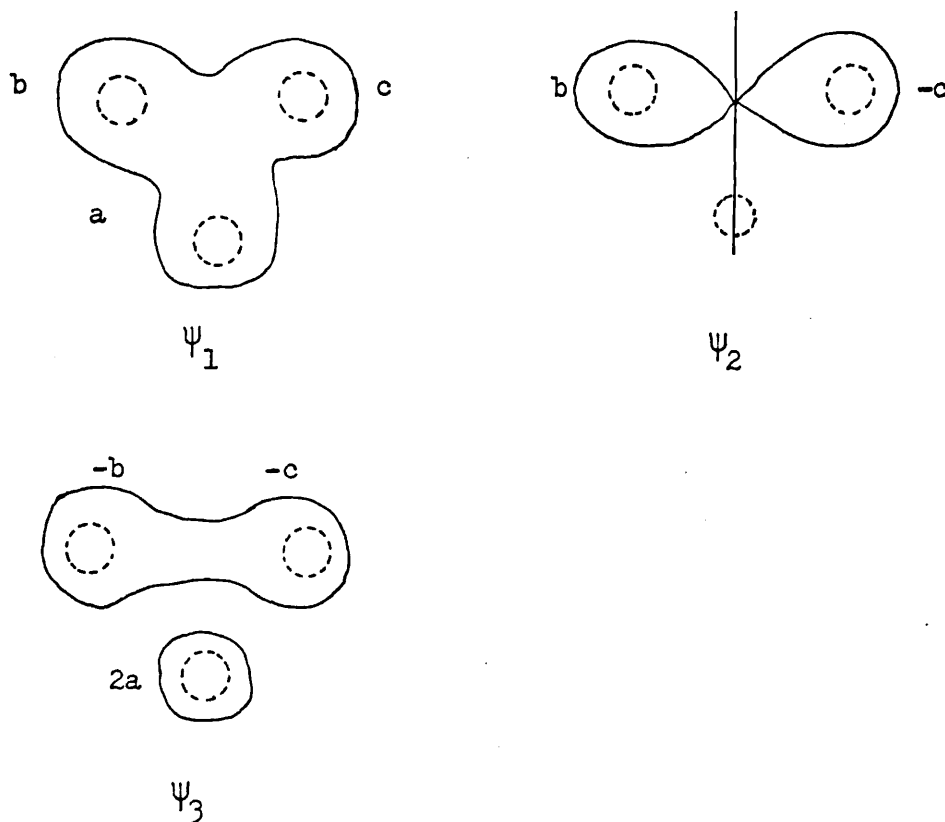
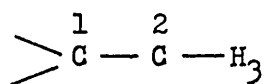


Fig. 8. Diagram showing the combination of the three hydrogen 1s orbitals (a,b,c) to form the group orbitals ψ_1 , ψ_2 and ψ_3 .

The quantitative treatment for MO calculations involves development of parameters for the $-H_3$ group on the basis of it being a single pseudo-atom. Thus for the fragment -



the parameters k_{12} and h_2 and k_{2H_3} and h_{H_3} must be evaluated.

However, although hyperconjugation has been found to be very much the dominant mechanism in hyperfine coupling in β -protons,⁵⁴⁻⁵⁶ there

is nevertheless still a small contribution from spin polarisation and this has to be taken into account when evaluating a_H for β -protons.^{57,58} The contributions to a_H for β -protons from these two mechanisms is normally expressed in the form^{51,59-61} -

$$a_H = B_0 + B_2 \cos^2 \theta \quad (32)$$

where B_0 is the contribution from spin polarisation and θ is the angle of twist between the α -carbon $2p_z$ orbital and the plane containing the β -proton C-H bond.

This hyperconjugation model can similarly be applied to the amino-group where two molecular orbitals can be formed from the two hydrogen $1s$ orbitals.

$$\psi_1 = \frac{1}{\sqrt{2}} (a + b) \quad (33)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (a - b) \quad (34)$$

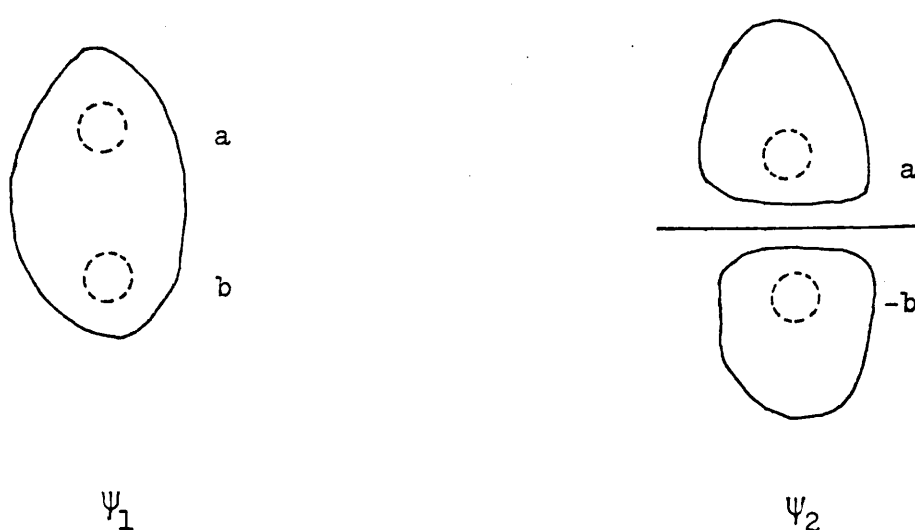


Fig. 9. Diagram showing the combination of the two hydrogen $1s$ orbitals to form the group orbitals ψ_1 and ψ_2 .

Ψ_1 has σ -symmetry about the C-N bond while Ψ_2 has a nodal plane in the axis of the C-N bond and has an element of π -symmetry perpendicular to the C-N bond axis through which it may interact directly with the ring p^π -system.

Chapter II.

EXPERIMENTAL

II.1. Materials

Many of the materials used in the syntheses of the radical precursors, which were commercially available, were used without further purification (Table (1)). Some commercially available starting materials were, however, purified before use (Table (2)). Other compounds were synthesised using methods given in the literature (Table (3)), and, where it was possible to obtain them, had physical constants in good agreement with those in the cited literature.

In certain cases, no attempts were made at isolating, and obtaining physical constants from, the immediate radical precursor. Aminohydroquinones, for example, undergo rapid aerial oxidation and, therefore, could not be isolated. Also, certain azido derivatives were not obtained dry due to their explosive nature.

II.2. Instrumentation

E.s.r. spectra were recorded on a Varian E4 spectrometer operating at a fixed microwave frequency of ca. 9.5 GHz with a linearly varied static magnetic field strength of ca. 3400 G. (0.34 T).

II.3. Generation of Radicals

All radicals were generated in static autoxidation conditions at room temperature. Although p-semiquinones can be obtained from the corresponding quinones, spectra so obtained are less well resolved due to exchange broadening and wherever possible hydroquinones were used as radical precursors. In the few cases where quinones were used, in situ reduction was achieved by the use of alkaline sodium dithionite solution as the radical generator.

Table (1)Commercial Materials Used Without Further Purification

Adrenochrome
Catechol (1,2-dihydroxybenzene)
Diazald* (N-methyl-N-nitroso-p-toluenesulphonamide)
1,4-Dihydroxybenzene
1,2-Dimethoxybenzene
1,4-Dimethoxybenzene
Ethyl diazoacetate
Glyoxal sodium bisulphite
Guaiacol (2-methoxyphenol)
5-Hydroxyisoquinoline
8-Hydroxyquinoline
4-Methylamino-1,2-naphthoquinone
Palladium 10% on charcoal
Silver nitrate
Sodium azide
Sodium 1,2-naphthoquinone-4-sulphonate
Sulphanilic acid

Dimethylformamide (DMF)
Ethanol
Potassium t-butoxide
Sodium dithionite

*Diazald is a registered trademark of the Aldrich Chemical Co. Inc.

Table (2)

Commercial Materials Purified Before Use

Compound	Method	Physical Data
Acetyl chloride	Distillation	b.p. 51° (lit. ⁶² 51-52°)
Benzoyl chloride	Distillation	b.p. 197° (lit. ⁶² 197°)
1,4-Benzoquinone	Steam distillation	yellow needles m.p. 115° (lit. ⁶² 115.7°)
2,3,5,6-Tetrachloro- 1,4-benzoquinone	Recrystallisation from toluene and benzene	yellow prisms m.p. 285° (lit. ⁶² 290° sealed tube)
2,3-Dichloro- 1,4-naphthoquinone	Recrystallisation from ethanol	yellow needles m.p. 194° (lit. ⁶² 193°)
1,4-Naphthoquinone	Recrystallisation from benzene	yellow needles m.p. 127° (lit. ⁶³ 125°)

Table (3)

Synthesis of Materials

Compound	Method	Physical Data
2-Nitro-1,4-dihydroxybenzene (a)	Nitration of 1,4-dimethoxybenzene ⁶⁴	m.p. 133-134° (lit. ⁶⁶ 133-134°)
2,3-Dinitro-1,4-dihydroxybenzene (a)	Nitration of 1,4-dimethoxybenzene ^{64,65}	m.p. 98-100° (lit. ⁷² 98-100°)
2,5-Dinitro-1,4-dihydroxybenzene (a)	Nitration of 1,4-dimethoxybenzene ^{64,65}	m.p. 201-202° (lit. ⁷² 201-203°)
2,6-Dinitro-1,4-dihydroxybenzene	Nitration of benzoylhydroquinone ⁶⁶	m.p. 135° (lit. ⁶⁶ 134-135°)
2,3,5,6-Tetraazido-1,4-benzoquinone	Reaction of 2,3,5,6-tetrachloro-1,4-benzoquinone with sodium azide ⁶⁷	(b)

(continued)

Table (3) (cont.)

Compound	Method	Physical Data
3-Nitrocatechol (a)	Nitration of guaiacol using acetyl chloride/silver nitrate ⁶⁸	m.p. 86° (lit. ⁶⁹ 84°)
4-Nitrocatechol	Nitration of catechol ⁶⁹	m.p. 176° (lit. ⁶⁹ 176°)
3,4-Dinitrocatechol	Nitration of catechol ⁶⁹	m.p. 147-148° (lit. ⁶⁹ 147-148°)
3,5-Dinitrocatechol	Nitration of catechol diacetate ⁷⁰	m.p. 164° (lit. ⁷³ 164°)
3,6-Dinitrocatechol (a)	Further nitration of 3-nitroguaiacol ⁶⁸	m.p. of 3,6-dinitroguaiacol 69° (lit. ⁶⁸ 69-70°)
4,5-Dinitrocatechol (a)	Nitration of 1,2-dimethoxybenzene ⁷¹	m.p. 167° (lit. ⁷¹ 166.5-167.5°)
3,4,6-Trinitrocatechol (a)	Further nitration of 3-nitroguaiacol ⁶⁸	m.p. of 3,4,6-trinitroguaiacol 108° (lit. ⁶⁸ 108-109°)

(continued)

Table (3) (cont.)

Compound	Method	Physical Data
2,3-Triazolo-1,4-dihydroxybenzene (a)	From 2,3-dinitro-1,4-dimethoxybenzene ⁷⁴	calc. for C ₆ H ₅ N ₃ O ₂ : C, 47.7; N, 27.8 found: C, 46.9; N, 26.8
4,5-Triazolo-1,2-dihydroxybenzene (a)	From 4,5-dinitro-1,2-dimethoxybenzene ⁷⁴	(c)
Quinoline quinone	From 8-hydroxyquinoline ⁷⁵	m.p. 120-121° (decomp.) (lit. ⁷⁶ 121-122° (decomp.))
Isoquinoline quinone	From 5-hydroxyisoquinoline ⁷⁵	(c)
2,3-Diazido-1,4-naphthoquinone	Reaction of 2,3-dichloro-1,4-naphthoquinone with sodium azide ⁶⁷	m.p. 136° (lit. ⁶⁷ 136°)
4-Azido-1,2-naphthoquinone	Reaction of sodium 1,2-naphthoquinone-4-sulphonate with sodium azide ⁷⁷	(b)

(continued)

Table (3) (cont.)

Compound	Method	Physical Data
5,8-Dihydroxyquinoxaline (a)	Condensation of 2,3-diamino-1,4-dimethoxybenzene with glyoxal sodium bisulphite ⁷⁸	m.p. 236° (lit. ⁷⁹ 236-237°)
3-Carboxy-lin-naphthindazole-4,9-quinone	Reaction of ethyl diazoacetate with 1,4-naphthoquinone ⁸⁰	m.p. 186° (lit. ⁸⁰ 186.5°)
Benzo [1,2-C:4,5-C'] dipyrazole-4,8(1H,5H)dione	Reaction of diazomethane with 1,4-benzoquinone ⁸¹	decomp. 284-285° (lit. ⁸¹ decomp. 285°)

(a) - Demethylation of these compounds was achieved by refluxing with 48% hydrobromic acid.

(b) - These compounds could not be purified due to their instability.

(c) - This compound was not isolated and the spectra were obtained from the reaction solution after the final stage.

In a typical experiment, one drop of 10% sodium hydroxide solution was added to 5 cm³ of a solution containing approximately 0.001 moles of radical precursor. In some cases, the base used was potassium t-butoxide, particularly as this removes the possibility of sodium-splitting in the spectra of o-semiquinones.

In the case of the aminohydroquinones, their nitro precursors (1g in 25 cm³ of ethanol) were reduced by hydrogenation over 10% palladium on charcoal catalyst (100 mg, 4 atm., 20°C) until the theoretical uptake of hydrogen had taken place. The catalyst was then quickly filtered off and the resulting solution used immediately for the generation of e.s.r. spectra.

All spectra were obtained from ethanolic solutions though in many instances solvent-shifted spectra were also obtained by the addition of water or N,N-dimethylformamide to the ethanolic solution. These solvent-affected spectra were often useful in the analysis of the more complex splitting patterns.

Chapter III

RESULTS

III.1. McLachlan S.G.F. Parameters

Previous investigations on phenoxy radicals have led to a set of parameters which were found to give calculated values of coupling constants in reasonable agreement with experimental data and these formed the basis of the calculations performed in this investigation.^{14,28}

Initial studies on substituted phenoxy radicals led to the oxygen parameters $h_O = 1.6$ and $k_{CO} = 1.3$ and these have been successfully used for a number of aminophenoxy radicals and aminosemiquinones. The two nitrogen parameters $h_N = 1.3$ and $k_{CN} = 1.0$ subsequently used were formulated by finding the parameters which most closely reproduced the experimental coupling constants in the aniline radical cation.⁸²

These four parameters formed the starting point for a further investigation to see if any improvements could be made. This was achieved by performing exhaustive calculations. In these, the experimental couplings and Q values were set and the four parameters h_O , k_{CO} , h_N and k_{CN} were simultaneously varied over a fixed range of values by set increments. Thus, the set of parameters which gave the closest correlation with experiment was established. This procedure was repeated for each of the compounds under study. In fact each compound produced a slightly different set of 'ideal' parameters but overall, the four parameters previously established were found to give the best results and the calculated values quoted are based on them. These are -

$$\begin{aligned} h_O &= 1.6 \\ k_{CO} &= 1.3 \\ h_N &= 1.3 \\ k_{CN} &= 1.0 \end{aligned}$$

The only other parameter required in this investigation was the k_{NN} resonance integral. The best value found for this was $k_{NN} = 1.0$.

III.2. Aminosemiquinones

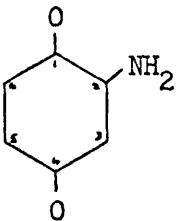
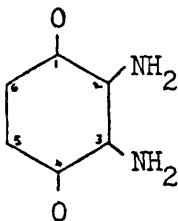
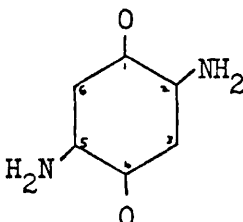
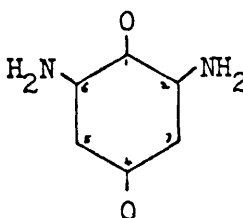
Although there have been many e.s.r. investigations of amino-substituted free radicals,^{3-5,83} there have been very few reports of spectra obtained from aminosemiquinones in which the amino-group is not protected by substitution. This is due to the highly reactive nature of both the dihydroxy and quinonoid precursors of these radicals, which undergo rapid aerial oxidation.

The successful approach in this investigation was by means of catalytic hydrogenation of the stable nitrohydroxybenzene precursor in ethanolic solution. On removal from the hydrogenator it was essential to filter off the catalyst and use the aminohydroxybenzene solution as quickly as possible before the radical precursor underwent total destruction from aerial oxidation. The aminohydroquinones underwent autoxidation in the usual way and, in general, well resolved intense e.s.r. spectra could be obtained from the aminosemiquinone solution for several minutes after generation of the radical. Spectra were obtained from all of the mono- and di-aminosemiquinones as well as 3,4,6-triamino-1,2-semiquinone and tetraamino-1,4-semiquinone, and the results obtained are given in Tables (4) and (5).

Although the aminohydroquinone precursor itself could not be isolated and identified, there is no doubt that the spectra obtained are indeed of the corresponding aminosemiquinones. Catalytic hydrogenation is a well established and successful method of cleanly reducing nitro-compounds to the corresponding amino-compounds and the identity of all the nitro-precursors was confirmed. Furthermore, all the spectra obtained had splitting patterns consistent with those expected from the aminosemiquinones and having obtained all the possible mono- and di-aminosemi-

Table (4)

E.s.r. Coupling Constants (a/Gauss) for Amino-1,4-semiquinones (calculated values in parentheses).

Radical Skeleton	a_2	a_3	a_5	a_6
I 	$a_N = 1.70$ (2.14)	-0.20 (-1.20)	4.72 (5.28)	1.50 (1.31)
	$a_{NH}^H = 0.85$			
II 	$a_N = 0.60$ (0.58)	$a_N = 0.60$ (0.58)	3.10 (3.77)	3.10 (3.77)
	$a_{NH}^H = 0.00$	$a_{NH}^H = 0.00$		
III 	$a_N = 2.80$ (2.41)	0.80 (-1.54)	$a_N = 2.80$ (2.41)	0.80 (-1.54)
	$a_{NH}^H = 1.00$		$a_{NH}^H = 1.00$	
IV 	$a_N = 1.10$ (1.50)	1.30 (0.50)	1.30 (0.50)	$a_N = 1.10$ (1.50)
	$a_{NH}^H = 0.25$			$a_{NH}^H = 0.25$

(continued)

Table (4) (cont.)

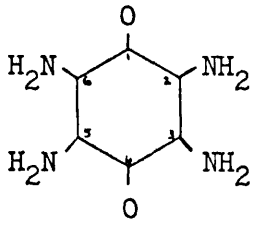
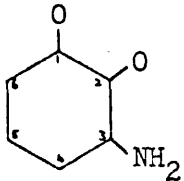
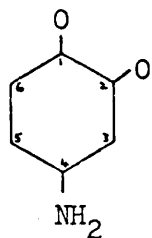
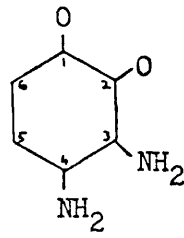
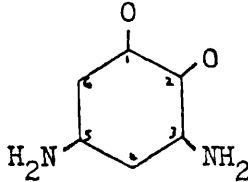
Radical Skeleton	a_2	a_3	a_5	a_6
<p>V</p> 	$a_N = 1.10$ (0.73)	$a_N = 1.10$ (0.73)	$a_N = 1.10$ (0.73)	$a_N = 1.10$ (0.73)
	$a_{NH}^H = 0.20$	$a_{NH}^H = 0.20$	$a_{NH}^H = 0.20$	$a_{NH}^H = 0.20$

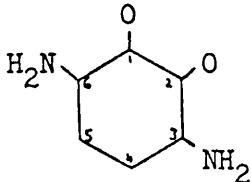
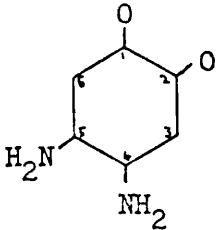
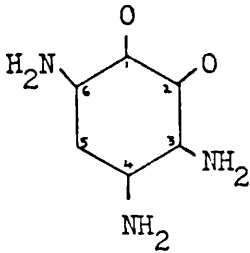
Table (5)

E.s.r. Coupling Constants (a/Gauss) for Amino-1,2-semiquinones (calculated values in parentheses).

Radical Skeleton	a_3	a_4	a_5	a_6
VI 	$a_N = 1.65$ (2.25)	0.00 (-1.15)	5.10 (4.46)	-0.85 (-1.73)
	$a_{NH}^H = 0.70$			
VII 	1.88 (-1.52)	$a_N = 2.10$ (2.20)	3.07 (5.39)	0.85 (1.02)
		$a_{NH}^H = 3.95$		
VIII 	$a_N = 0.16$ (-0.12)	$a_N = 1.62$ (1.54)	4.94 (5.83)	2.82 (0.13)
	$a_{NH}^H = 0.68$	$a_{NH}^H = 1.00$		
IX 	$a_N = 1.21$ (1.50)	4.06 (0.57)	$a_N = 1.21$ (1.84)	0.21 (-0.89)
	$a_{NH}^H = 0.21$		$a_{NH}^H = 1.21$	

(continued)

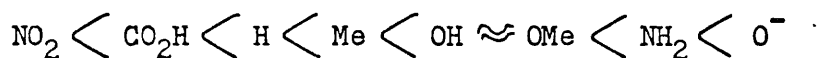
Table (5) (cont.)

Radical Skeleton	a_3	a_4	a_5	a_6
X 	$a_N = 0.68$ (0.56)	2.04 (1.30)	2.04 (1.30)	$a_N = 0.68$ (0.56)
	$a_{NH}^H = 0.68$			$a_{NH}^H = 0.68$
XI 	0.55 (-1.58)	$a_N = 2.30$ (0.56)	$a_N = 2.30$ (0.56)	0.55 (-1.58)
		$a_{NH}^H = 0.17$	$a_{NH}^H = 0.17$	
XII 	$a_N = 1.12$ (0.98)	$a_N = 2.40$ (2.65)	0.15 (-1.23)	$a_N = 1.85$ (2.50)
	$a_{NH}^H = 0.76$	$a_{NH}^H = 2.35$		$a_{NH}^H = 1.82$

quinones, there is no ambiguity as to which species a particular spectrum came from.

In some cases, the assignments of the coupling constants are unambiguous due to the symmetry of the species. These include the symmetrical diaminosemiquinones (radicals II, III, IV, X and XI) (Figs. 15, 16, 17, 25 and 26) and tetraamino-1,4-semiquinone (radical V) (Fig. 18) .

The problem of assignment of coupling constants in the asymmetrical aminosemiquinones has been dealt with on the basis of previous work done on substituted phenoxylys.²⁸ This clearly shows that in a given class of radicals, the observed splitting patterns can be expected to change in a smooth way with substitution and that the substituent effects are in a similar order to their electron donating power. The observed trend in the change of spin density distribution by substituents is^{28,88} -



and amino-substituted radicals would be expected to fit the observed pattern.

For any given substitution pattern, graphs may be drawn which give rise to smooth curves, showing that points which fall on the same curve must correspond to each other.^{28,88,89} This simple graphical procedure has been used to assign the coupling constants in the three mono-substituted aminosemiquinones (Figs. 13, 19,20). Figs. 10-12 show graphs in which corresponding splittings of a number of similarly substituted semiquinones are plotted against each other. The assignments of the aromatic proton coupling constants are based on their fit with the appropriate curves. In all three cases the splittings from the aminosemiquinones fitted on to

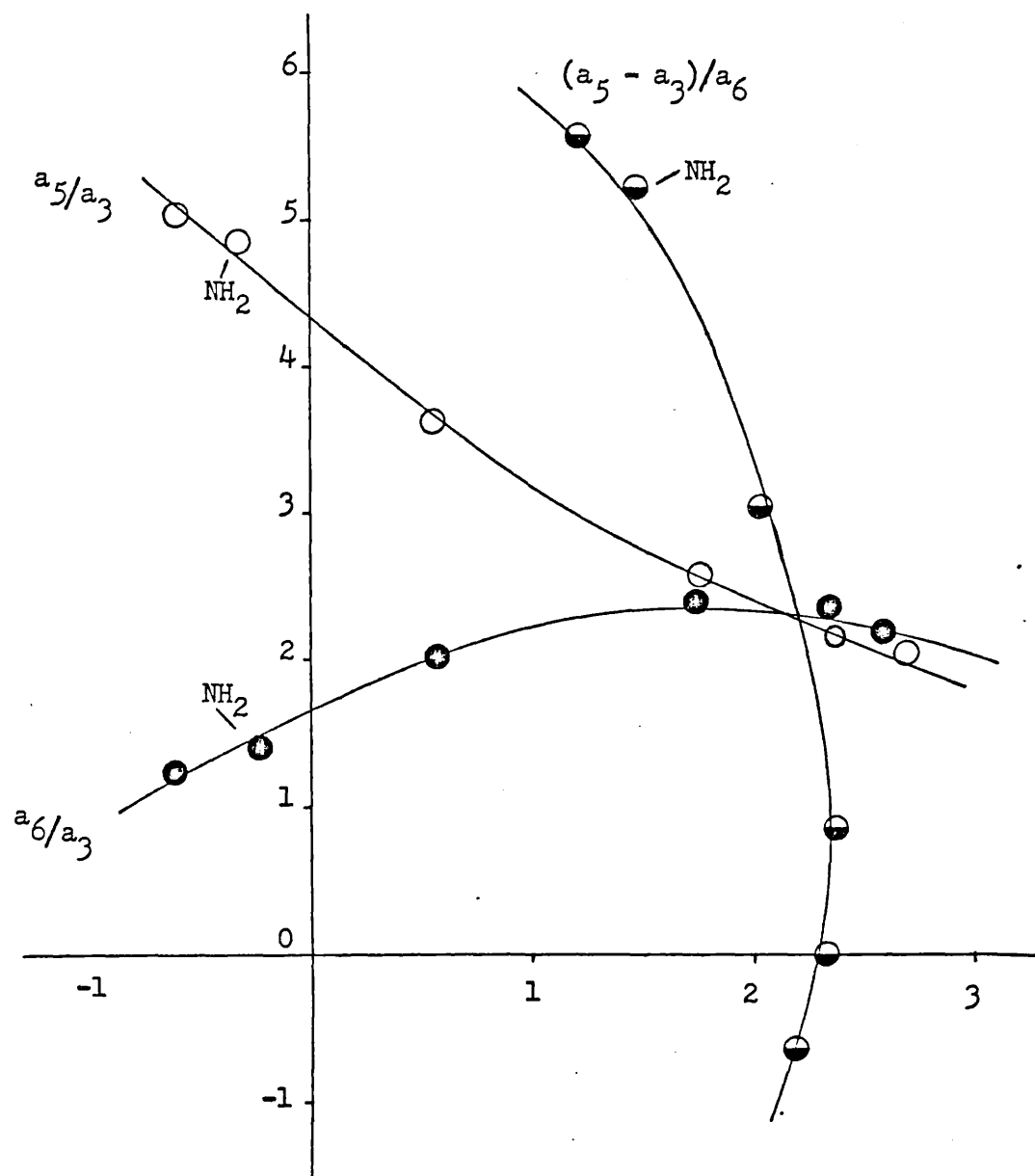


Fig. 10 - Graph showing the method of assignment of coupling constants for 2-amino-1,4-semiquinone.

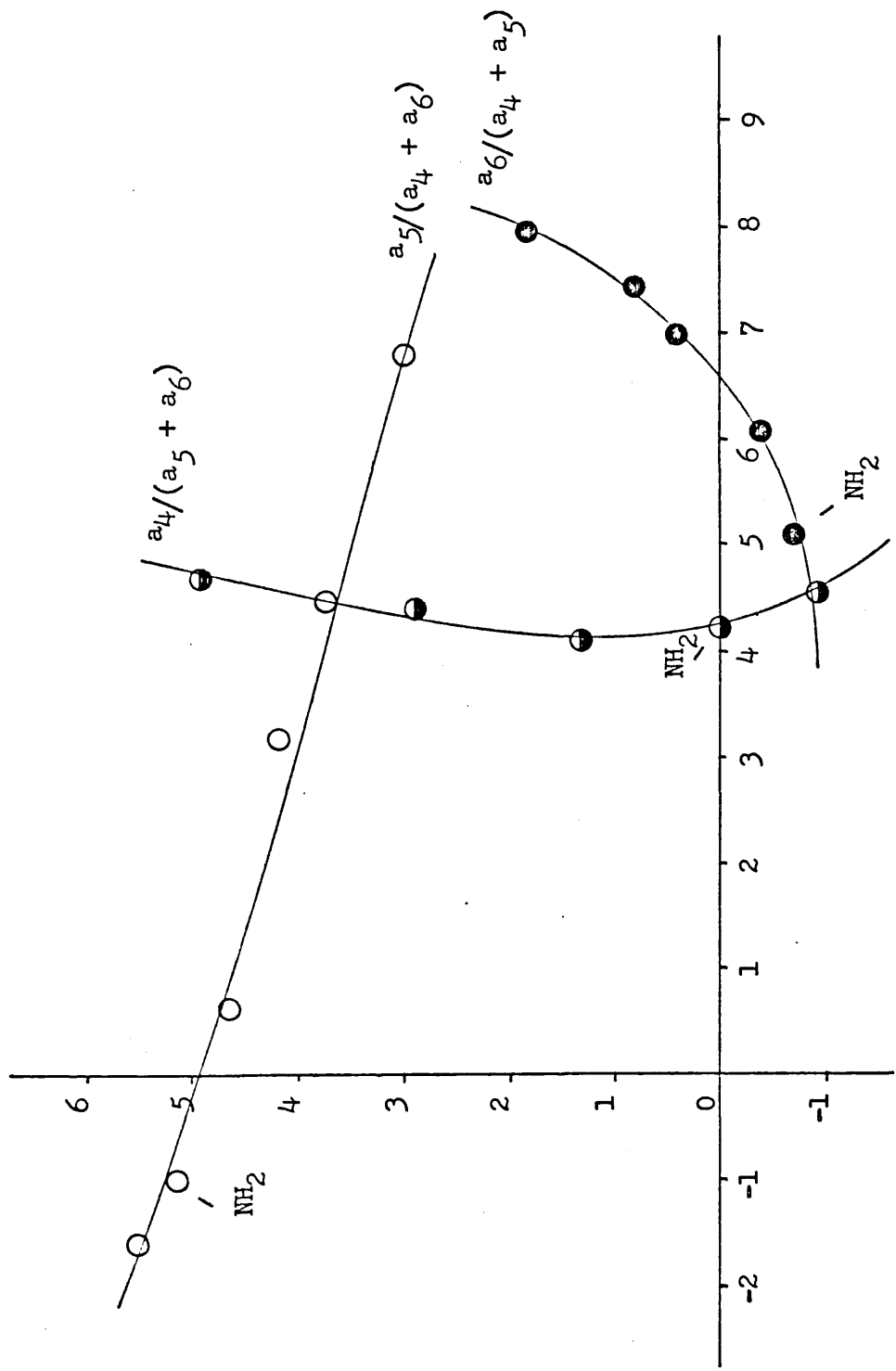


Fig. 11. - Graph showing the method of assignment of coupling constants for 3-amino-1,2-semiquinone.

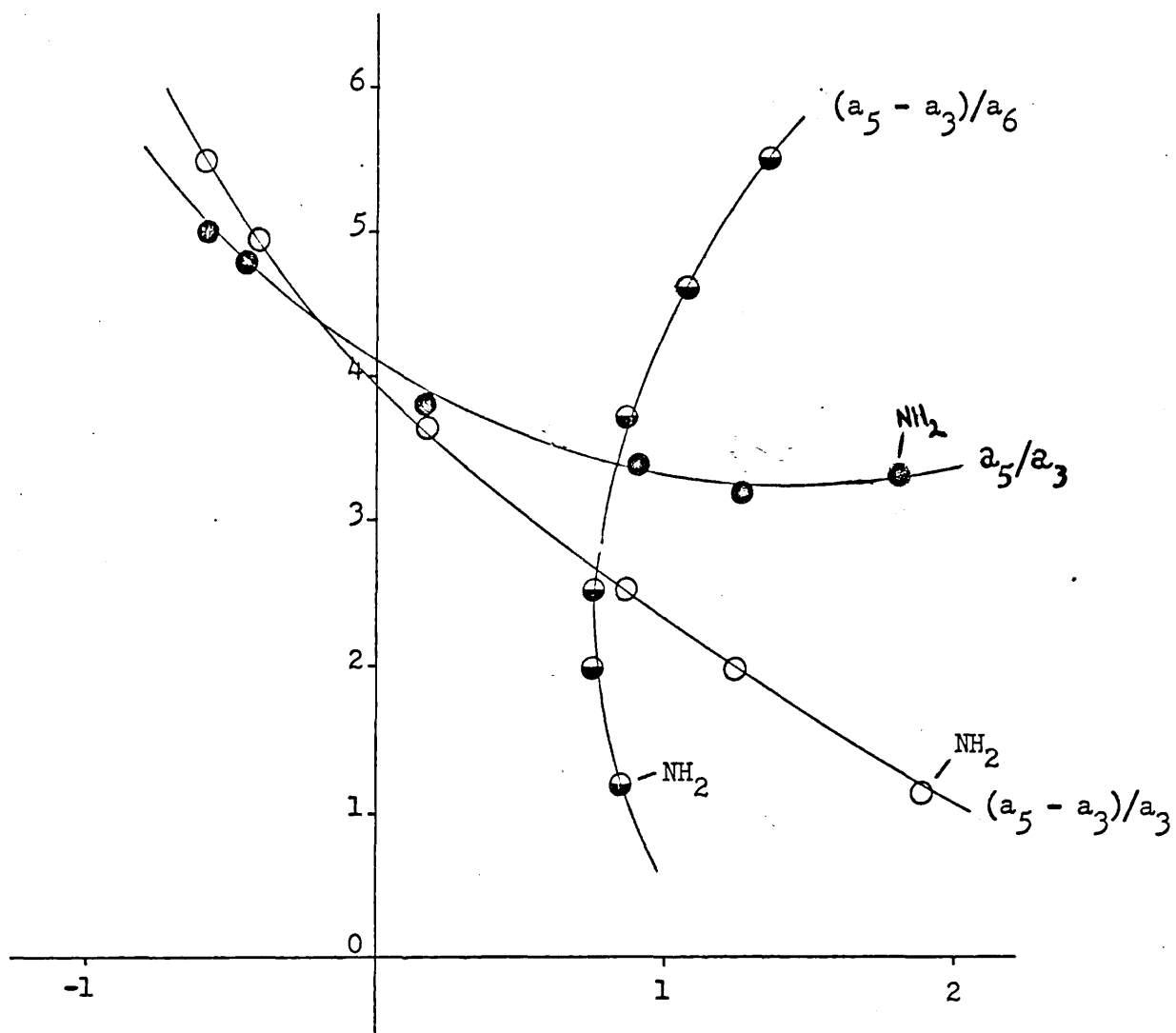
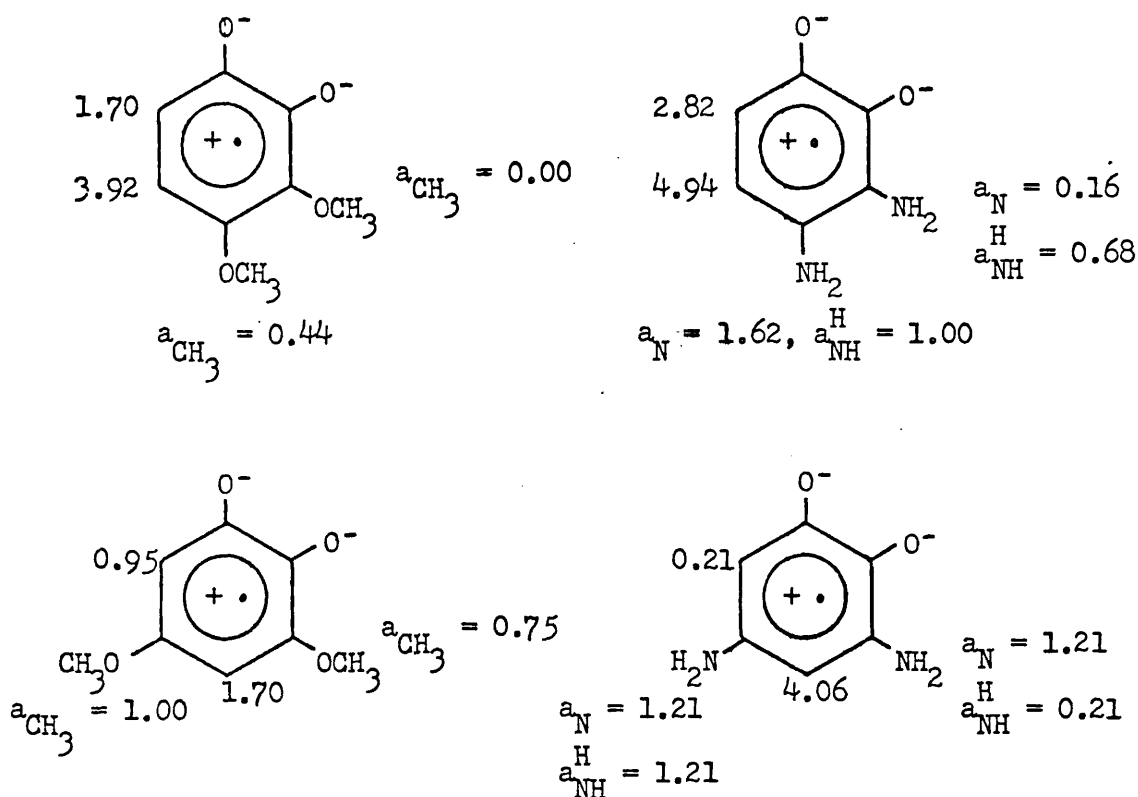


Fig. 12. - Graph showing the method of assignment of coupling constants for 4-amino-1,2-semiquinone.

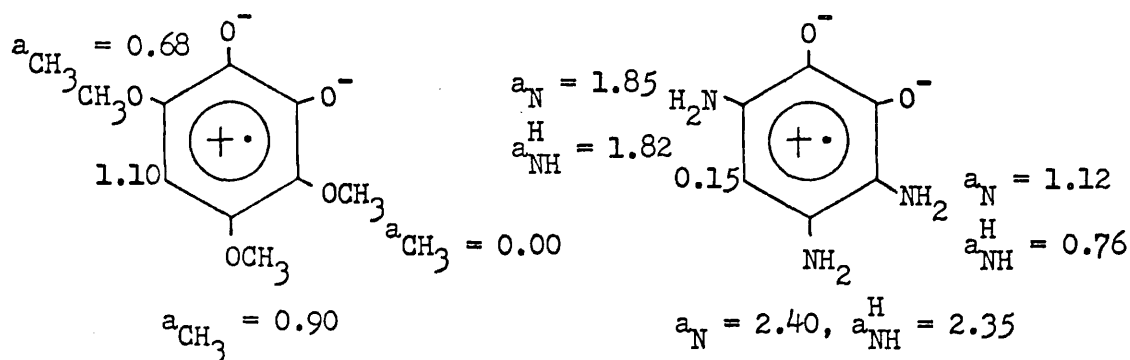
the respective curves, confirming the validity of this approach.

Because of the smooth variation of splitting patterns it is possible to assign coupling constants in a certain species by comparison with the splitting pattern of a similarly substituted compound. Since amino- and methoxy-groups are similar in their effect on spin density distribution in these radicals, the assignments for the two asymmetrical diamino-semiquinones VIII and IX (Figs. 21, 22) have been made by comparison with the correspondingly substituted dimethoxysemiquinones⁸⁹ (Scheme 1).



Scheme 1. - Comparison of splittings (a/Gauss) for radicals VIII and IX with corresponding methoxy-substituted semiquinones.

Although slightly more tenuous, assignments for the triaminosemi-quinone XII (Fig. 27) have also been made by comparison with the corresponding methoxy-substituted compound (Scheme 2).



Scheme 2. - Comparison of splittings ($a/10^{-4}$ T) for radical XII with the corresponding methoxy-substituted semiquinone.

In all cases, the assignments of the coupling constants to the relative positions on the molecule were confirmed by McLachlan S.C.F. calculations.

Although well resolved, the spectra of the aminosemiquinones were, generally, complex and in most cases there was extensive overlap of spectral lines. As a result, wherever possible, spectra were obtained not only in ethanolic solution, but also in ethanol-water and ethanol-DMF mixtures. Changes in coupling constants due to solvent effects are well known⁸⁴⁻⁸⁷ and these solvent-affected spectra were very useful as an aid to analysis. Two examples where the change in coupling constants due to solvent effects is particularly striking are provided by the spectra of 3,5-diamino-1,2-semiquinone (radical IX) and 3,4,6-triamino-1,2-semiquinone (radical XII). The spectra of radical IX in ethanol and in ethanol-water solutions are shown in Figs. 22 and 24 respectively, while

those of radical XII in the same solutions are shown in Figs. 27 and 28 respectively.

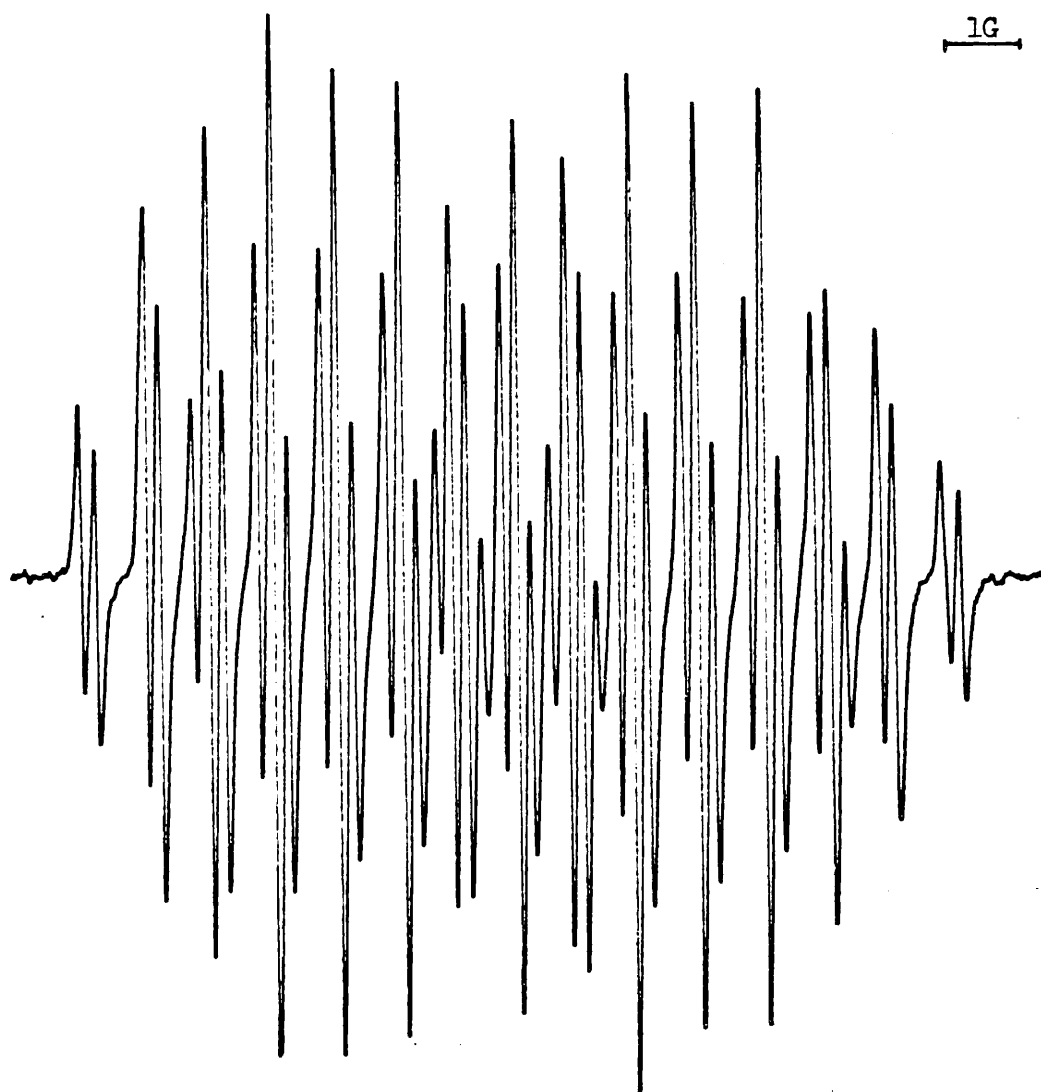


Fig. 13. - Spectrum of 2-amino-1,4-semiquinone.

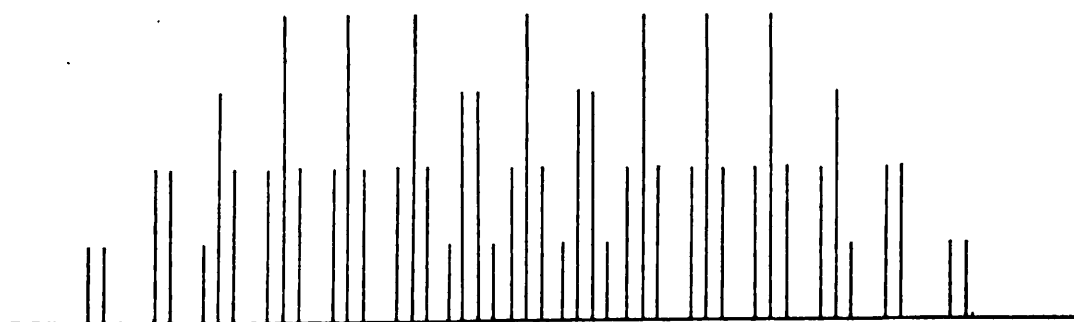
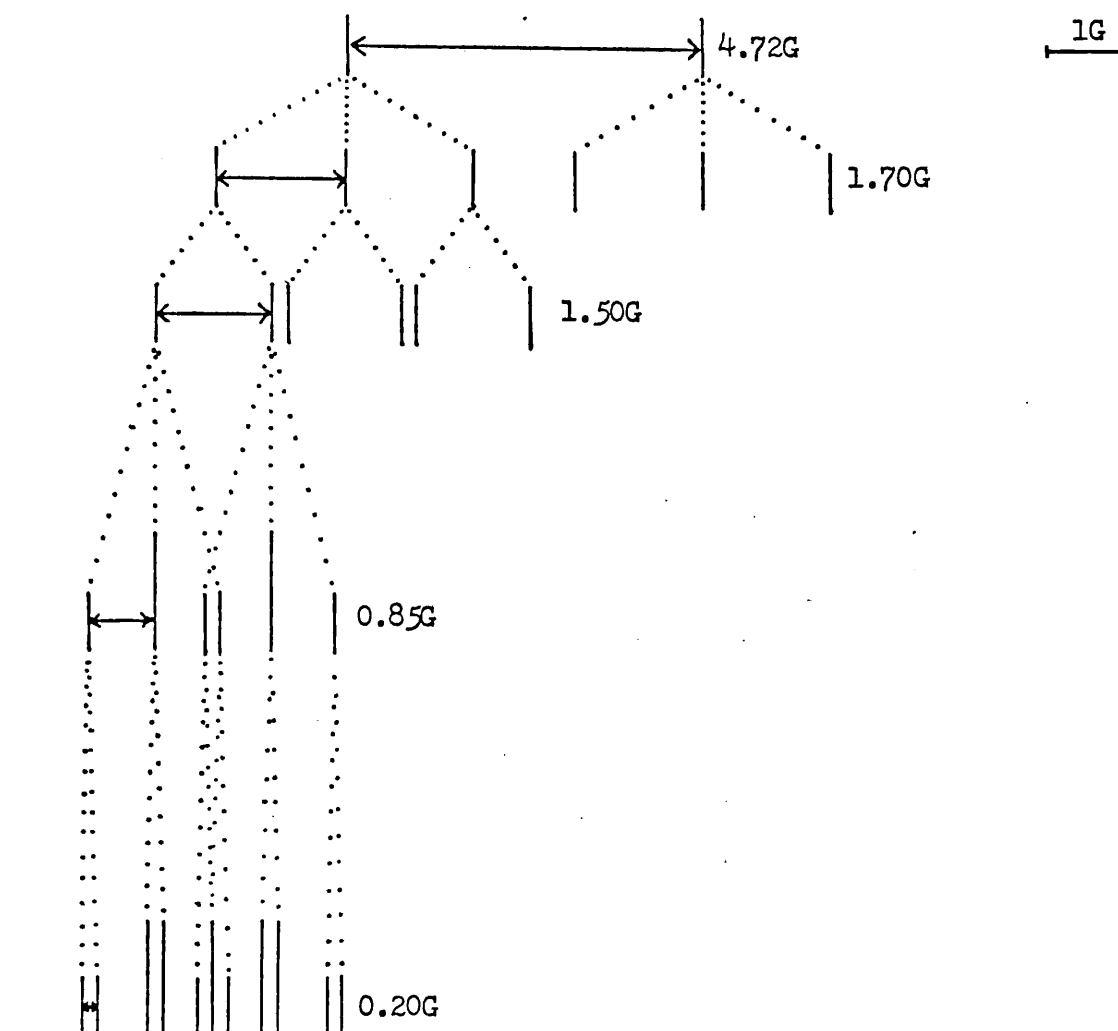


Fig. 14 - Reconstruction of the spectrum of 2-amino-1,4-semiquinone.

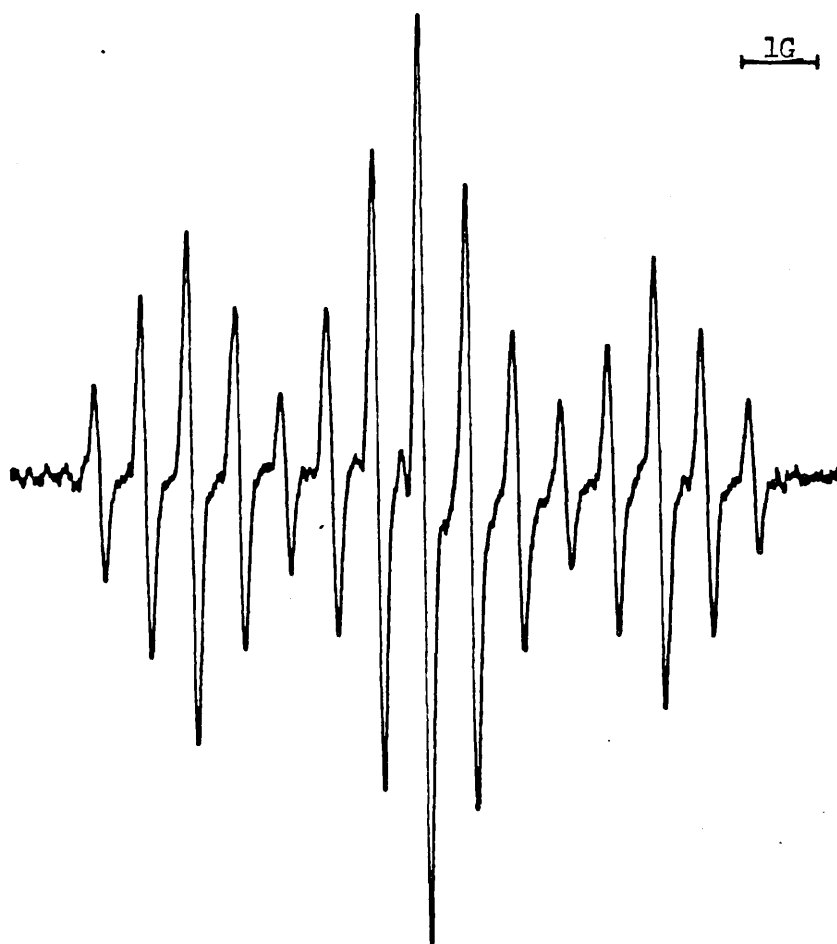


Fig. 15. - Spectrum of 2,3-diamino-1,4-semiquinone.

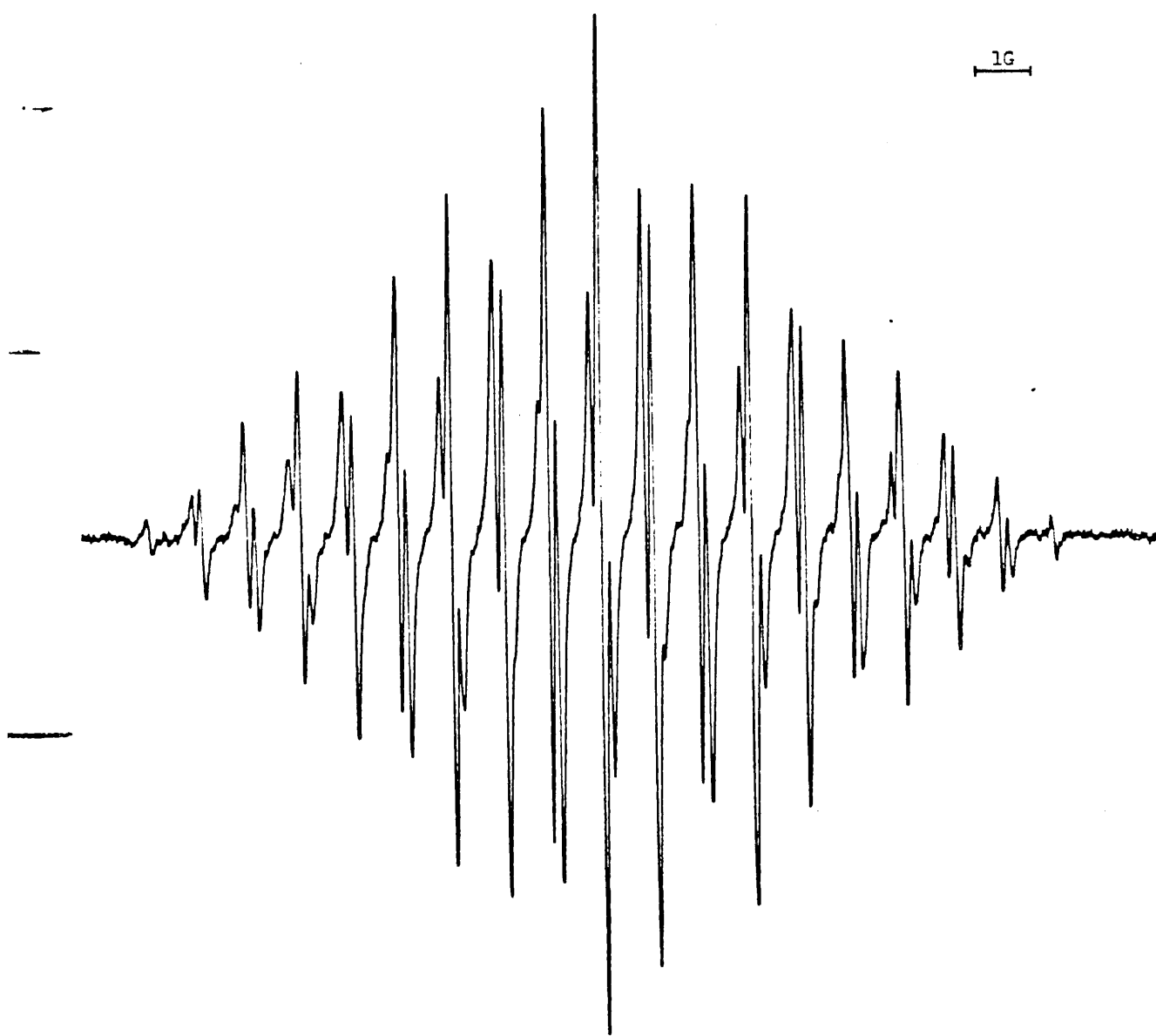


Fig. 16. - Spectrum of 2,5-diamino-1,4-semiquinone.

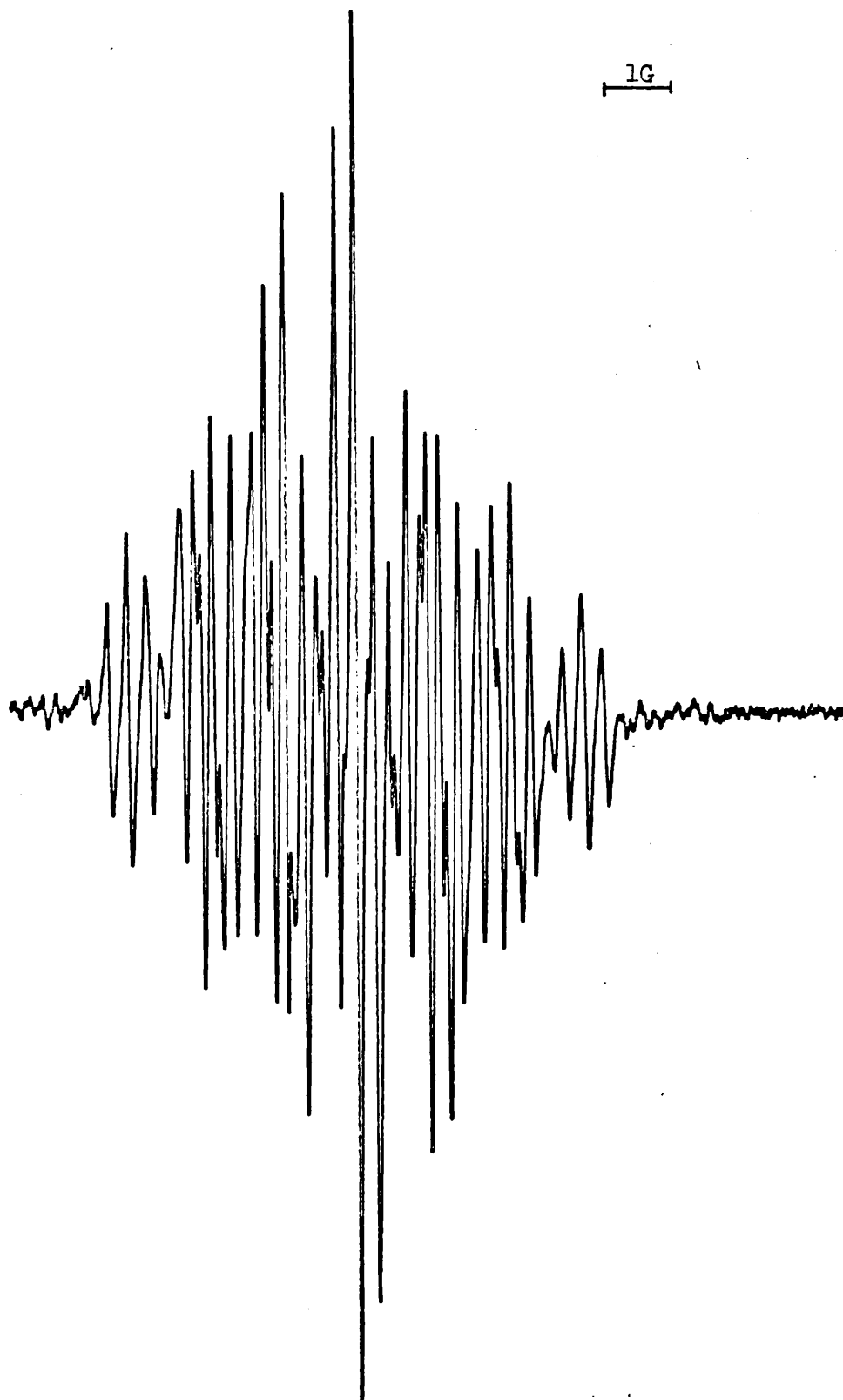


Fig. 17. - Spectrum of 2,6-diamino-1,4-semiquinone.

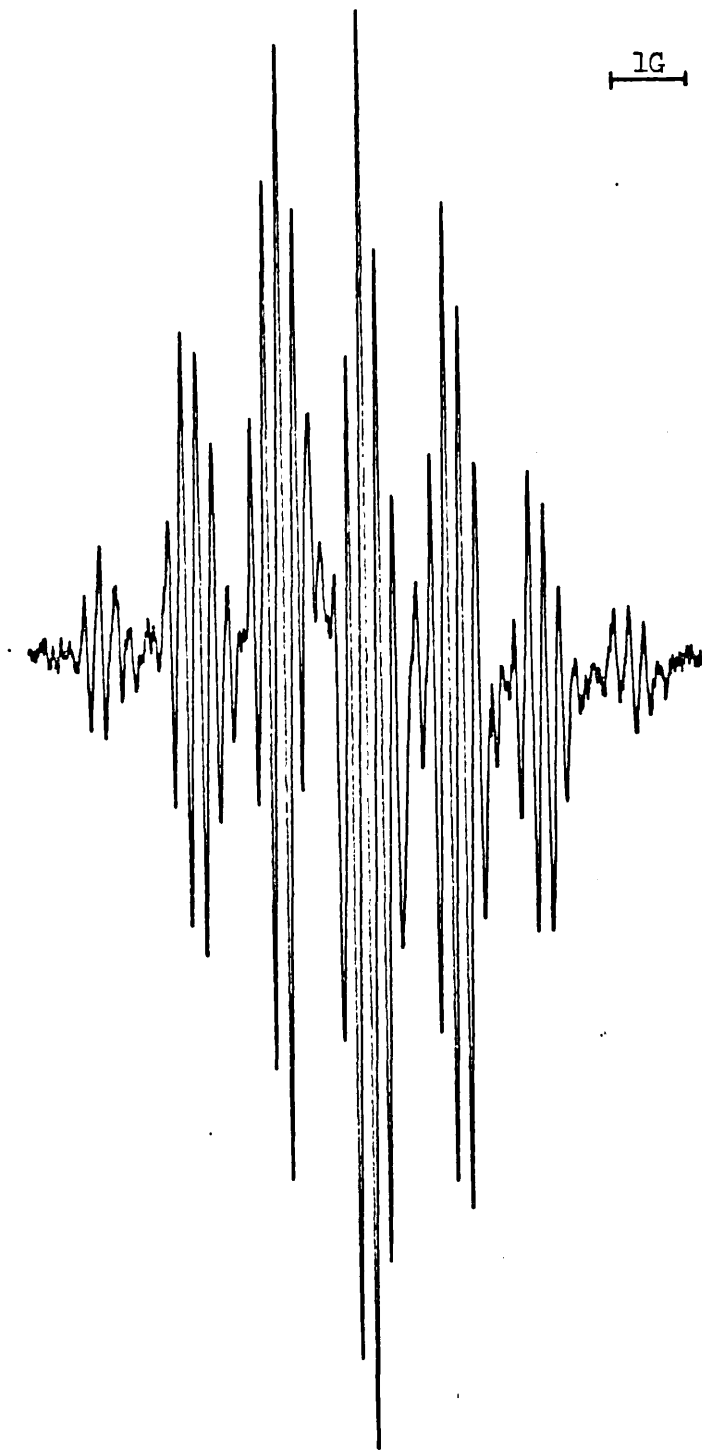


Fig. 18. - Spectrum of 2,3,5,6-tetraamino-1,4-semiquinone.

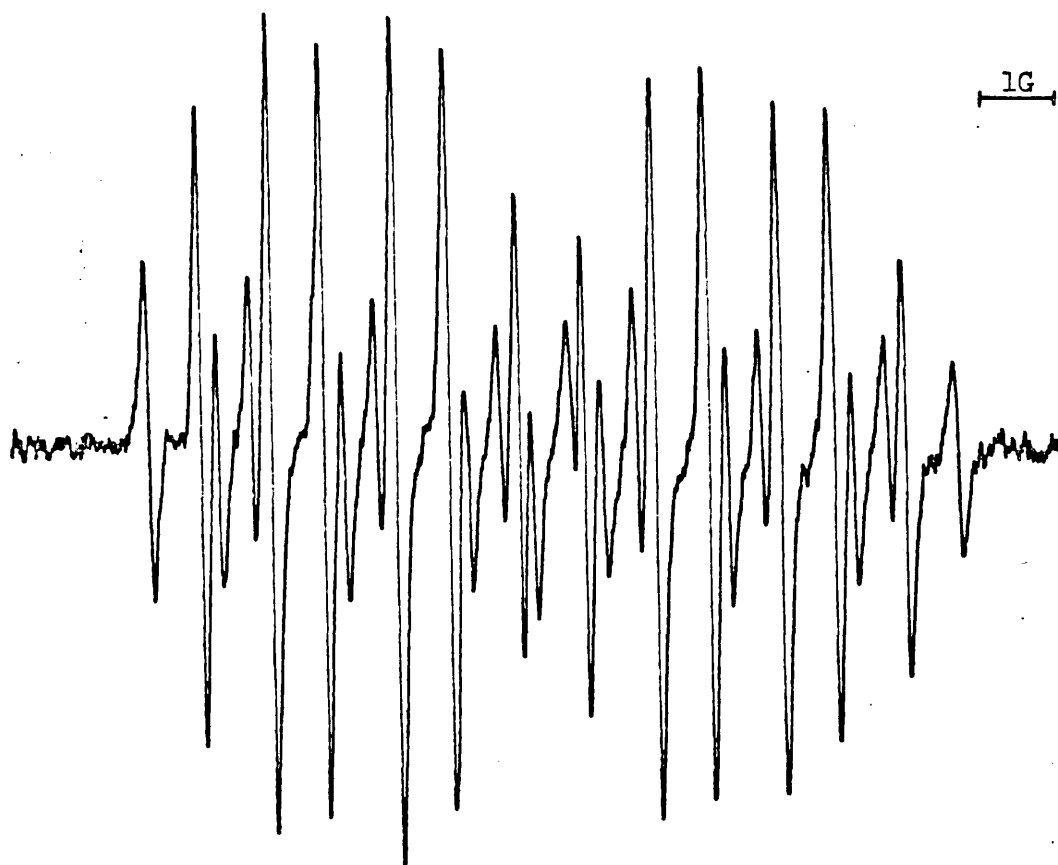


Fig. 19. - Spectrum of 3-amino-1,2-semiquinone.

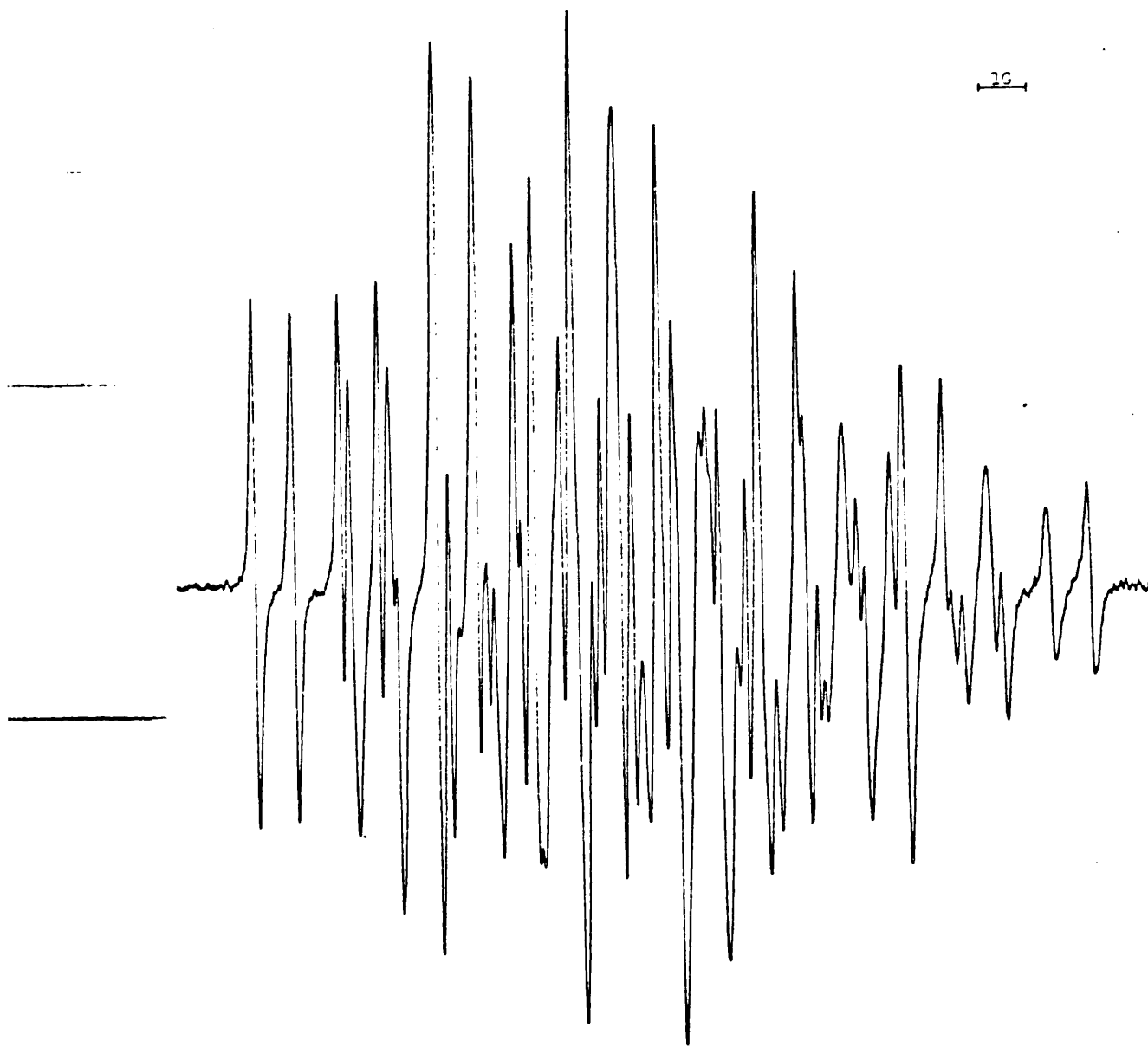


Fig. 11. - Spectrum of 4-amino-1,2-semiquinone.

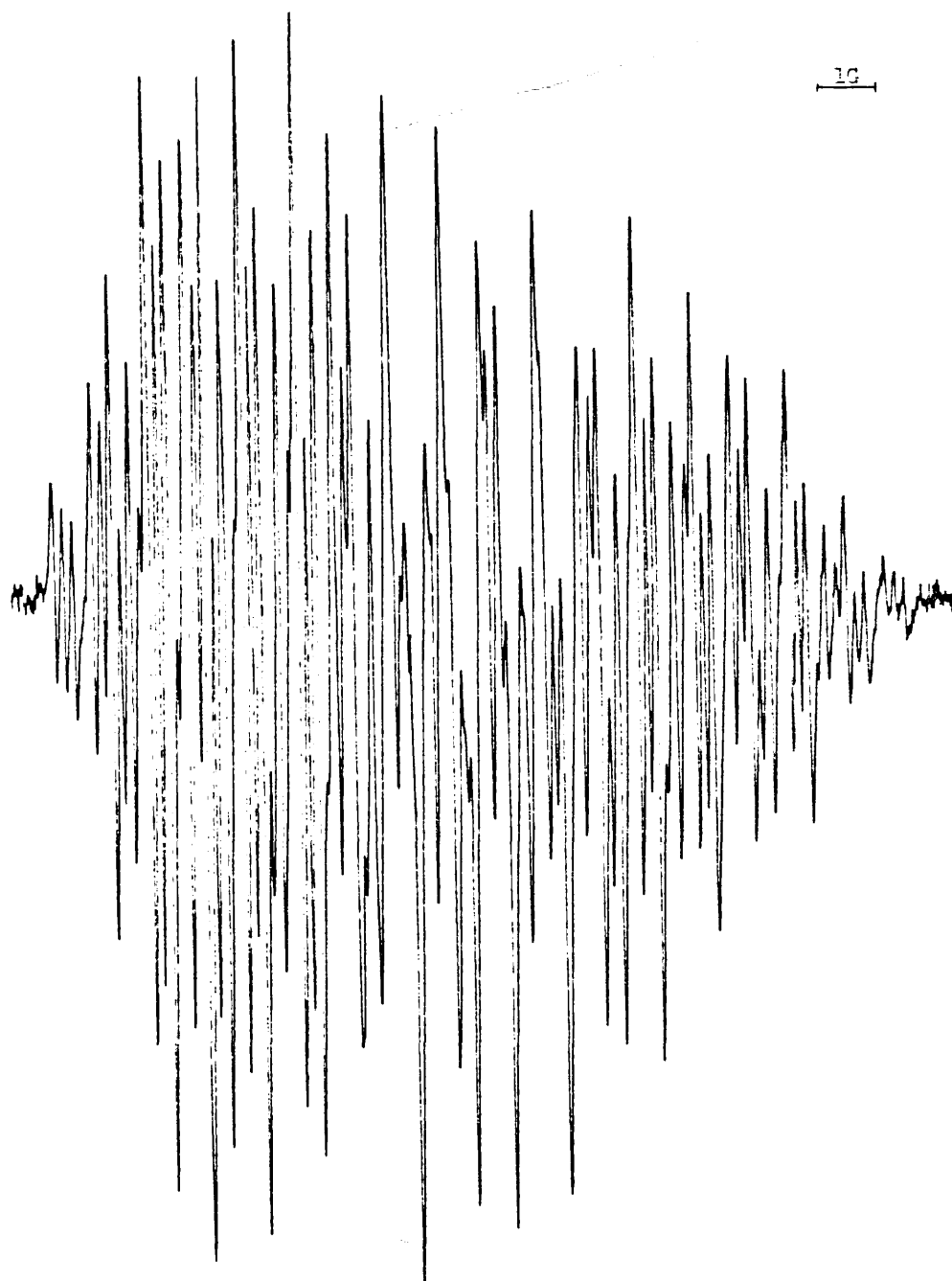


Fig. 11. - Spectrum of 3,4-diamino-1,2-semiquinone.

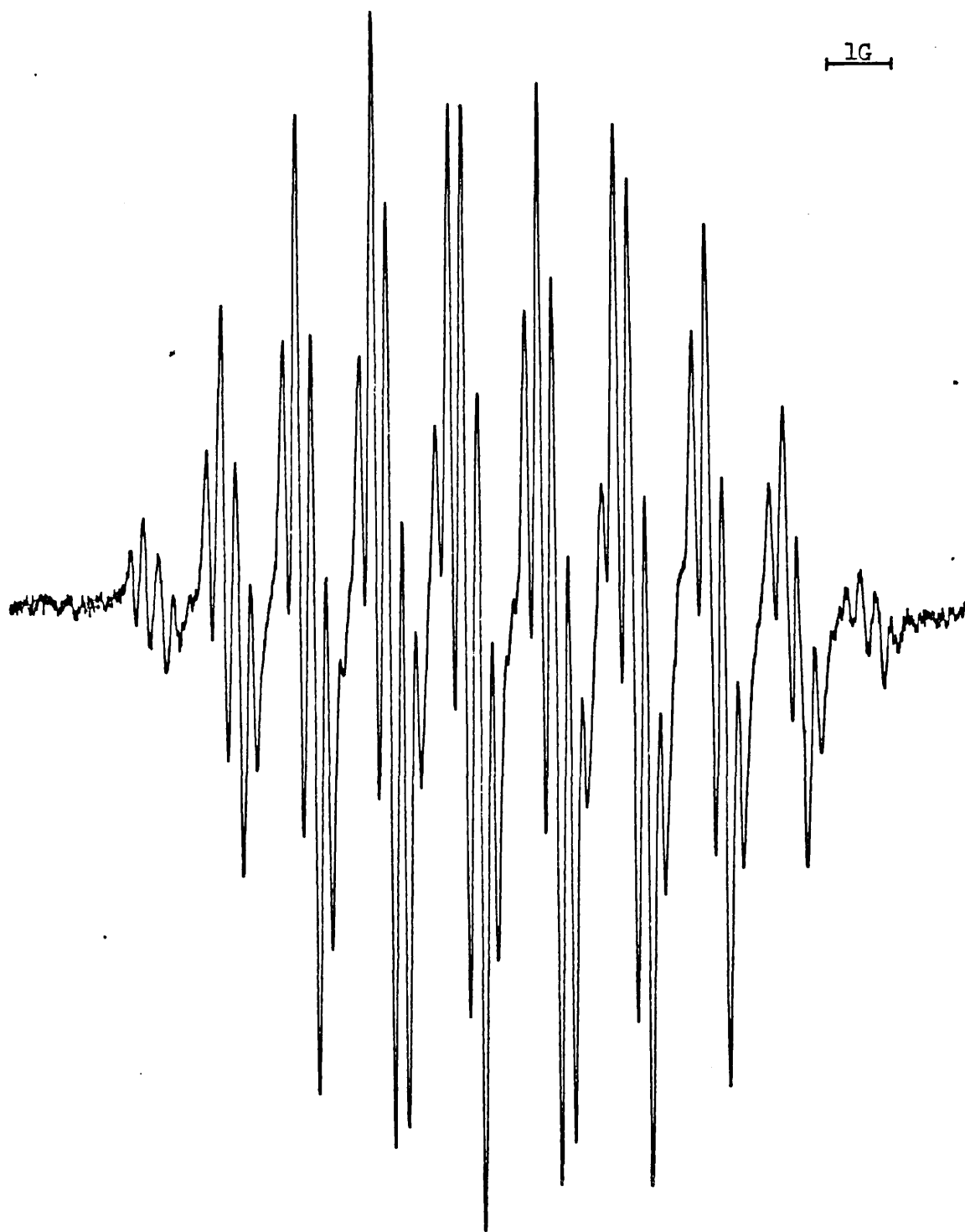


Fig. 22. - Spectrum of 3,5-diamino-1,2-semiquinone (in ethanol).

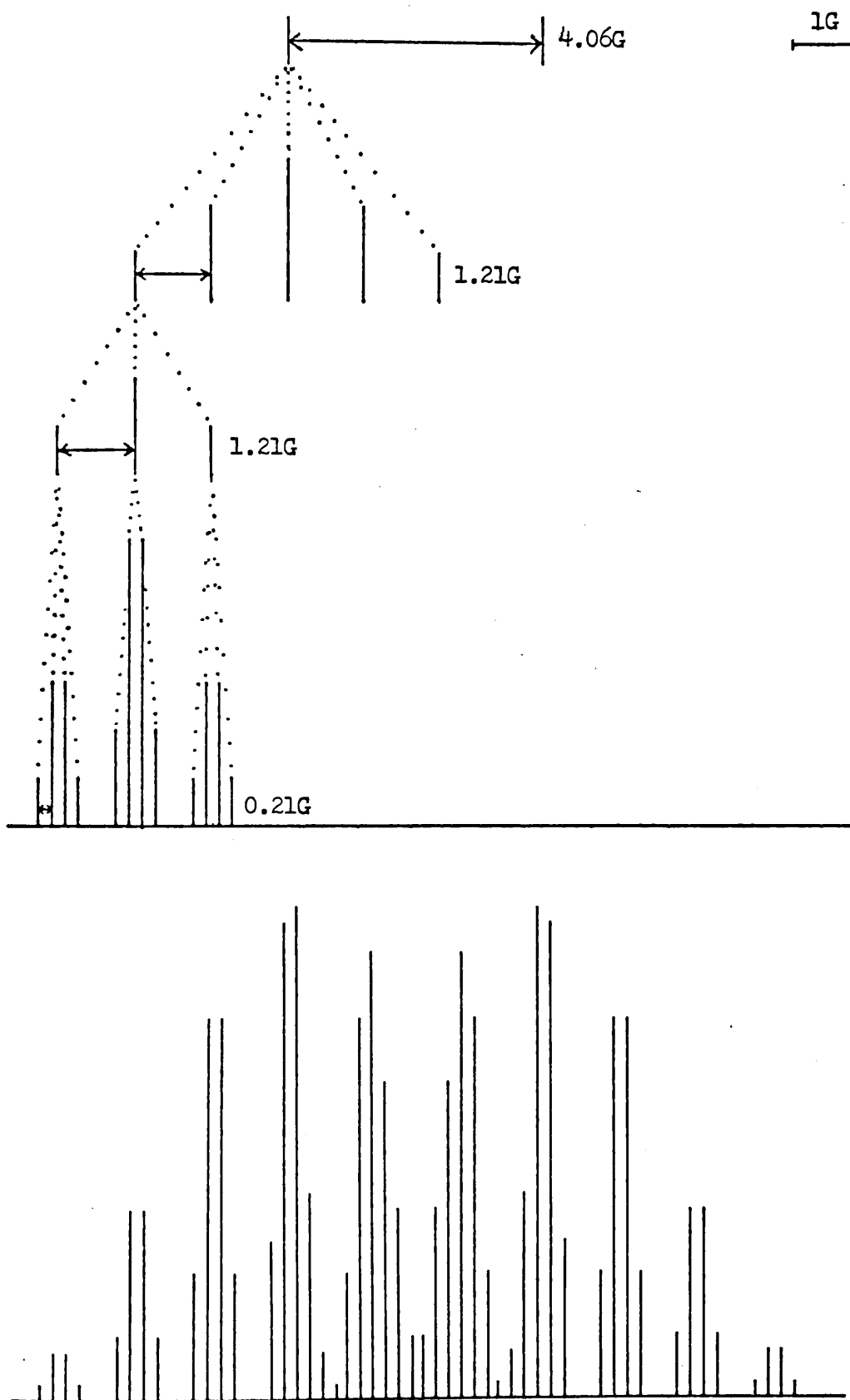


Fig. 23. - Reconstruction of the spectrum of 3,5-diamino-1,2-semiquinone (in ethanol).

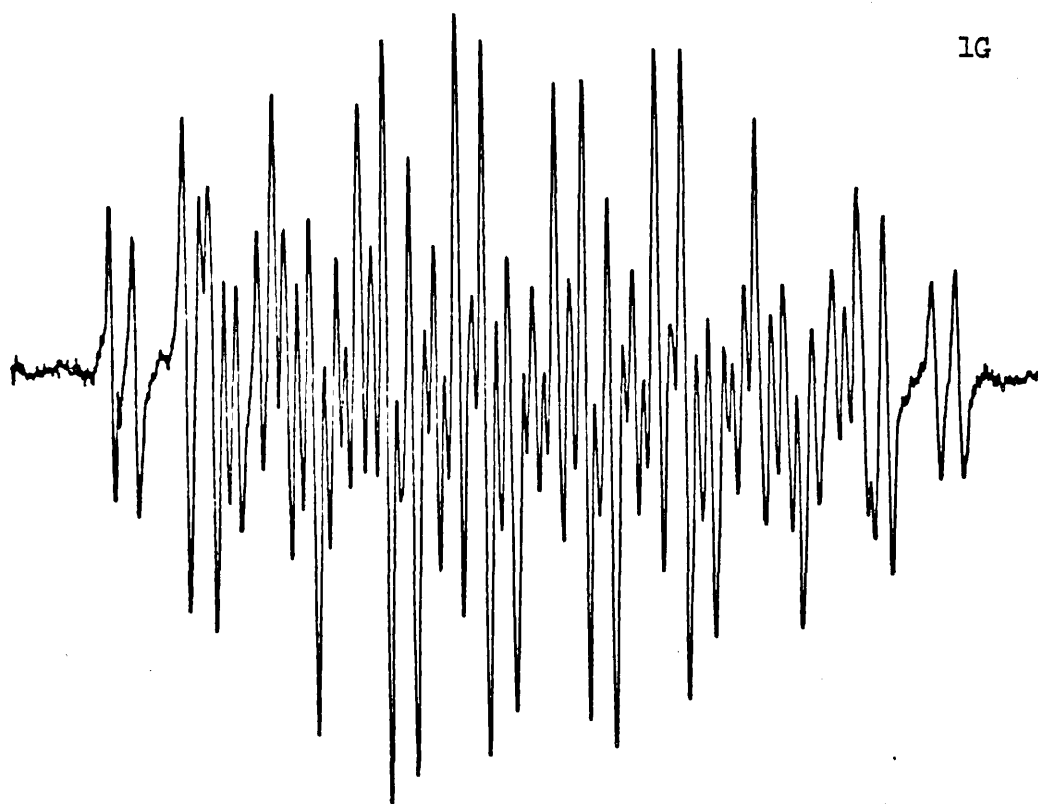


Fig. 24. - Spectrum of 3,5-diamino-1,2-semiquinone (in ethanol/water).

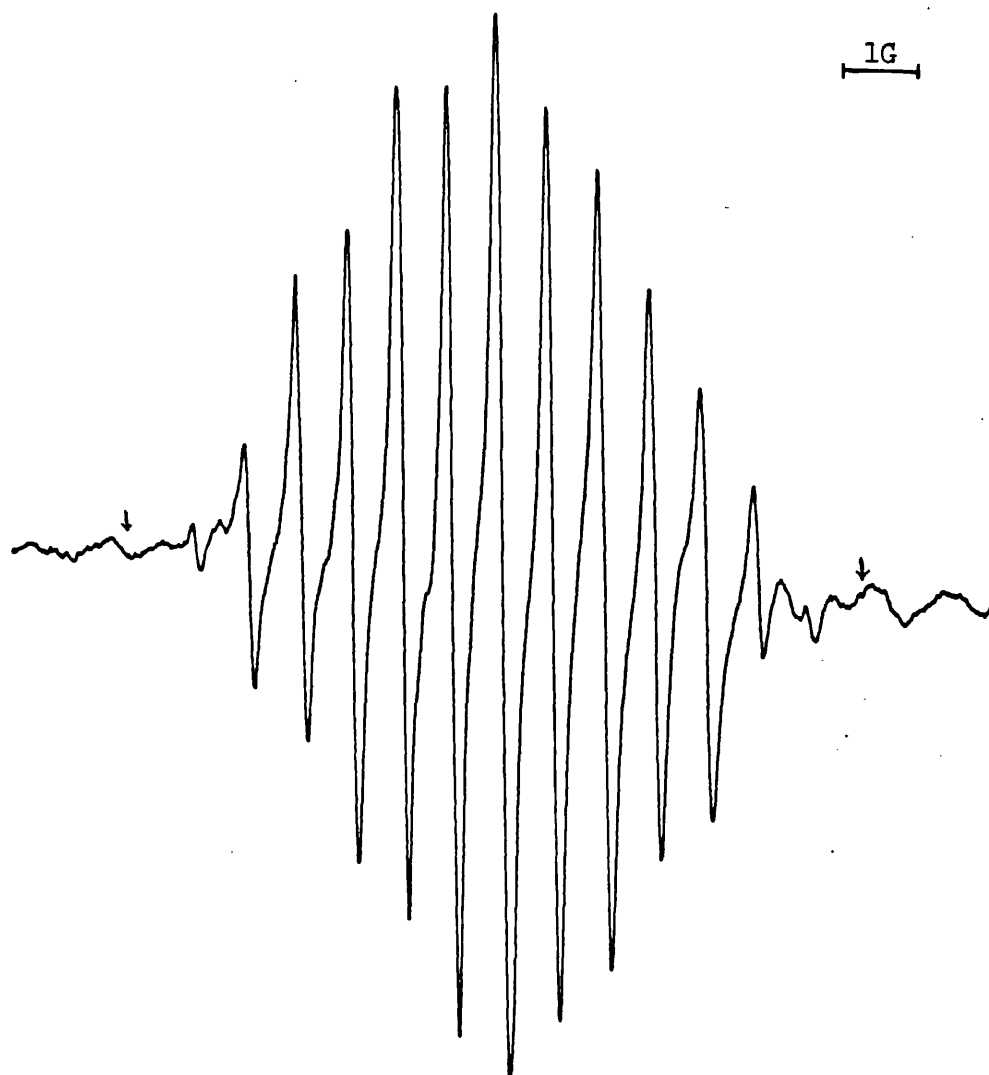


Fig. 25. - Spectrum of 3,6-diamino-1,2-semiquinone.

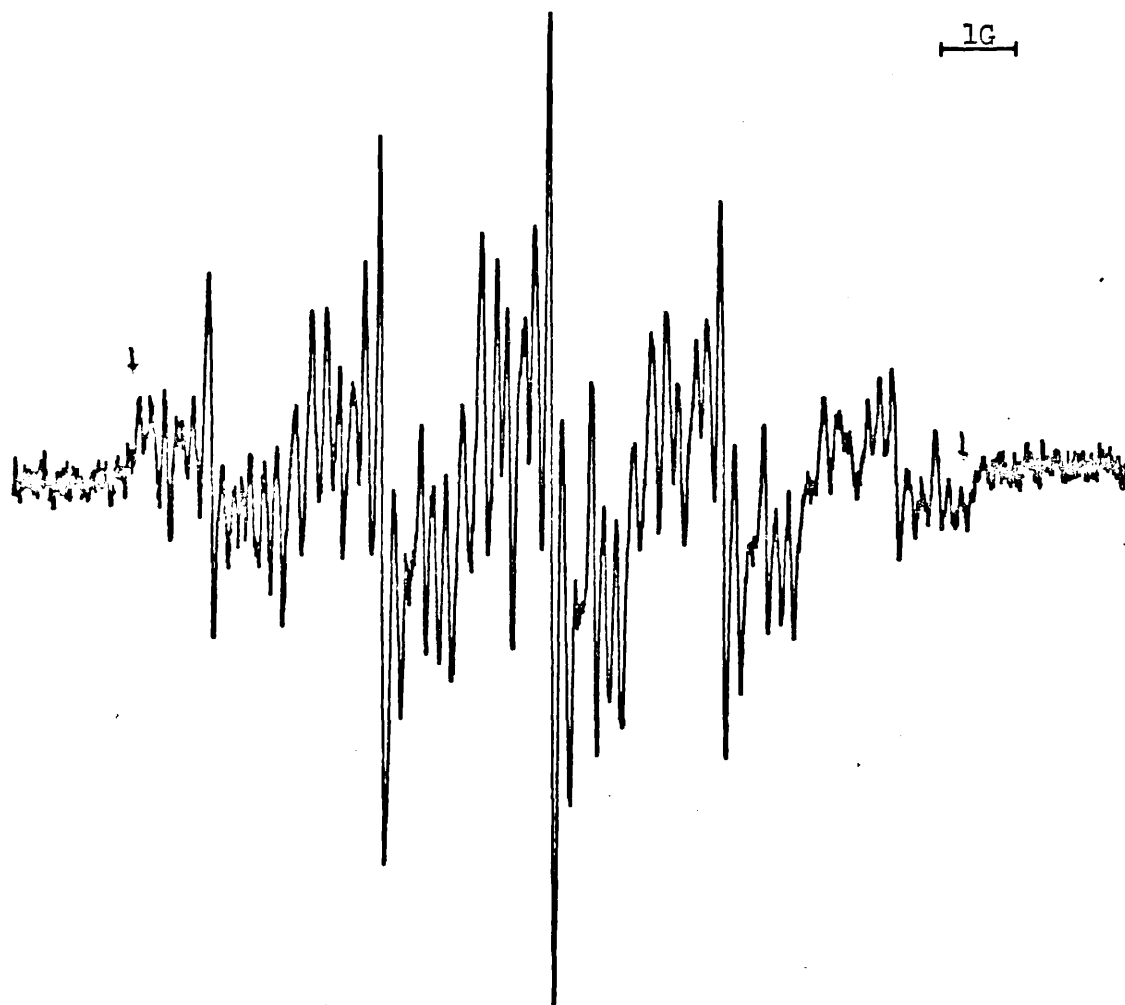


Fig. 26. - Spectrum of 4,5-diamino-1,2-semiquinone.

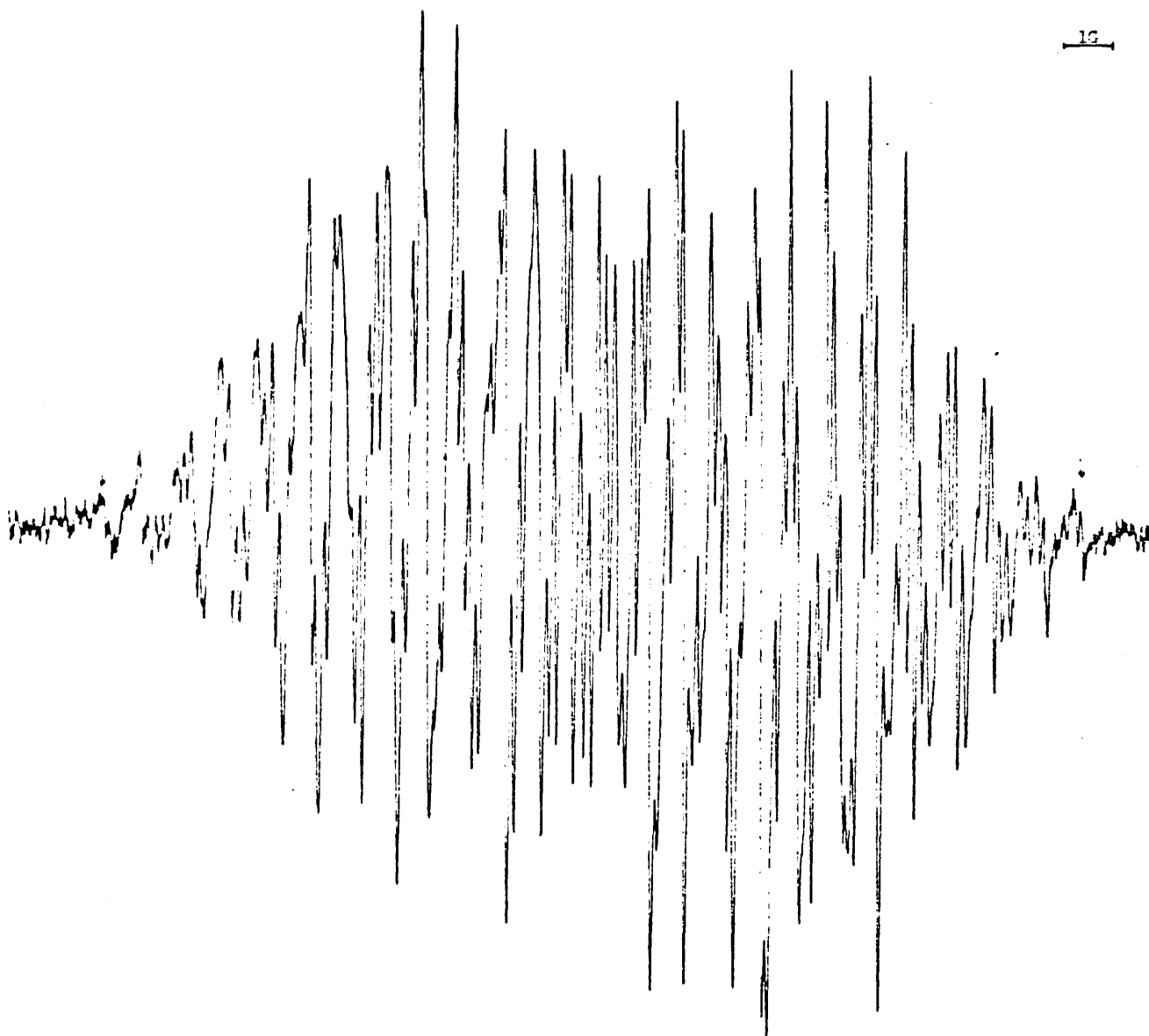


Fig. 7. - Spectrum of 3,4,6-triamino-1,2-semiquinone (in ethanol).

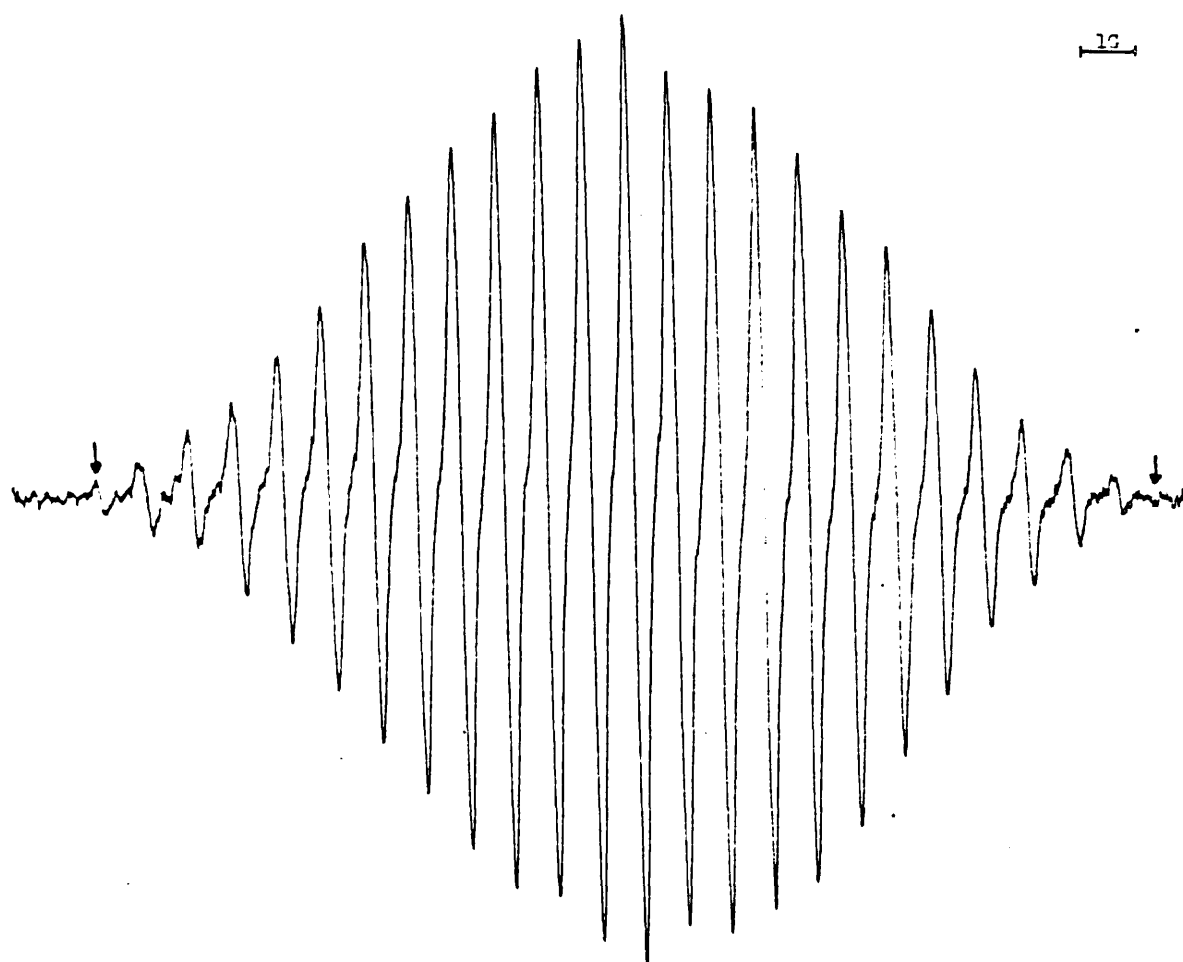
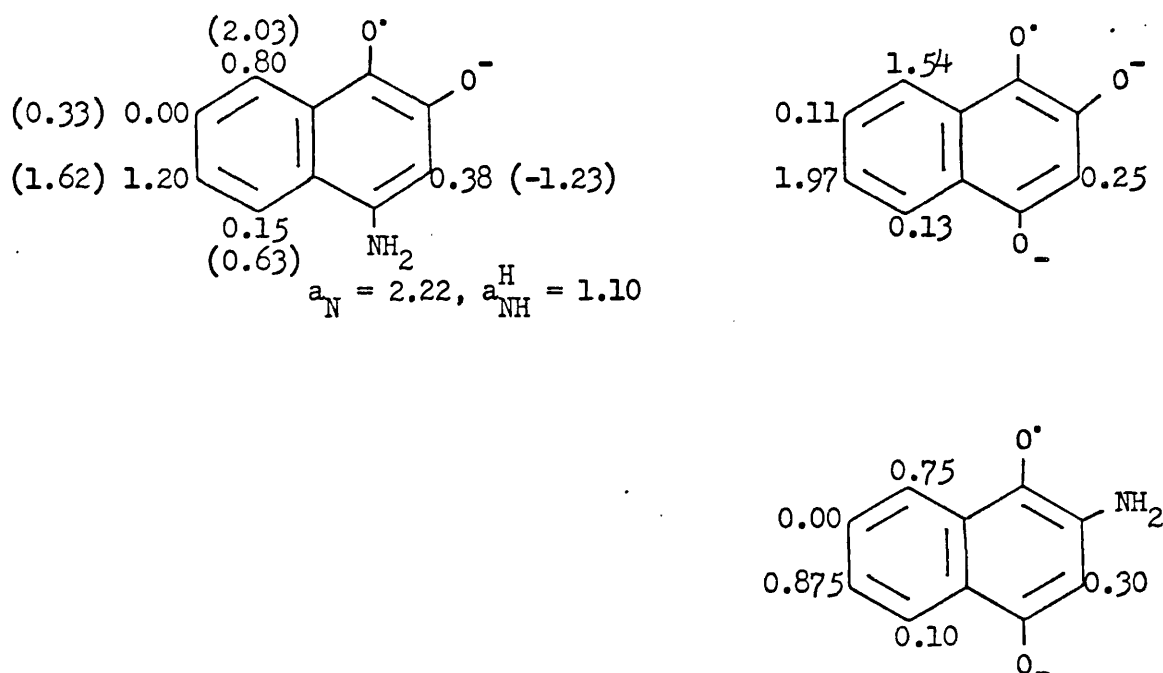


Fig. 28. - Spectrum of 3,4,6-triamino-1,2-semiquinone (in ethanol/water).

III.2.1. 4-Amino-1,2-naphthosemiquinone

4-Amino-1,2-naphthosemiquinone gave a spectrum which analysed as four non-equivalent protons with splittings of 0.15G, 0.38G, 0.80G and 1.20G, two equivalent protons with a splitting of 1.10G and a nitrogen with the splitting of 2.22G. The assignment of the splittings from the amino-group is unambiguous and the assignment of the splittings from the ring protons have been made on the basis of comparison with other 1,2,4-substituted naphthoquinone systems (Scheme 3). McLachlan S.C.F. calculations support this assignment.

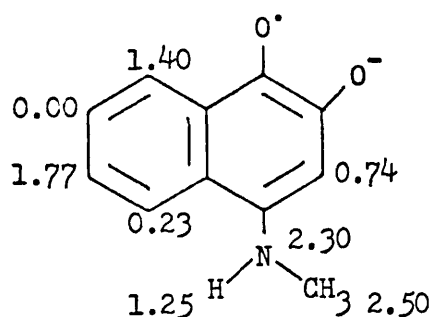


Scheme 3. - Assignment of coupling constants (a/Gauss) in 4-amino-1,2-naphthosemiquinone by comparison with other 1,2,4-substituted systems (1,2,4-trihydroxynaphthalene⁹⁰ and 2-amino-1,4-naphthosemiquinone⁸²) (calculated values in parentheses).

III.2.2. 4-Methylamino-1,2-naphthosemiquinone

4-Methylamino-1,2-naphthosemiquinone gave a spectrum which analysed as five non-equivalent protons with splittings of 0.23G, 0.74G, 1.25G, 1.40G and 1.77G, a nitrogen with a splitting of 2.30G and three equivalent protons with a splitting of 2.50G.

The assignments of the nitrogen splitting and the methyl-proton splitting are obvious, but the single-proton coupling constants are ambiguous. They have tentatively been assigned as in Scheme 4. on the basis of comparison with 4-amino-1,2-naphthosemiquinone (Scheme 3).



Scheme 4. - Assignment of coupling constants (a/Gauss) in 4-methylamino-1,2-naphthosemiquinone.

III.3. Heterocyclic Semiquinones

Well resolved spectra of a variety of heterocyclic semiquinones were obtained. The examples of heterocyclic semiquinones selected were chosen in order to illustrate the effects of nitrogen on the unpaired electron spin density distribution in a variety of compounds where nitrogen appears in many different heterocyclic environments.

3.1. Quinoline- and Isoquinoline-5,8-semiquinones

All of the ring positions in quinoline- and isoquinoline-5,8-semiquinones are chemically non-equivalent and although equivalency of coupling constants occurs, this is purely fortuitous. This asymmetry also leads to ambiguity in the assignment of the coupling constants to the various ring positions. The assignments have been made on the basis of comparison with equivalent naphtho-1,4-semiquinone systems and with the aid of McLachlan S.C.F. calculations. This method of assignment has also helped to define the position in which oxygen (O^-) is substituted into the two secondary radicals.

3.1.1. Quinoline-5,8-semiquinone

Analysis of the spectrum of quinoline-5,8-semiquinone (Fig. 29) showed there to be five non-equivalent protons with splittings of 3.16G, 3.05G, 0.80G, 0.32G and 0.12G, and an absence of a nitrogen splitting.

The assignment of coupling constants are shown in Scheme 5., with calculated values and values for the equivalent naphtho-1,4-semiquinone system.

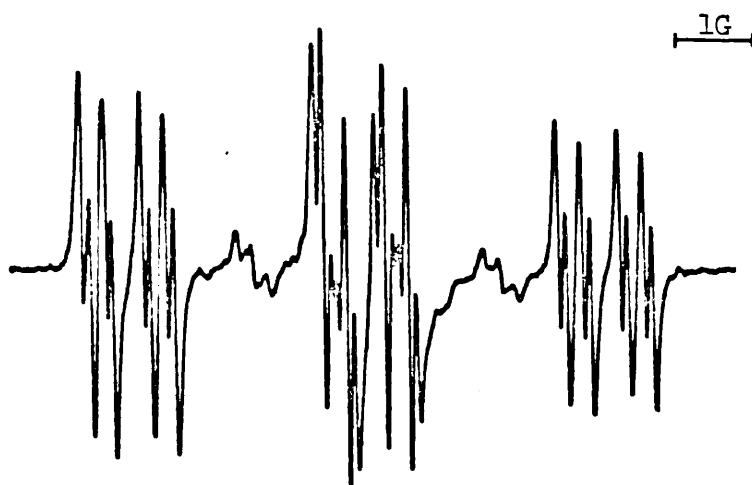
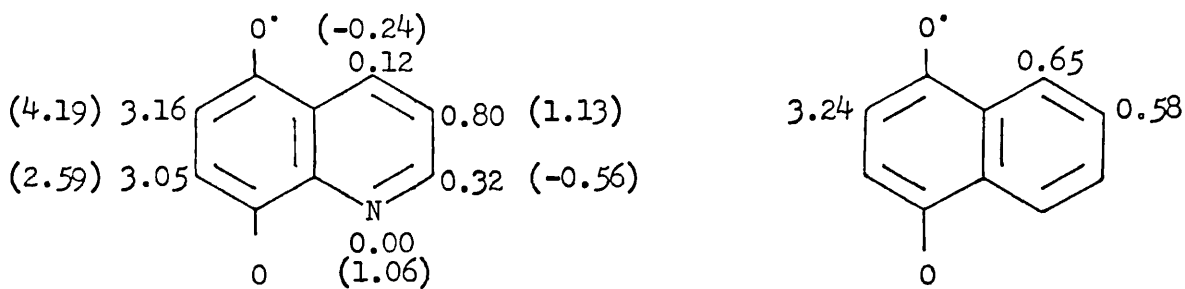


Fig. 29. - Spectrum of quinoline-5,8-semiquinone.

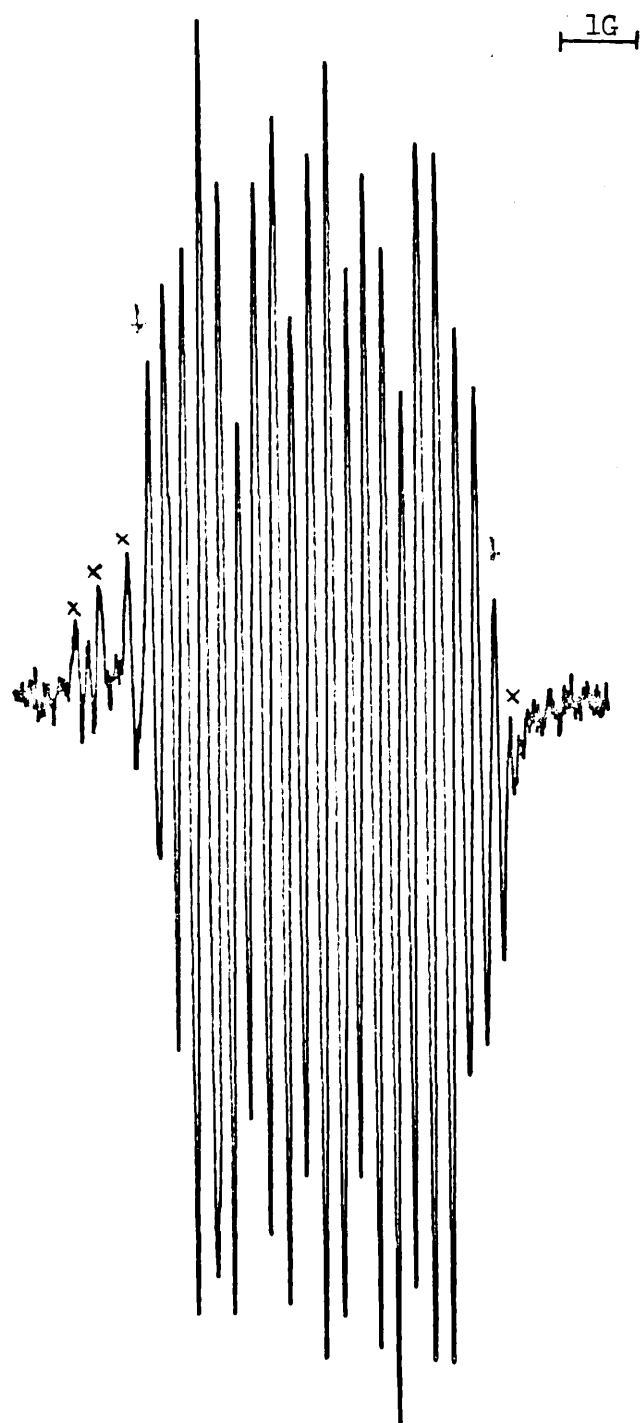


Scheme 5. - Assignment of coupling constants (a /Gauss) in quinoline-5,8-semiquinone by comparison with naphtho-1,4-semiquinone (calculated values in parentheses).

3.1.2. Quinoline-5,8-semiquinone (secondary radical)

The spectrum of the secondary radical was obtained when excess base was added to an aqueous solution of quinoline-5,8-quinone. The primary radical was initially observed but after about 10 minutes this decayed and yielded the secondary radical (Fig. 30).

The spectrum consisted of 20 lines, all 0.25 cm apart, and analysis was achieved by close inspection of the line intensities and a building up of the individual splitting patterns to reproduce the observed spectrum as shown in Fig. 31. The analysis showed there to be a nitrogen splitting of 0.75G and four proton splittings of 2.25G, 0.50G, 0.25G and 0.25G. Assignment of these coupling constants are shown Scheme 6.



(x - Spurious lines from another species)

Fig. 30. - Spectrum of quinoline-5,8-semiquinone (secondary radical).

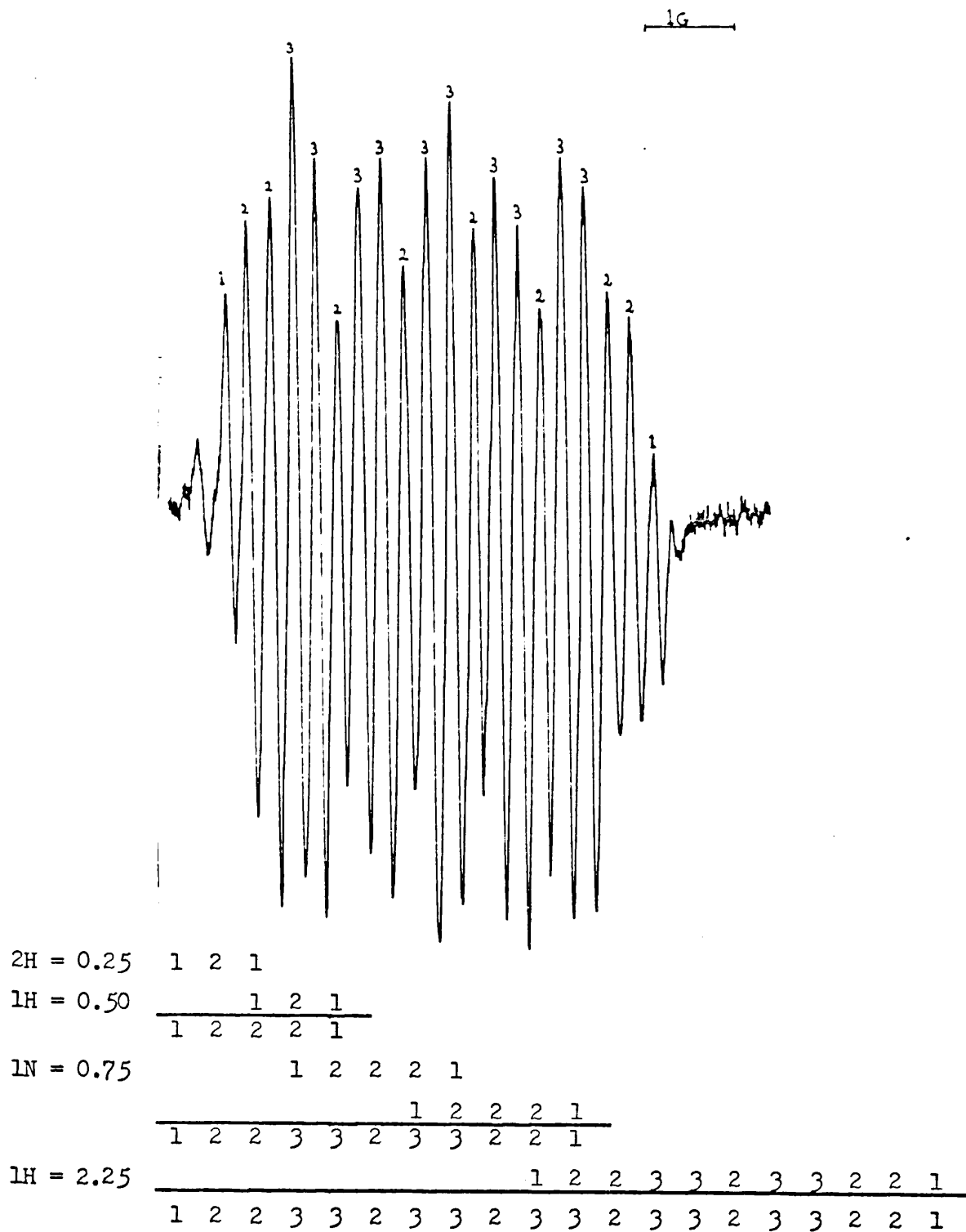
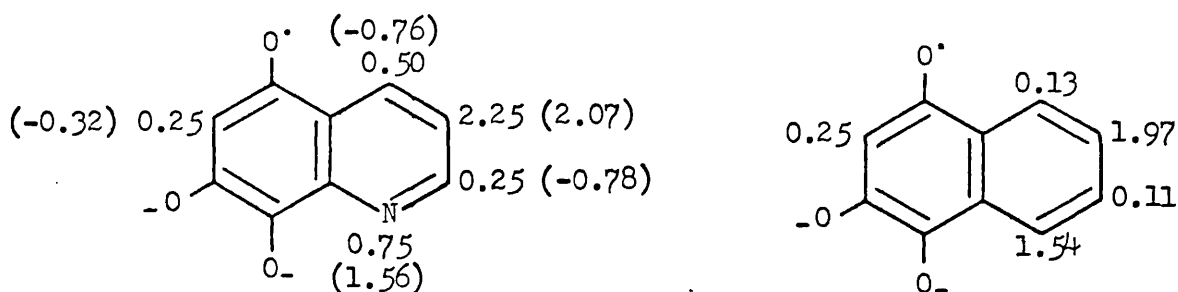


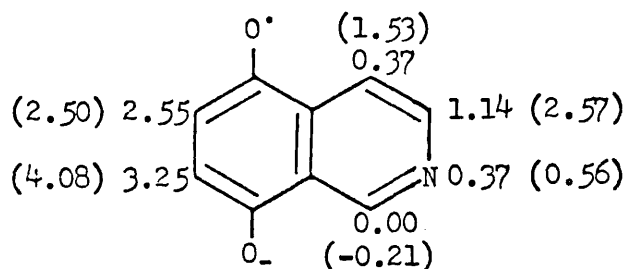
Fig. 31. - Build-up of line-intensity pattern in spectrum of quinoline-5,8-semiquinone (secondary radical).



Scheme 6. - Assignment of coupling constants (a/Gauss) in the secondary radical of quinoline-5,8-semiquinone by comparison with the secondary radical of naphtho-1,4-semiquinone (calculated values in parentheses).

3.1.3 Isoquinoline-5,8-semiquinone

Analysis of the spectrum of isoquinoline-5,8-semiquinone (Fig. 32) showed there to be a nitrogen splitting of 0.37G and four non-equivalent protons with splittings of 3.25G, 2.55G, 1.14G and 0.37G, leaving one proton with a coupling constant of zero. The assignment of coupling constants are shown in Scheme 7.



Scheme 7. - Assignment of coupling constants (a/Gauss) in isoquinoline-5,8-semiquinone by comparison with naphtho-1,4-semiquinone (calculated values in parentheses).

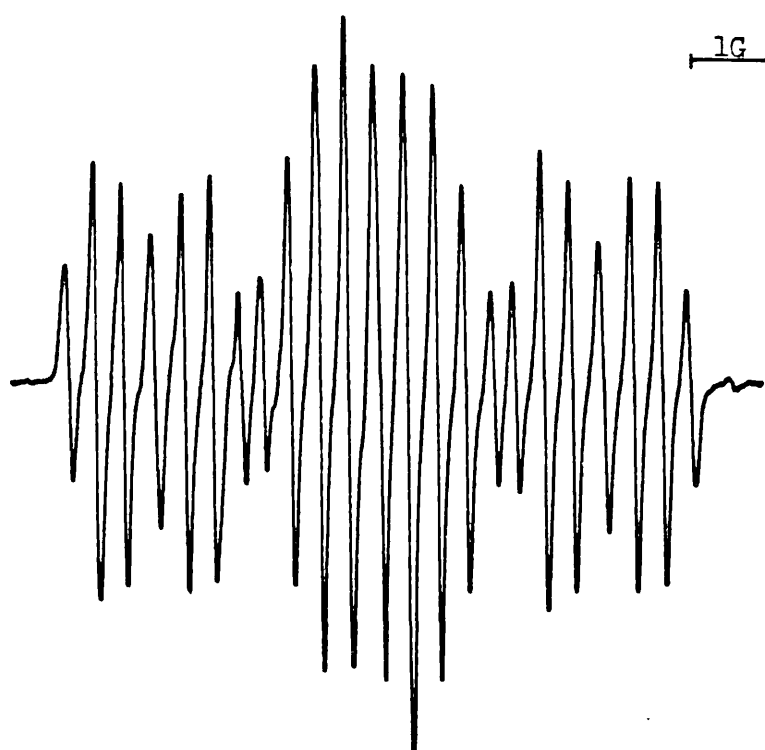
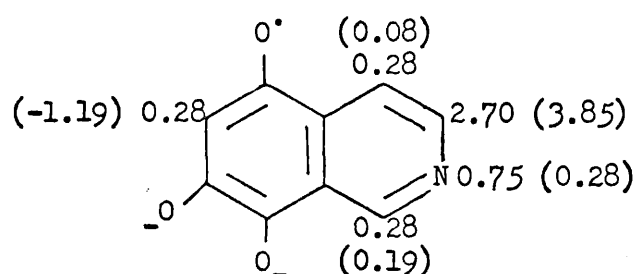


Fig. 32. - Spectrum of isoquinoline-5,8-semiquinone.

3.1.4. Isoquinoline-5,8-semiquinone (secondary radical)

Like the secondary radical of quinoline-5,8-semiquinone, the secondary radical of isoquinoline-5,8-semiquinone was generated by addition of excess base to the parent quinone and allowing the primary radical to decay and yield the secondary species after about ten minutes.

Analysis of the spectrum (Fig. 33) showed there to be a nitrogen splitting of 0.75G, three proton splittings of 0.28G and a single proton splitting of 2.70G. The assignment of coupling constants are shown in Scheme 8.



Scheme 8. - Assignment of coupling constants (a/Gauss) in the secondary radical of isoquinoline-5,8-semiquinone by comparison with the secondary radical of naphtho-1,4-semiquinone (calculated values in parentheses)

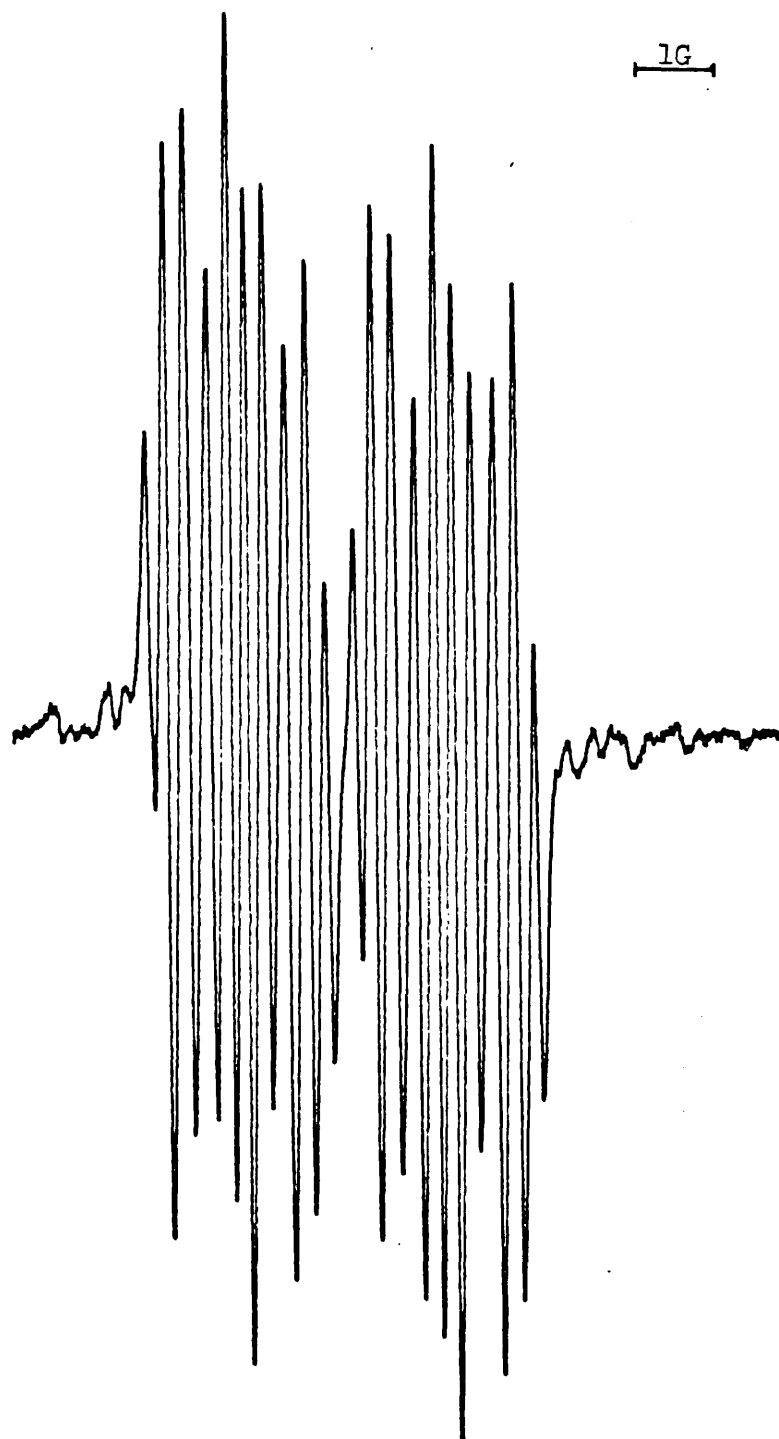


Fig. 33. - Spectrum of isoquinoline-5,8-semiquinone (secondary radical).

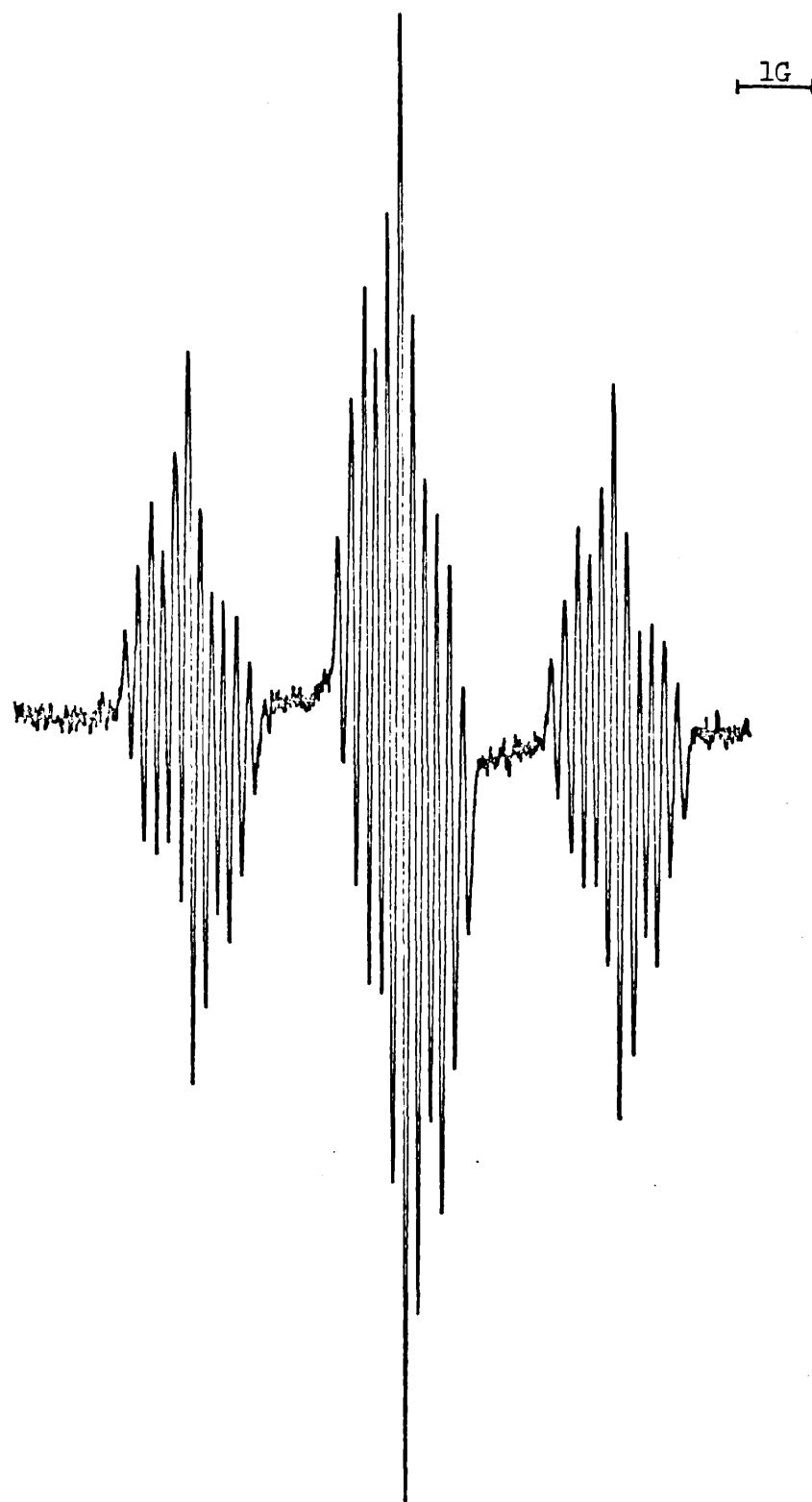


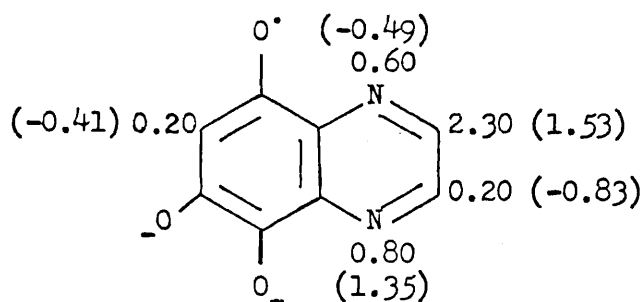
Fig. 34. - Spectrum of quinoxaline-5,8-semiquinone.

3.2.2. Quinoxaline-5,8-semiquinone (secondary radical)

If excess base was used in the radical generation process then after about 15 minutes the primary radical of quinoxaline-5,8-semiquinone decayed and a secondary radical was formed which gave rise to the spectrum in Fig. 35.

The spectrum showed splittings due to two non-equivalent nitrogens of 0.80 and 0.60G respectively, two protons of 0.20G and a single proton of 2.30G.

As with the quinoline and isoquinoline semiquinones the assignment of the coupling constants is based on comparison with the equivalent naphtho-1,4-semiquinone radical and on McLachlan S.C.F. calculations (Scheme 12).



Scheme 12. - Assignment of coupling constants (a/Gauss) in the secondary radical of quinoxaline-5,8-semiquinone (calculated values in parentheses).

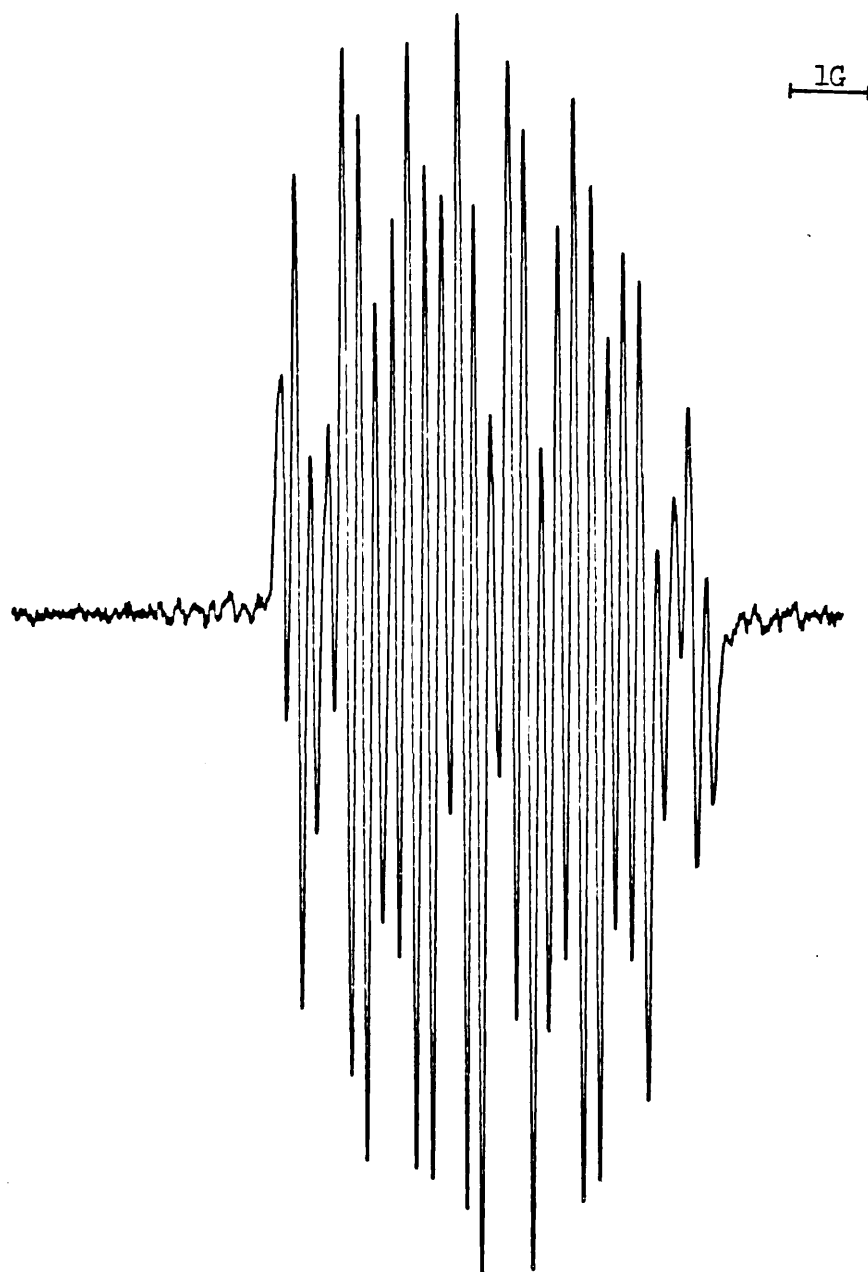
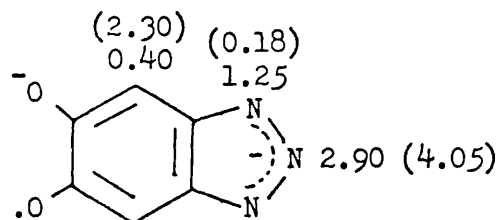


Fig. 35. - Spectrum of quinoxaline-5,8-semiquinone (secondary radical).

3.3. Triazolosemiquinones

3.3.1. 4,5-Triazolo-1,2-semiquinone

The spectrum of 4,5-triazolo-1,2-semiquinone (Fig. 36) analyses as two equivalent nitrogens with a splitting of 1.25G, a single nitrogen with a splitting of 2.90G and two equivalent protons with a splitting of 0.40G. The assignment of the coupling constants is unambiguous due to the symmetry of the species.



Scheme 13 - Assignment of coupling constants (a/Gauss) in 4,5-triazolo-1,2-semiquinone (calculated values in parentheses).

3.3.2. 2,3-Triazolo-1,4-semiquinone

The spectrum of 2,3-triazolo-1,4-semiquinone (Fig. 37) is the same as that obtained previously by a different method.¹⁴ The analysis is confirmed as a splitting of 0.90G due to two equivalent nitrogens, a splitting of 0.65G due to a single nitrogen and a splitting of 3.40G due to two equivalent protons. The assignment of the coupling constants is unambiguous due to the symmetry of the species (Scheme 14).

One interesting comparison between the two spectra of this compound (Figs. 37 and 38) is the much greater line broadening effect at the high field end of the spectrum in Fig. 38. The spectrum in Fig. 38 was obtained in D.M.F. solution, whereas that in Fig. 37. was obtained in

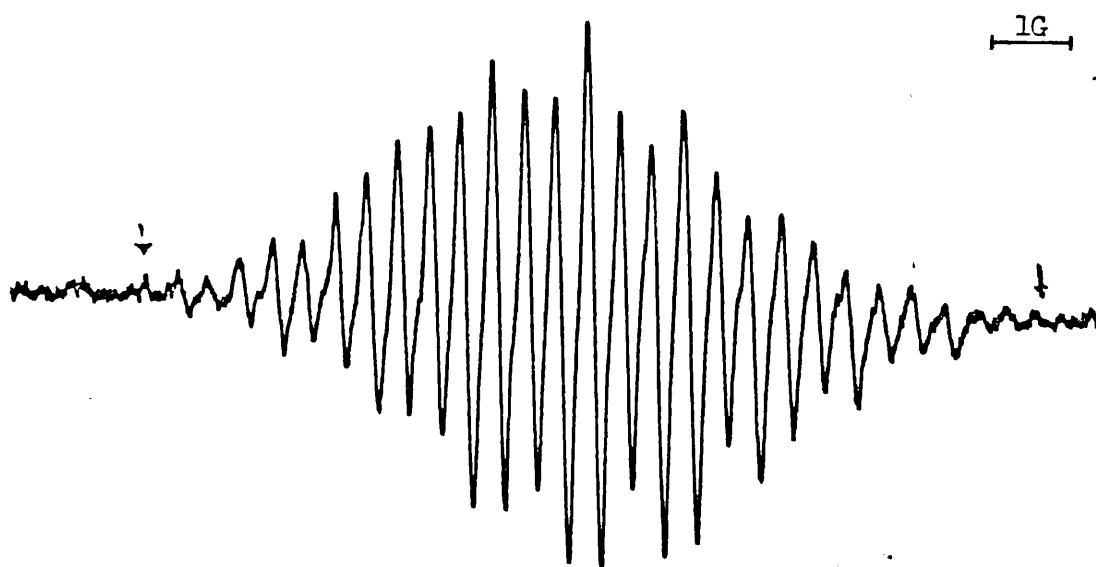
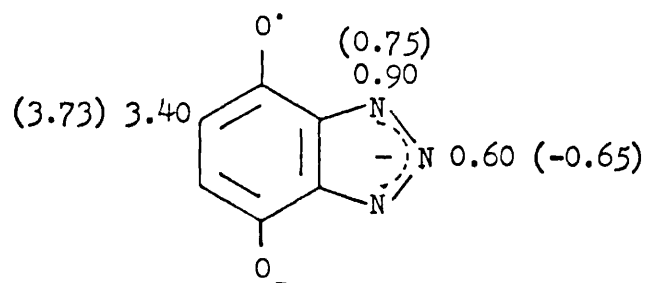


Fig. 36. - Spectrum of 4,5-triazolo-1,2-semiquinone.

ethanolic solution. The greater line broadening effect in Fig. 38. is caused by slow tumbling of the radical⁹¹ in the more viscous D.M.F. solution.



Scheme 14. - Assignment of coupling constants (a/Gauss) in 2,3-triazolo-1,4-semiquinone (calculated values in parentheses).

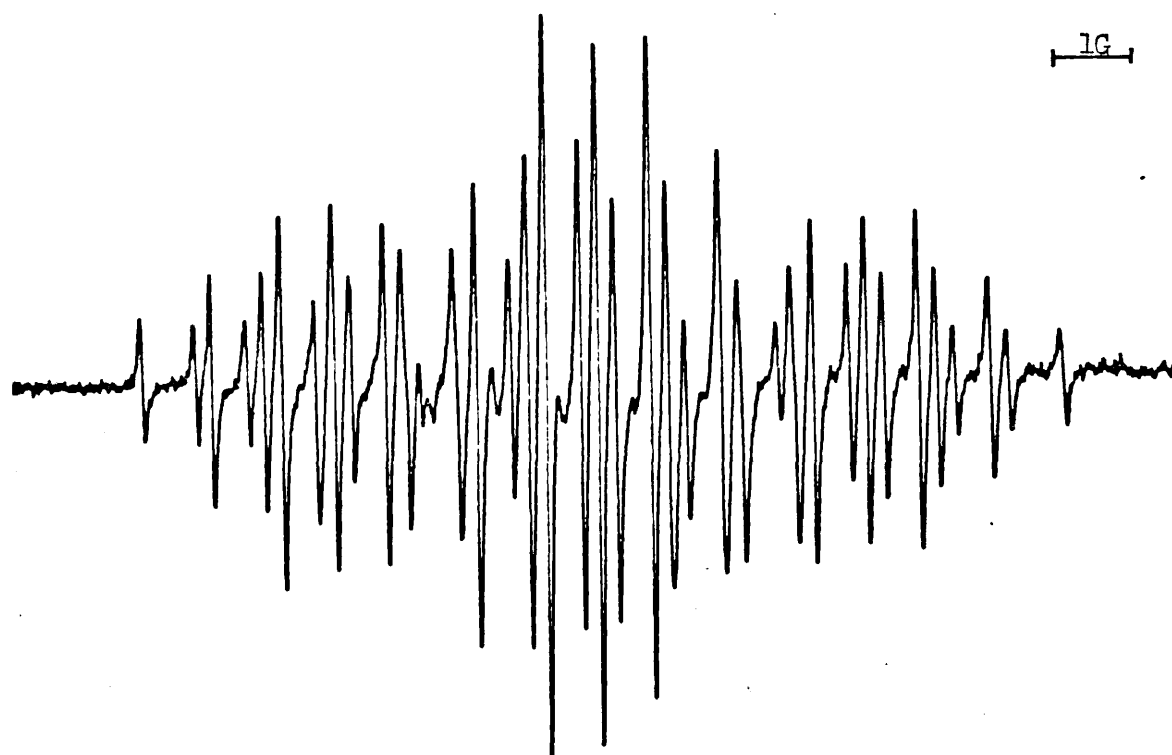


Fig. 37. - Spectrum of 2,3-triazolo-1,4-semiquinone (in ethanol).

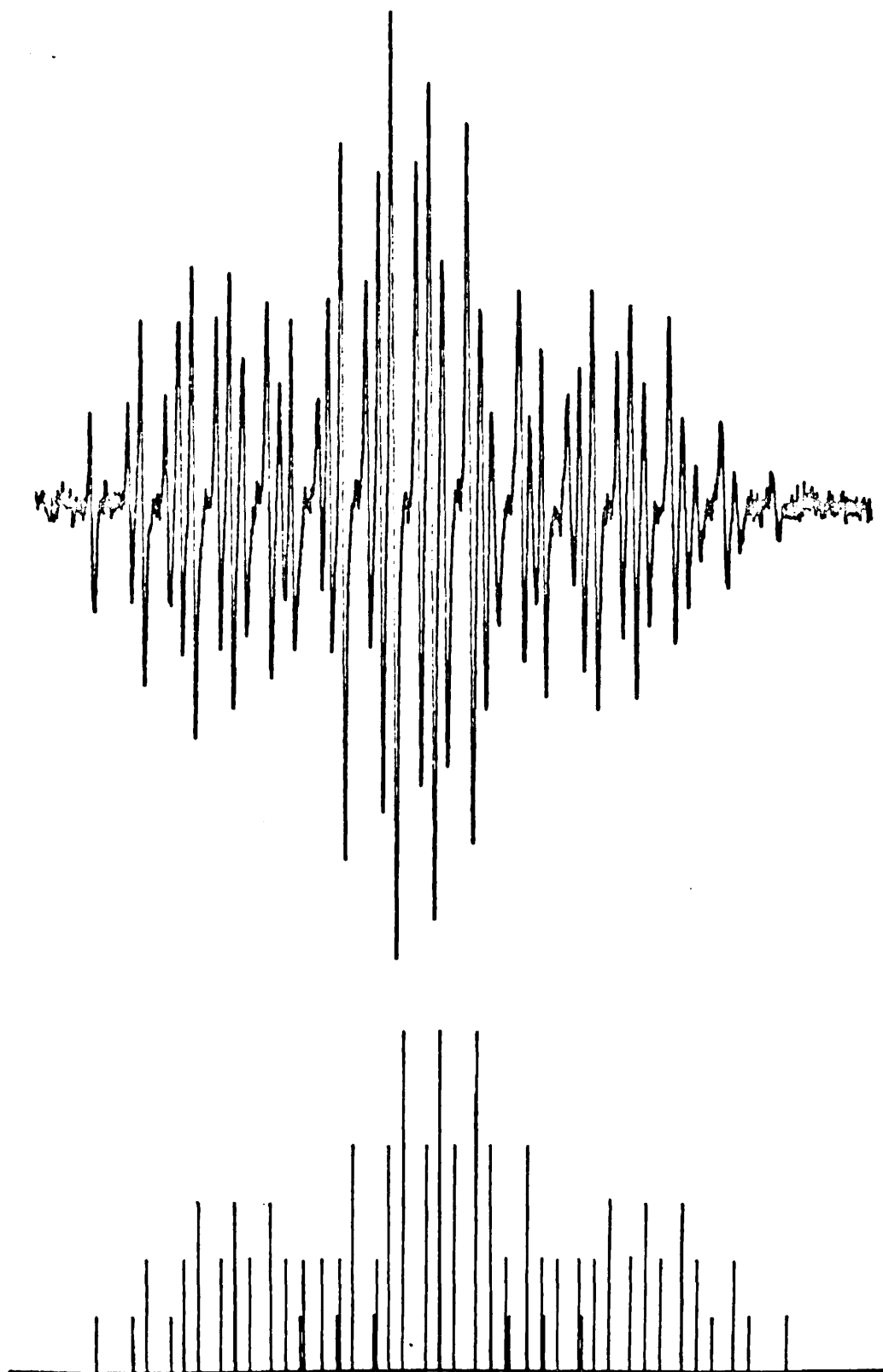
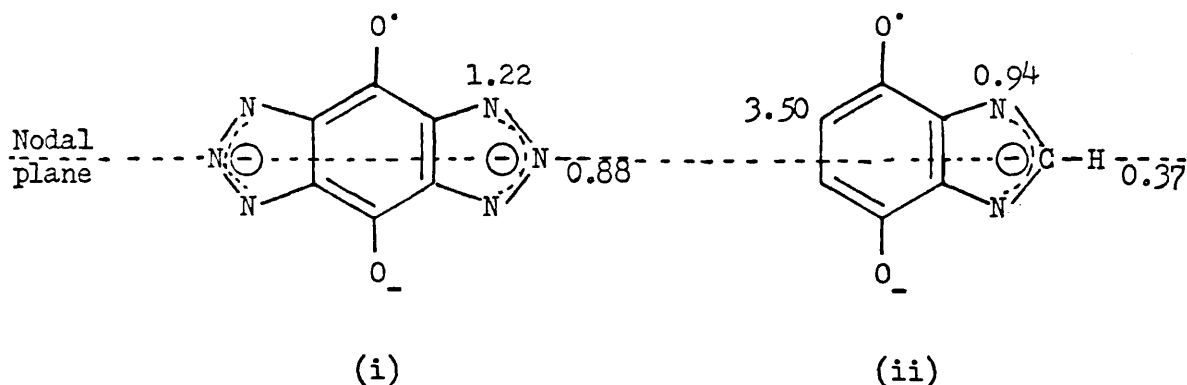


Fig. 38. - Spectrum of 2,3-triazolo-1,4-semiquinone (in DMF).

III.3.4 Benzo [1,2-C:4,5-C'] dipyrazole-4,8(1H,5H)dione

The spectrum of benzo [1,2-C:4,5-C'] dipyrazole-4,8(1H,5H)dione (Fig. 39) is made up of splittings from two pairs of equivalent protons of 2.04G and 1.04G respectively, and two pairs of equivalent nitrogens of 2.04G and 0.40G respectively.

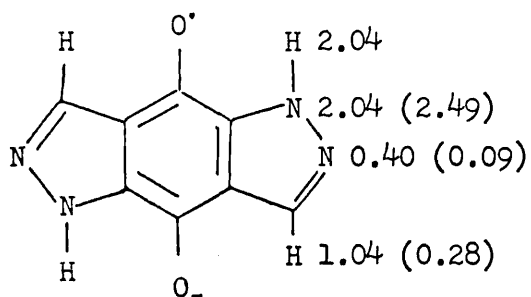
The assignment of the coupling constants is not obvious and has been done on the basis of comparison with similar systems and with the aid of McLachlan S.C.F. calculations. A general feature of 1,4-semiquinones with fused, symmetrical three-membered rings is that when the odd electron is in an antisymmetrical orbital, atoms in the nodal plane exhibit small coupling constants (Scheme 15).



Scheme 15. - Assignment of coupling constants (a/Gauss) of two 1,4-semiquinones with fused, symmetrical three-membered rings:

- (i) - Bis-triazolo-1,4-semiquinone¹⁴
(ii) - Imidazo-1,4-semiquinone⁹

Although benzo [1,2-C:4,5-C'] dipyrazole-4,8(1H,5H)dione does not itself have a plane of symmetry, it is similar to the symmetrical systems and thus the two nitrogen splittings have been assigned as in Scheme 16.



Scheme 16 - Assignment of coupling constants (a/Gauss) in benzo [1,2-C:4,5-C']dipyrazole-4,8(1H,5H)dione (calculated values in parentheses).

The assignment of the splittings due to the two pairs of protons is less easy. However, previous studies have shown that in compounds where hydrogen is attached to a heterocyclic nitrogen, the relationship $a_N \approx a_{NH}^H$ is valid.^{2,3} Therefore, the proton splittings have been assigned as in Scheme 16., and McLachlan S.C.F. calculations lend support to this assignment.

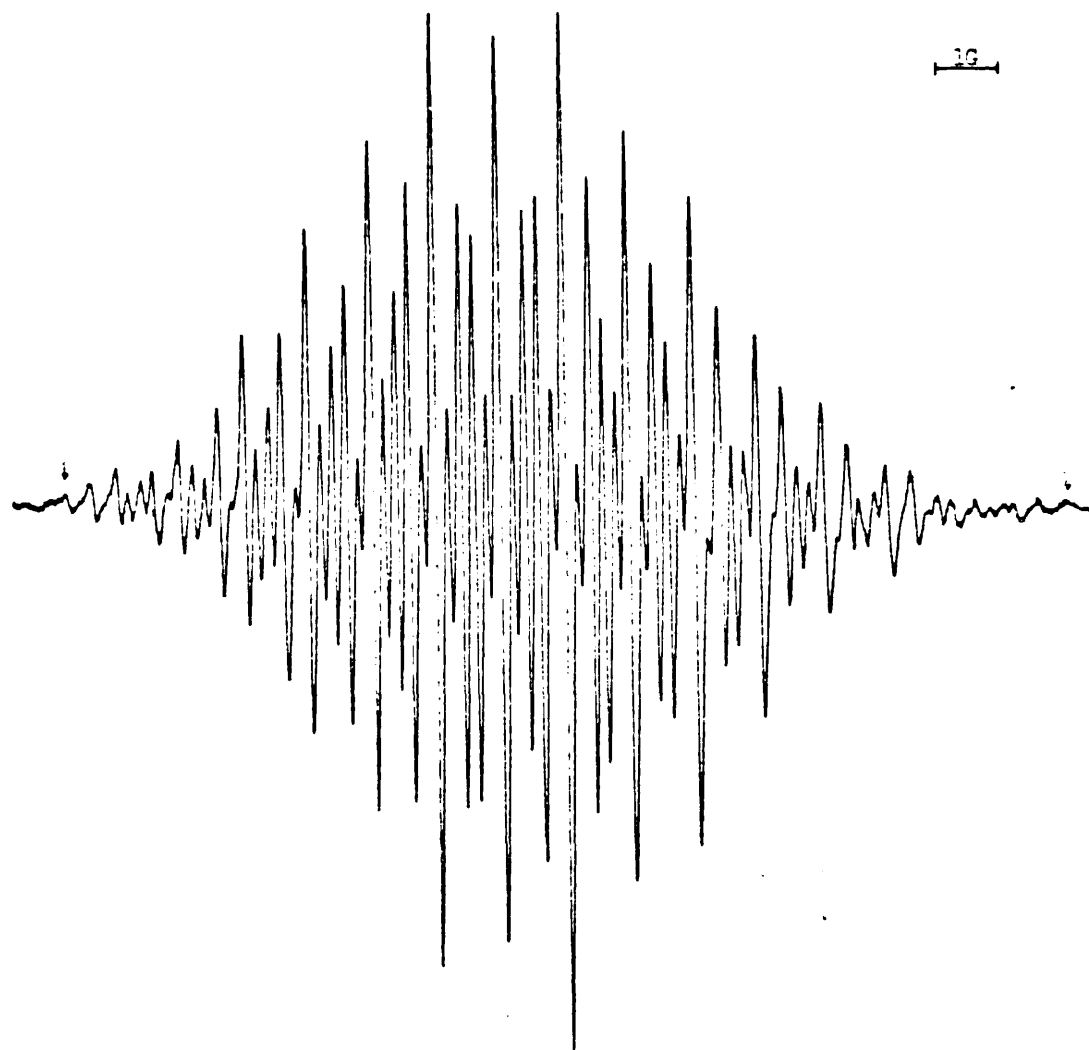
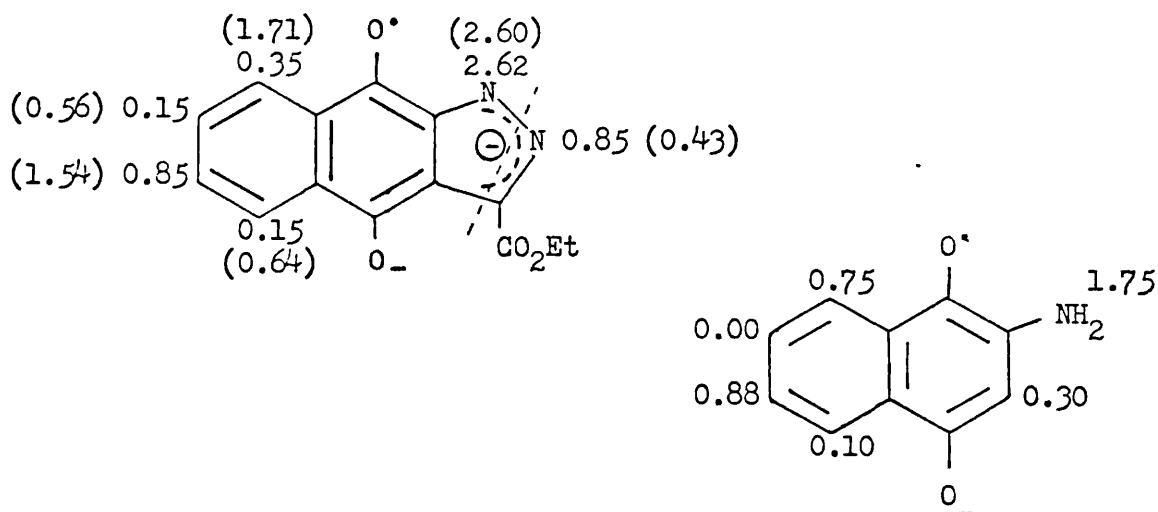


Fig. 39. - Spectrum of benzo[1,2-C:4,5-C']dipyrazole-4,8(1H,5H)dione.

III.3.5. 3-Carbethoxy-lin-naphthindazole-4,9-quinone

3-Carbethoxy-lin-naphthindazole-4,9-quinone gave a spectrum made up of splittings due to four non-equivalent protons and two non-equivalent nitrogens (Fig. 40).

The assignment of the nitrogen splittings has been made on a similar basis to that used for benzo [1,2-C:4,5-C'] dipyrazole-4,8(1H,5H)dione. Furthermore, the magnitude of $a_{N(1)}$ in this compound suggests that there may be little delocalisation in the hetero-ring, thus enabling a comparison to be drawn with 2-substituted naphthoquinones (Scheme 17), and it is on this basis that the assignment of the ring protons has been made. The assignment is supported by McLachlan S.C.F. calculated values.



Scheme 17. - Assignment of coupling constants (a/Gauss) in 3-carbethoxy-lin-naphthindazole-4,9-quinone by comparison with 2-amino-1,4-naphthoquinone (calculated values in parentheses).

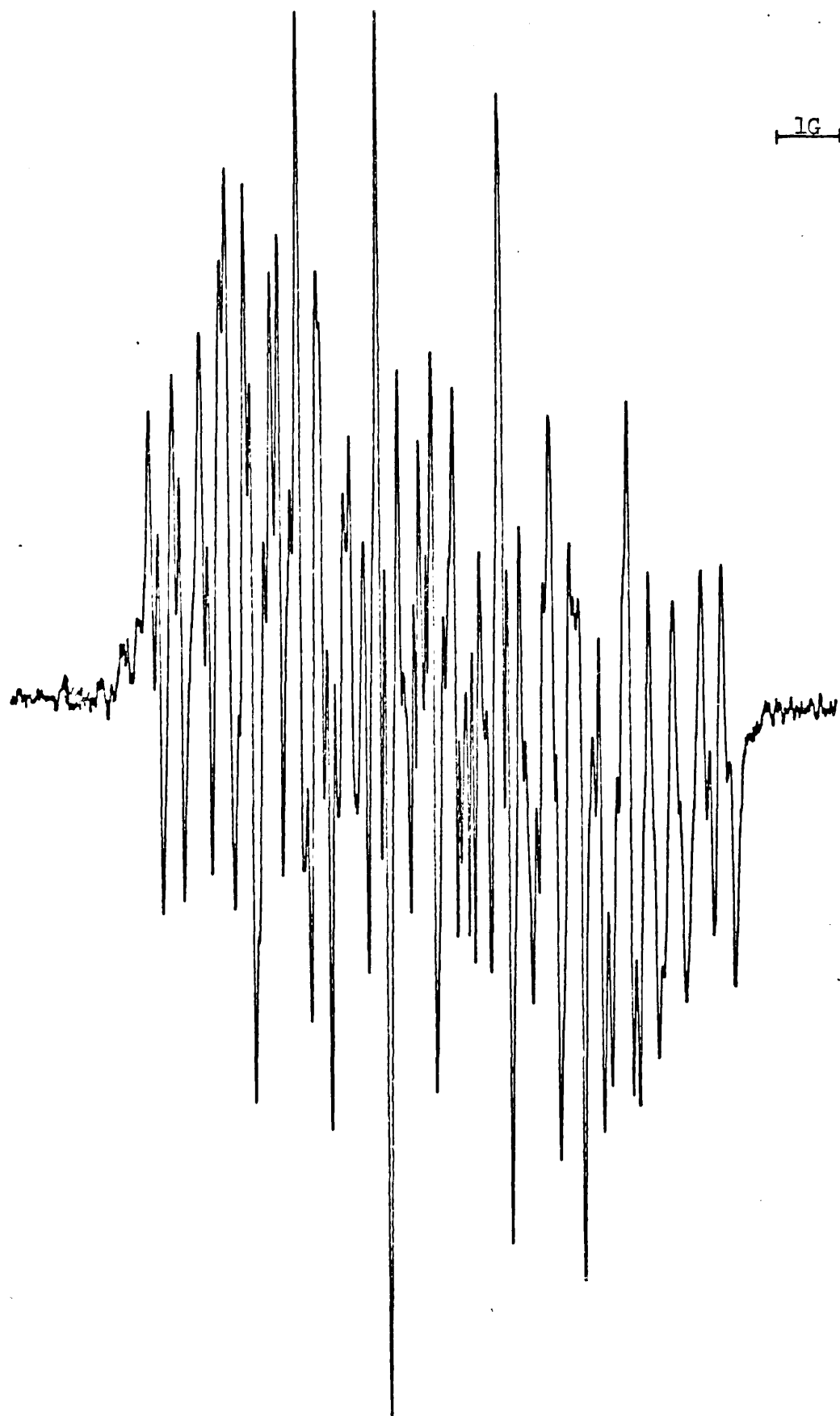
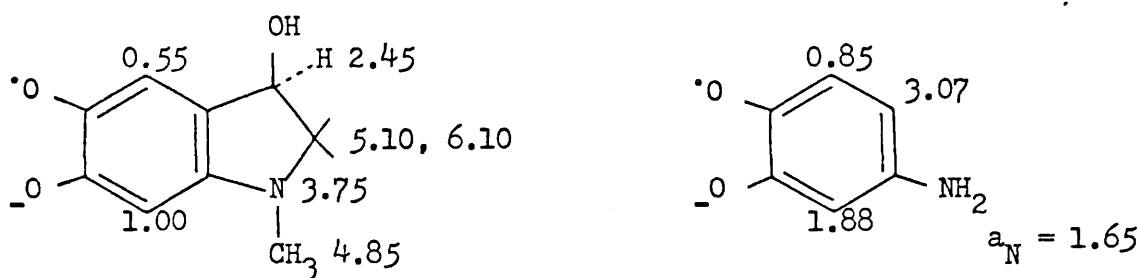


Fig. 40. - Spectrum of 3-carbethoxy-lin-naphthindazole 4,9-quinone.

III.4. Adrenochrome

The spectrum of adrenochrome (Fig. 41) analysed as five non-equivalent protons with splittings of 0.55G, 1.00G, 2.45G, 5.10G and 6.10G, a nitrogen with a splitting of 3.75G and three equivalent protons with a splitting of 4.85G.

The assignment of the nitrogen coupling constant and the splitting due to the three equivalent protons is unambiguous. The two smallest splittings have been assigned to the quinonoid ring as shown in Scheme 18, by comparison with 4-amino-1,2-semiquinone. Since there is no delocalisation in the heterocyclic ring this is a valid comparison.



Scheme 18. - Assignment of coupling constants (a/Gauss) in adrenochrome by comparison with 4-amino-1,2-semiquinone.

The three remaining splittings have been assigned to protons in the heterocyclic ring on the basis of their stereochemistry. The two protons at the position adjacent to the nitrogen atom are in an axial position and therefore able to undergo a large degree of hyperconjugation with the nitrogen π -orbital. Thus a large quantity of unpaired electron spin density can occur at this position. Furthermore, because these protons are stereochemically in very similar environments they would be expected to have splittings of a similar magnitude. Therefore, the two largest splittings of 5.10G and 6.10G have been assigned to these two protons (Scheme 18).

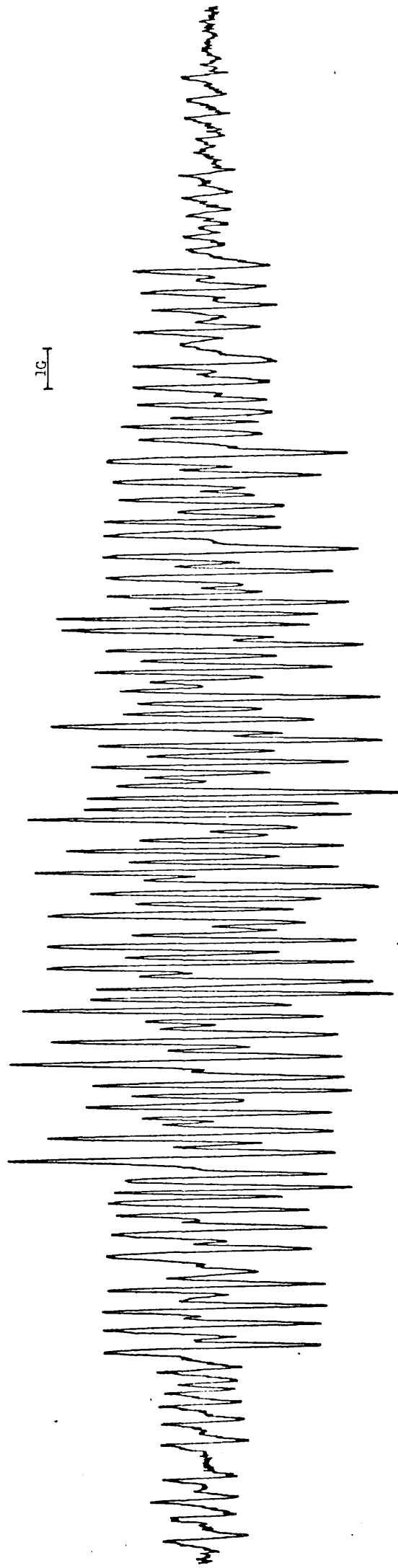


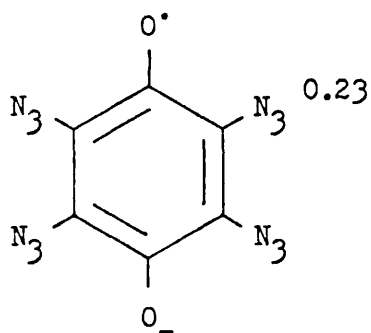
Fig. 41. - Spectrum of Adrenochrome.

III.5. Azidosemiquinones

During the process of synthesising other compounds, two azidoquinones, 2,3,5,6-tetraazidobenzoquinone and 2,3-diazido-1,4-naphthoquinone, were prepared. Under standard autoxidative conditions, both compounds were found to yield spectra which, on analysis, proved to be from azidosemiquinones.

5.1. 2,3,5,6-Tetraazido-1,4-semiquinone

2,3,5,6-Tetraazido-1,4-semiquinone (fig. 42) gave a spectrum consisting of nine lines in the intensity ratio 1:4:10:16:19:16:10:4:1 which is consistent with the splitting pattern of four equivalent nitrogens. All the lines were 0.23 G apart and the unambiguous assignment is as in Scheme 19.



Scheme 19. - Assignment of coupling constants (a/Gauss) in 2,3,5,6-tetraazido-1,4-semiquinone.

5.2. 2,3-Diazido-1,4-naphthosemiquinone

Analysis of the spectrum of 2,3-diazido-1,4-naphthosemiquinone (Fig. 43) is less straightforward and can only be done by close analysis

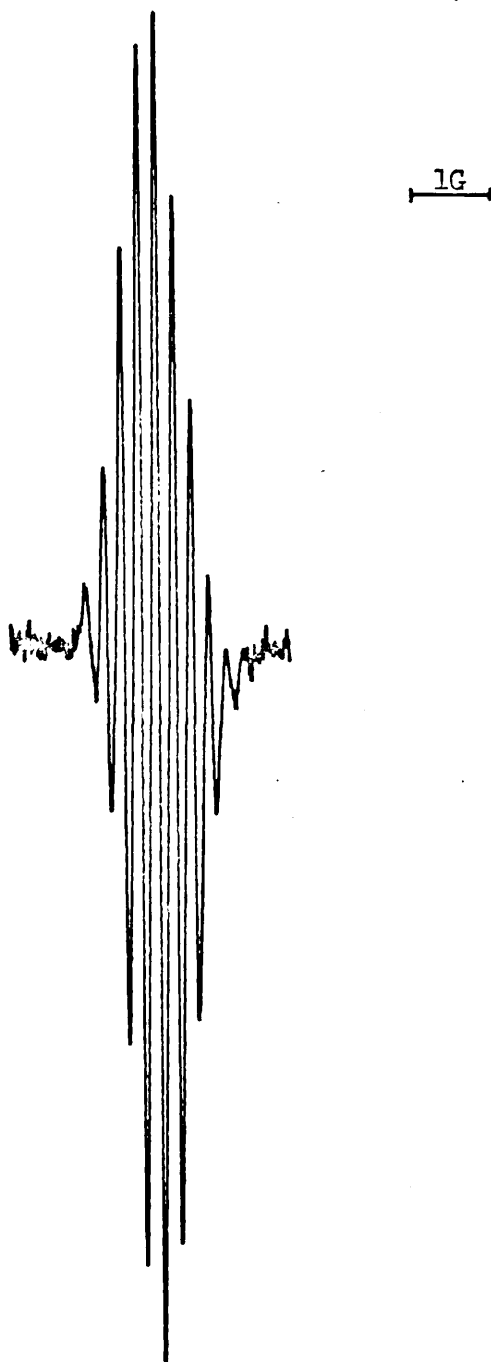
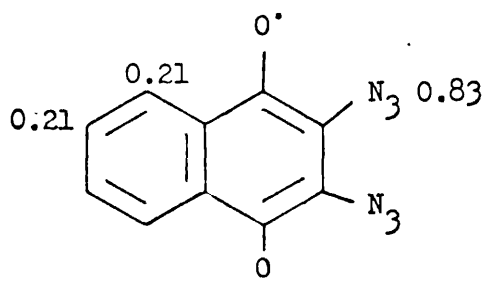


Fig. 42. - Spectrum of 2,3,5,6-tetraazido-1,4-semiquinone.

of the line intensities. The pattern found is consistent with four equivalent protons of coupling constant 0.21G and two equivalent nitrogens of coupling constant 0.83G. Due to the symmetry of the species, the assignment given (Scheme 20) is unambiguous.



Scheme 20. - Assignment of coupling constants (a/Gauss) in 2,3-diazido-1,4-naphthoquinone.

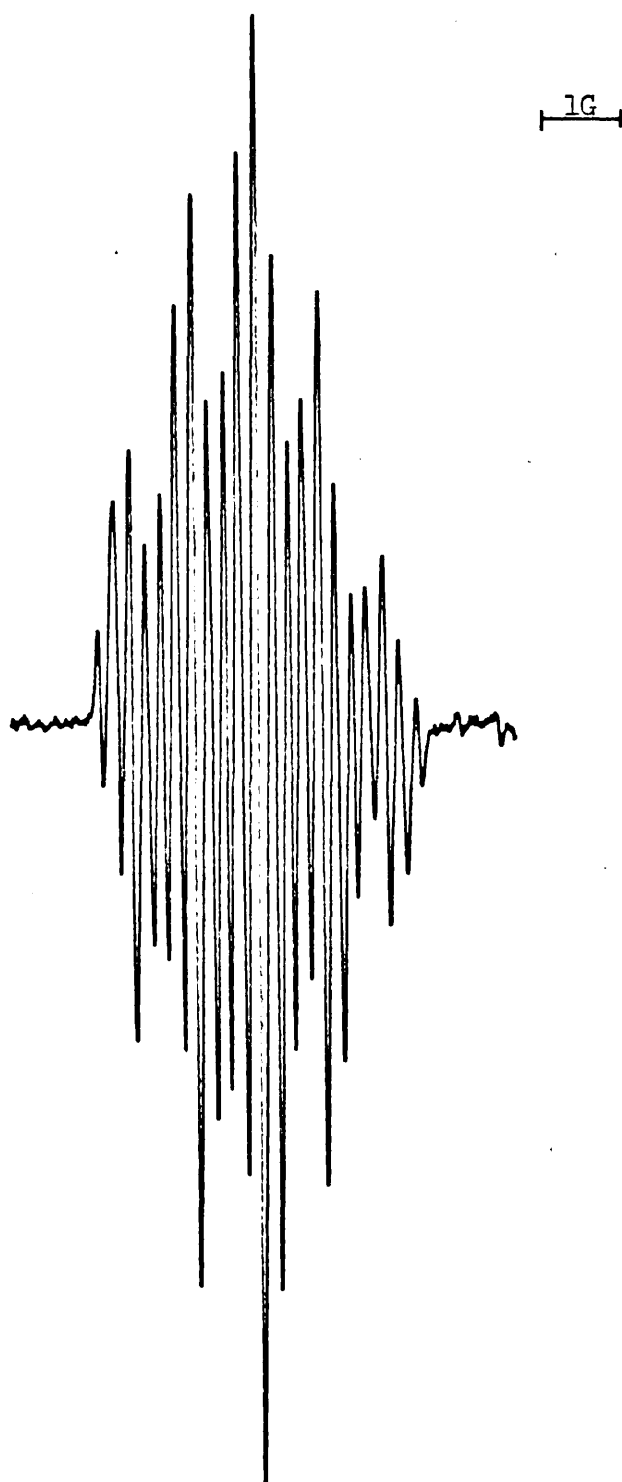


Fig. 43. - Spectrum of 2,3-diazo-1,4-naphthoquinone.

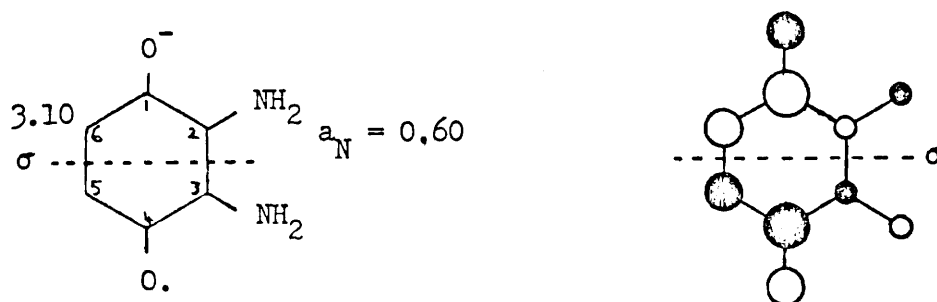
Chapter IV

DISCUSSION

IV.1. Assignment of Coupling Constants in Heterocycles

Nitrogen-containing heterocyclic radicals have been extensively studied and, in general, despite nitrogen being more electronegative than carbon, it has been found to have little effect on the spin density distribution relative to the non-heterocyclic analogue,⁹ a feature illustrated by the equivalence of the k_{CC} , k_{CN} and k_{NN} parameters in McLachlan S.C.F. calculations. The heterocycles studied in this report confirm this observation and lend credence to the methods of assignment of splittings used in Chapter III.

An investigation of the molecular orbitals in these compounds helps to illustrate why, in general, splitting patterns are similar in similarly substituted systems. The 1,2,3,4-substituted systems provide a good example. In these systems the unpaired electron is in an orbital which is anti-symmetric with respect to the symmetry plane, σ , bisecting the C_2-C_3 and C_5-C_6 bonds.^{28,92,93}



Scheme 21. - E.s.r. parameters (a/G) and coefficients of odd electron orbital in 2,3-diamino-1,4-semiquinone.

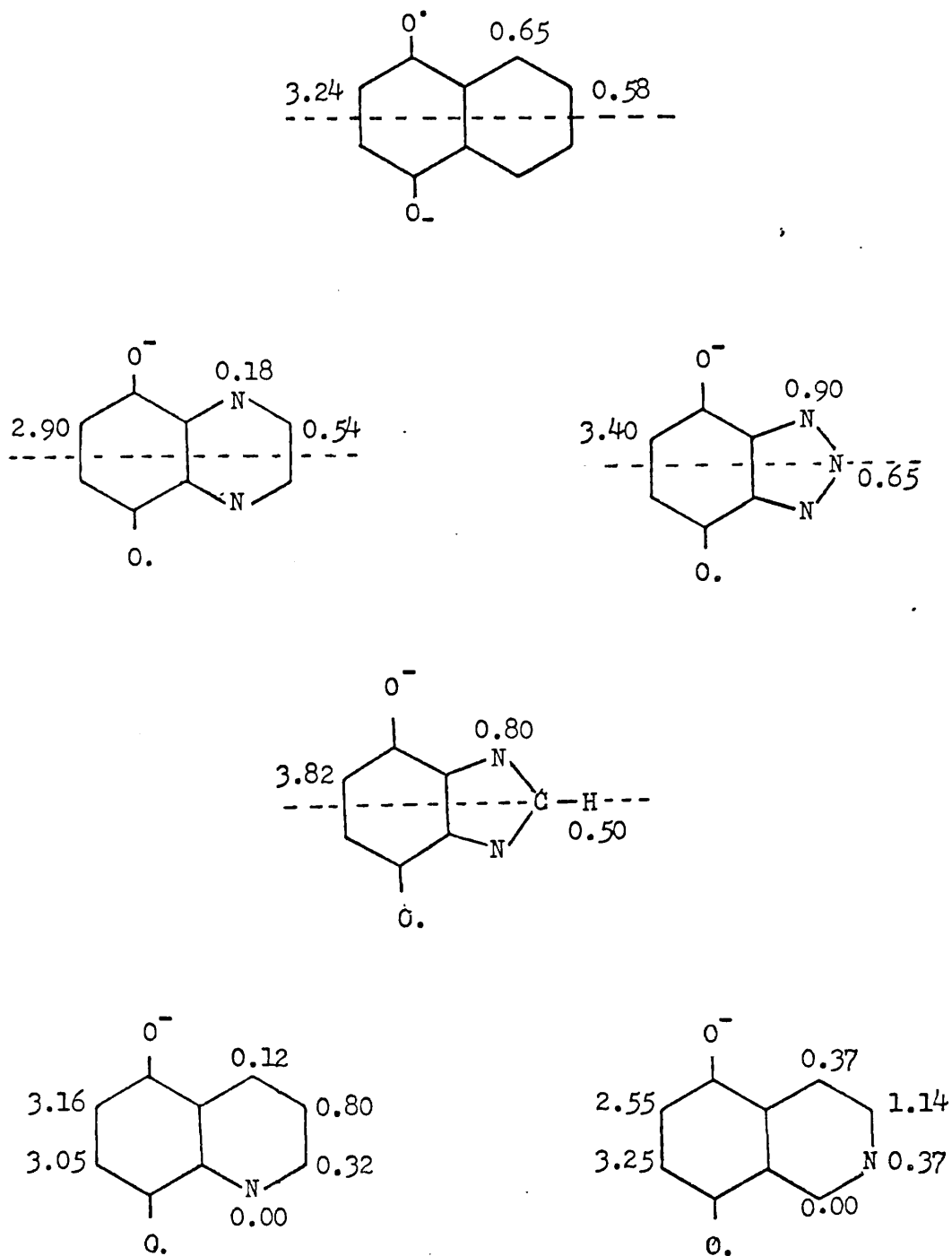
The splitting pattern in Scheme 21, confirmed by calculation, shows that the unpaired spin density is concentrated mainly at the 1,4,5,6-positions, with very little on the 2,3-substituents.

This feature is maintained in certain heterocycles which have a similar substitution pattern. Quinoxaline-5,8-semiquinone, imidazo-1,4-semiquinone⁹⁴ and 2,3-triazolo-1,4-semiquinone, for example, which may be regarded as N-substituted analogues of 2,3-diamino-1,4-semiquinone, exhibit the same pattern of unpaired spin density distribution, as do the primary radicals of quinoline- and isoquinoline-semiquinone which, although not symmetrical, can, nevertheless, be regarded as being 1,2,3,4-substituted systems (see Scheme 22).

These heterocycles, particularly those with four-membered side-rings, are also comparable to 1,4-naphthosemiquinone which may itself be loosely regarded as a 1,2,3,4-substituted system.

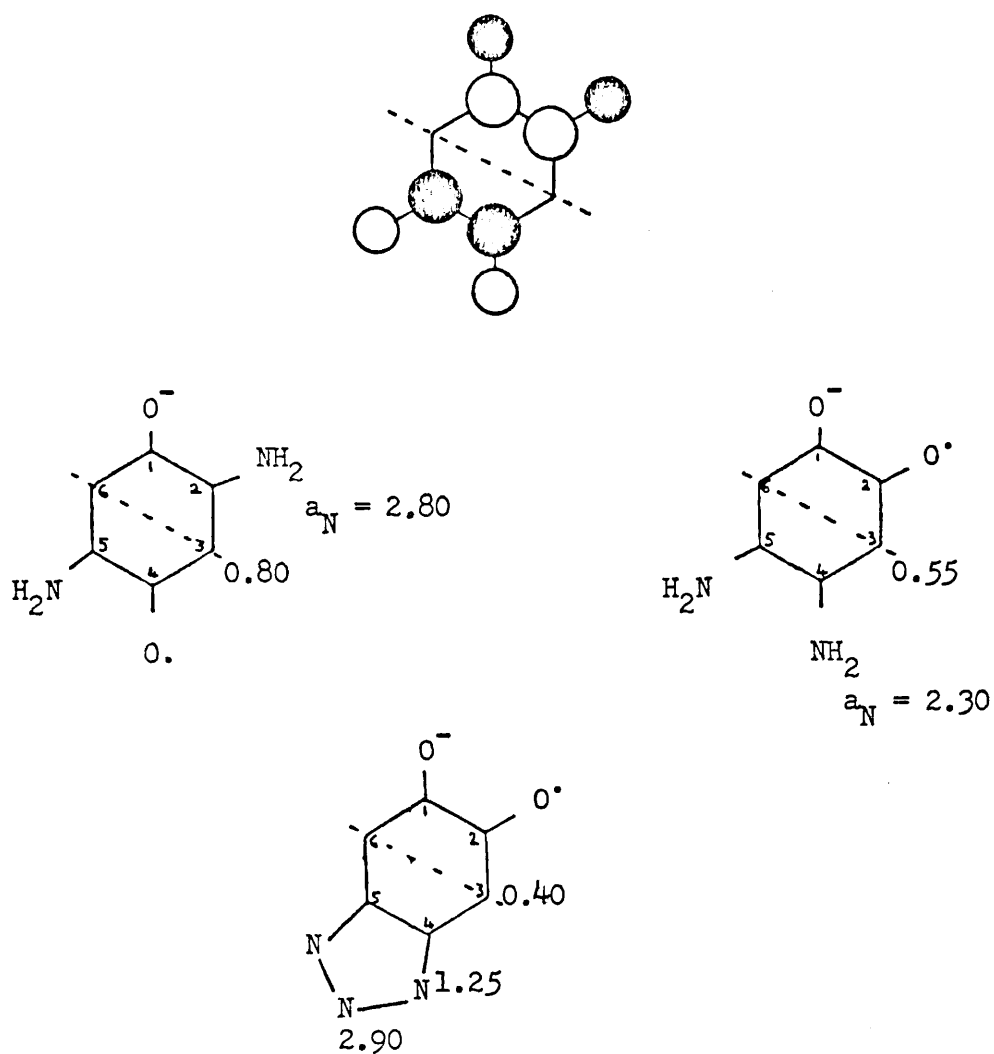
These results suggest that changes to the substituents in the 2,3-positions have very little effect on the overall spin distribution of the molecule, and, as expected, negative spin densities are predicted for atoms lying in the nodal plane of the molecular orbital such as the central nitrogen atom in 2,3-triazolo-1,4-semiquinone and the side-ring carbon atom in imidazo-1,4-semiquinone.

In 1,2,4,5-substituted systems the odd electron is also in an anti-symmetric orbital, with a nodal plane through the 3 and 6 ring positions, for which negative spin densities are predicted. As with the 1,2,3,4-substituted system, similarly substituted molecules exhibit similar spin distribution patterns. 2,5-Diamino-1,4-semiquinone, 4,5-diamino-1,2-semiquinone and 4,5-triazolo-1,2-semiquinone all exhibit similar spin distribution patterns (Scheme 23), with small coupling



Scheme 22. - Spin distribution (e.s.r. parameters, a/Gauss) in some 1,2,3,4-substituted heterocycles compared with that in 1,4-naphthosemiquinone.

constants in the positions corresponding to the nodal plane of the basic symmetrical system.



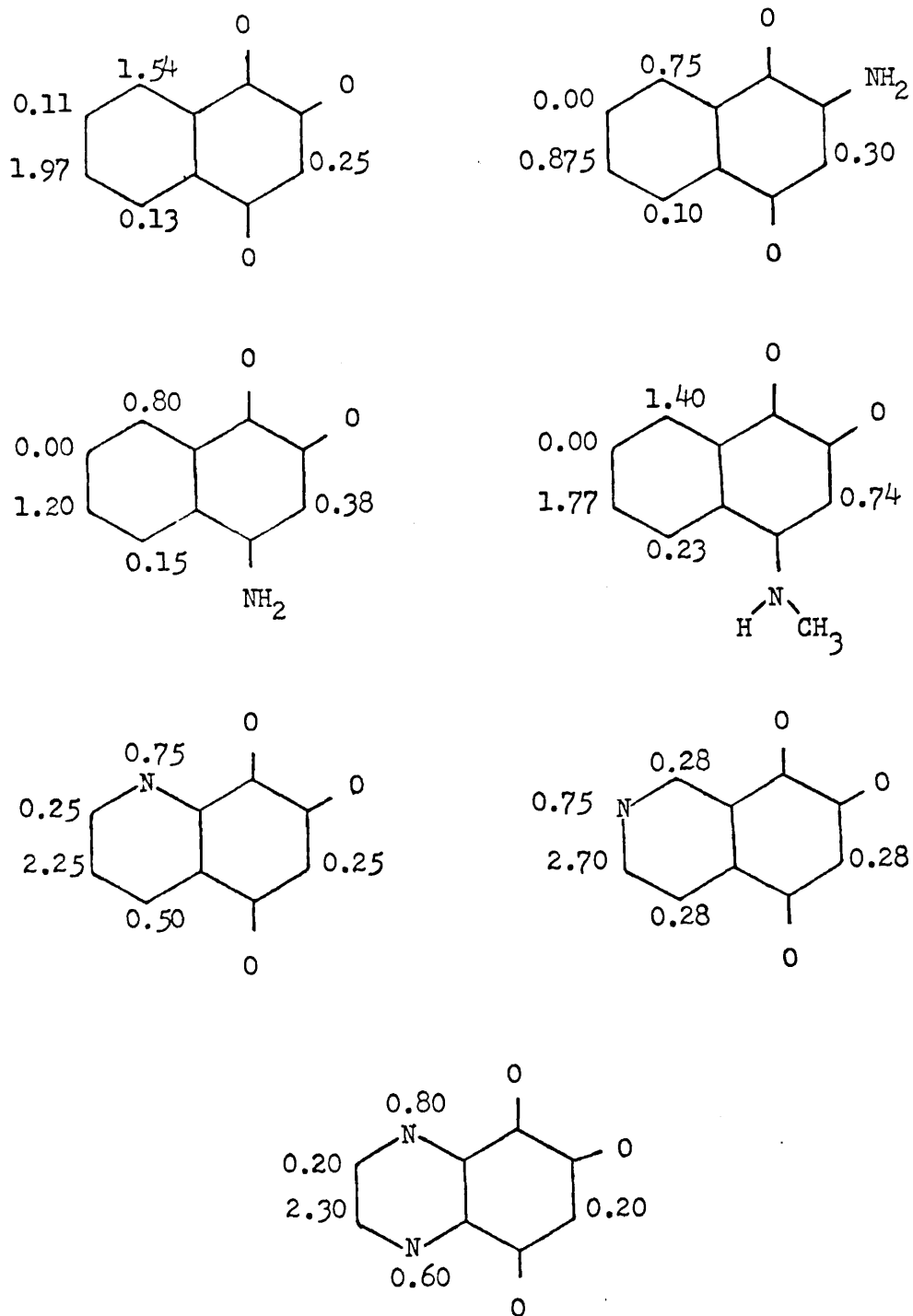
Scheme 23. - Spin distribution patterns (e.s.r. parameters, a /Gauss) in some 1,2,4,5-substituted systems showing small coupling constants in the positions corresponding to the nodal plane in the basic symmetrical system.

This simplistic approach can be extended to other systems where there is ambiguity in the assignment of coupling constants. For example, the comparison of the spin distribution pattern in 4-amino-1,2-semiquinone

with that in adrenochrome is useful in assigning the splittings to the aromatic ring positions (see Scheme 18., Chapter III., Section 4.).

The secondary radicals from the heterocycles quinoline- and isoquinoline-5,8-semiquinone and quinoxaline-5,8-semiquinone form a series which is similar to the 1,2,4-substituted naphthalene system. In these systems where there are several non-equivalent, single-proton coupling constants the assignments are ambiguous, but this simple approach enables assignments to be made. As shown in Scheme 24., these heterocycles along with the two 1,2,4-substituted naphthalenes, 4-amino-1,2-naphthosemi-quinone and 4-methylamino-1,2-naphthosemi-quinone, exhibit similar splitting patterns to those in 1,2,4-trihydroxynaphthalene⁹⁰ and 2-amino-1,4-naphthosemi-quinone.⁸²

Although the calculated values of the coupling constants do not closely agree with the experimental in the heterocycles, they do nevertheless tend to confirm the assignments made by reflecting the same relative order of magnitudes of coupling constants at the various positions within each system.



Scheme 24. - Splitting patterns (e.s.r. parameters, a/Gauss) in some 1,2,4-substituted naphthalenes and some similarly substituted heterocycles.

IV.2. Amino-group Spin Densities

Although the relationship $a_{\text{NH}}^{\text{H}} \approx a_{\text{N}}$ has been established for a large number of radicals,^{2,3,11} the values in Tables 4 and 5 (Chapter III, Section 2.) clearly show that, in general, the a_{NH}^{H} values in amino-semiquinones are smaller than those of other amino-substituted radicals.

As previously noted,¹⁴ the empirical relationship -

$$\left| a_{\text{NH}}^{\text{H}} \right| \approx \left| \rho_{\text{N}} \times 10 \times 10^{-4} \tau \right| \quad (35)$$

gives a closer fit with the observed data, though there is still no single a_{NH}^{H} value which consistently reproduces a_{NH}^{H} values in good agreement with the experimental. The low value of a_{NH}^{H} in equation (35) is unlikely to be due to a difference in total charge densities on the species,^{95,96} because for a number of pairs of aromatic hydrocarbons⁹⁵ and oxygenated radical ions,⁸⁹ the magnitude of the splittings of the cations exceeds that of the anions by only 15-20% .

The explanation is most likely to be found in terms of out-of-plane movement of the amino-group, leading to a contribution to a_{NH}^{H} from hyperconjugation. Although hyperconjugation has been shown to make a minimal contribution to a_{NH}^{H} in many amino-substituted radicals,^{3,11,46,97} in the case of semiquinones it is reasonable to expect that steric interactions between substituents will tend to prevent the amino-group from adopting a planar conformation relative to the molecule. Any contribution from hyperconjugation would be at a minimum when the protons were in the molecular plane ($\theta = 0^\circ$) and would increase as the angle θ increased.

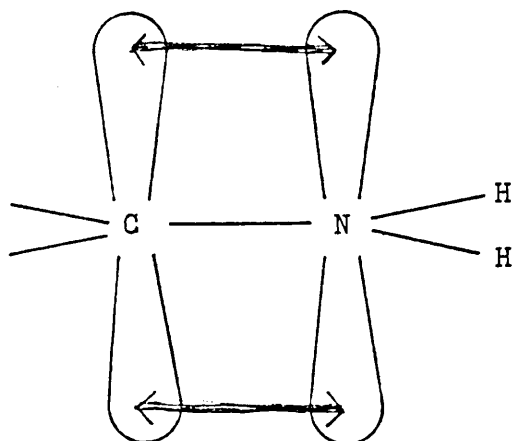
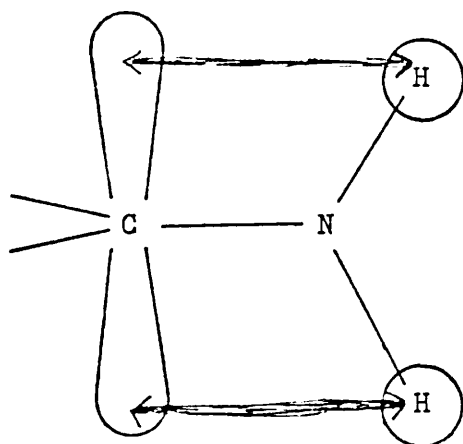
(i) $\theta = 0^\circ$ (ii) $\theta = 90^\circ$

Fig. 44. - Showing the situations (i) for minimum hyperconjugation effect ($\theta = 0^\circ$) and (ii) maximum hyperconjugation effect ($\theta = 90^\circ$)

Thus there would be two mechanisms⁹⁸⁻¹⁰³ contributing to the amino-proton spin density, spin polarisation and hyperconjugation. However, spin polarisation generates negative spin density at the proton,¹⁰⁴ proportional to ρ_N (equation (26), Chapter I, Section 5.1.), while hyperconjugation results in positive spin density at the proton, proportional to $\rho_{C(N)}$. The resultant spin density at the proton would therefore be the difference between the two contributions and, using previous nomenclature,^{105,106} equation (36) can be written -

$$a_{\text{NH}}^{\text{H}} = Q_{\text{NH}}^{\text{H}} \rho_{\text{N}} + Q_{\text{CNH}}^{\text{H}} \rho_{\text{C(N)}} \quad (36)$$

where Q_{NH}^{H} is negative and $Q_{\text{CNH}}^{\text{H}}$ is positive.

As shown in Fig. 44., the hyperconjugation parameter will vary with the angle θ and equation (36) will become -

$$a_{\text{NH}}^{\text{H}} = Q_{\text{NH}}^{\text{H}} \rho_{\text{N}} + Q_{\text{CNH}}^{\text{H}} \rho_{\text{C(N)}} \sin^2 \theta \quad (37)$$

There is, however, some doubt as to whether allowance should be made for any variation in the spin polarisation contribution as the amino-group rotates. In their treatment of rotating amino groups, Bullock and Howard neglect any variation in the spin polarisation contribution and use equation (37) unchanged.^{46,107} Other workers, such as Sullivan,¹⁰⁸⁻¹¹⁰ have, however, introduced an allowance for the variation of the spin polarisation contribution with θ and use an expression of the form -

$$a_{\text{NH}}^{\text{H}} = Q_{\text{NH}}^{\text{H}} \rho_{\text{N}} \cos^2 \theta + Q_{\text{CNH}}^{\text{H}} \rho_{\text{C(N)}} \sin^2 \theta \quad (38)$$

It would therefore be interesting to compare the results of the two approaches when applied to the amino-groups in the aminosemiquinones under study.

Of the parameters in equations (37) and (38), ρ_{N} and $\rho_{\text{C(N)}}$ can be calculated using McLachlan's S.C.F. calculations and the values of Q_{NH}^{H} and $Q_{\text{CNH}}^{\text{H}}$ have been evaluated by Bullock and Howard⁴⁶ as -32.5 and 38G respectively. However, in order to test the validity of these two interpretations it would be necessary to measure directly the relative

signs of a_{NH}^{H} , a facility not available in this investigation. The values of θ calculated have, therefore, been done so using both positive and negative values of a_{NH}^{H} .

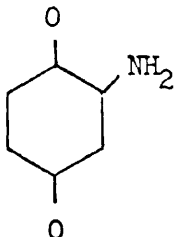
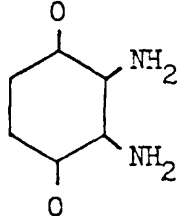
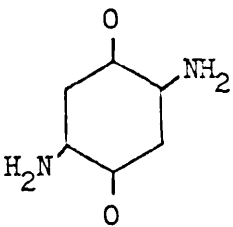
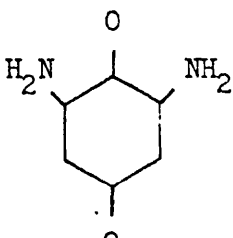
Tables (6) and (7) show the values of θ calculated from the approach of Bullock and Howard, using equation(37). Bearing in mind that the sign of a_{NH}^{H} has not been established, there are nevertheless some useful inferences to be drawn from these results. The most obvious feature is that, in general, where a positive value of a_{NH}^{H} has been used, equation (37) either gives a large value of θ or no meaningful result at all, whereas negative values of a_{NH}^{H} generally yield values of θ in the range of 30-50°.

Previous investigations have suggested that spin polarisation is very much the dominant mechanism for transferring unpaired spin density on to amino-protons.^{2,3,5,46} Furthermore, equation (37) shows that since the hyperconjugative contribution to a_{NH}^{H} varies with $\sin^2 \theta$, θ would have to be very large for this contribution to be greater than that from spin polarisation. Therefore, if spin polarisation is the dominant mechanism the sign of a_{NH}^{H} would be expected to be opposite to that of a_{N} . On this basis, since all the ρ_{N} and $\rho_{\text{C(N)}}$ values in Tables (6) and (7) are positive (with the exception of the 3-amino group in radical VIII) the a_{NH}^{H} values would be expected to be negative. It is therefore encouraging that if a_{NH}^{H} is negative, calculated values of θ are both more consistent and also smaller, results which are much more in line with previous work.

In the case of the 3-amino group in radical VIII, the ρ_{N} and $\rho_{\text{C(N)}}$ values are negative and spin polarisation would induce positive spin density at the proton. It is therefore the angle θ calculated from the positive value of a_{NH}^{H} that is comparable to the other results.

Table (6)

Calculated Values of θ° for Amino-groups in Amino-1,4-semiquinones
 [from eqn. (37)].

Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	θ° ($+a_{NH}^H$)	θ° ($-a_{NH}^H$)
	0.0856	0.1101	0.85	68.7	42.8
	0.0231	0.0119	0.00	-	-
	0.0964	0.1723	1.00	52.6	34.8
	0.0600	0.0792	0.25	58.8	48.7

(continued)

Table (6) (cont.)

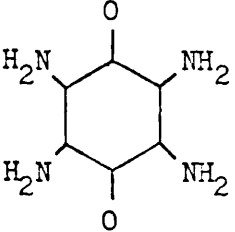
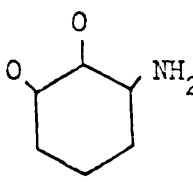
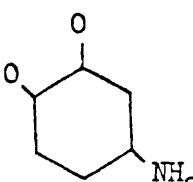
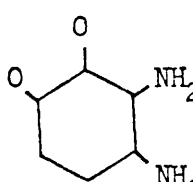
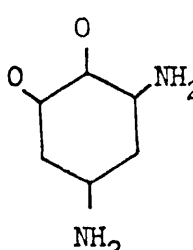
Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	θ° ($+a_{NH}^H$)	θ° ($-a_{NH}^H$)
	0.0290	0.0366	0.20	65.0	46.9

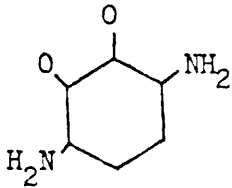
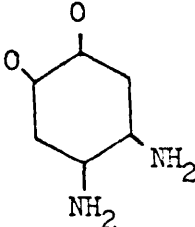
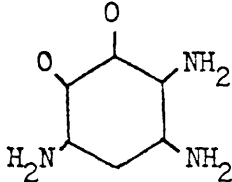
Table (7)

Calculated Values of θ° for Amino-groups in Amino-1,2-semiquinones
 [from eqn. (37)].

Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	θ° ($+a_{NH}^H$)	θ° ($-a_{NH}^H$)
	0.0900	0.1079	0.70	70.0	47.4
	0.0882	0.1148	3.95	-	30.0
	(3) -0.0046	-0.0360	0.68	38.5*	51.1*
	(4) 0.0614	0.0738	1.00	-	36.6
	(3) 0.0600	0.0777	0.21	58.8	50.1
	(4) 0.0736	0.1156	1.21	64.9	31.2

(continued)

Table (7) (cont.)

Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	e° ($+a_{NH}^H$)	e° ($-a_{NH}^H$)
	0.0223	0.0039	0.68	-	33.3
	0.0957	0.1708	0.17	45.3	42.3
	(3) 0.0393	0.0522	0.76	-	30.7
	(4) 0.1062	0.1856	2.35	65.1	23.3
	(6) 0.1002	0.1667	1.82	63.5	28.4

* See page 117.

The introduction, by Sullivan,¹⁰⁸⁻¹¹⁰ of a $\cos^2 \theta$ factor to account for the variation of the spin polarisation term with rotation is based on the argument that as the amino group is rotated out of plane by an angle θ the overlap integral, k_{CN} , decreases by a factor $\cos \theta$ and it was assumed that this results in a decrease in ρ_N by a factor $\cos^2 \theta$.

When the amino-group is coplanar with the rest of the molecule the nitrogen $2p_z$ orbital is in a position for maximum overlap with the p^π -conjugated system of the molecule. It is by means of this overlap that unpaired spin density is passed into the nitrogen $2p_z$ orbital and any reduction of this overlap as the C-N bond is rotated would be expected to result in a reduction of the unpaired spin density in the nitrogen $2p_z$ orbital. Since a_{NH}^H and a_N are both directly related to ρ_N^π , this would have the effect of reducing the size of these parameters, though both to the same degree.

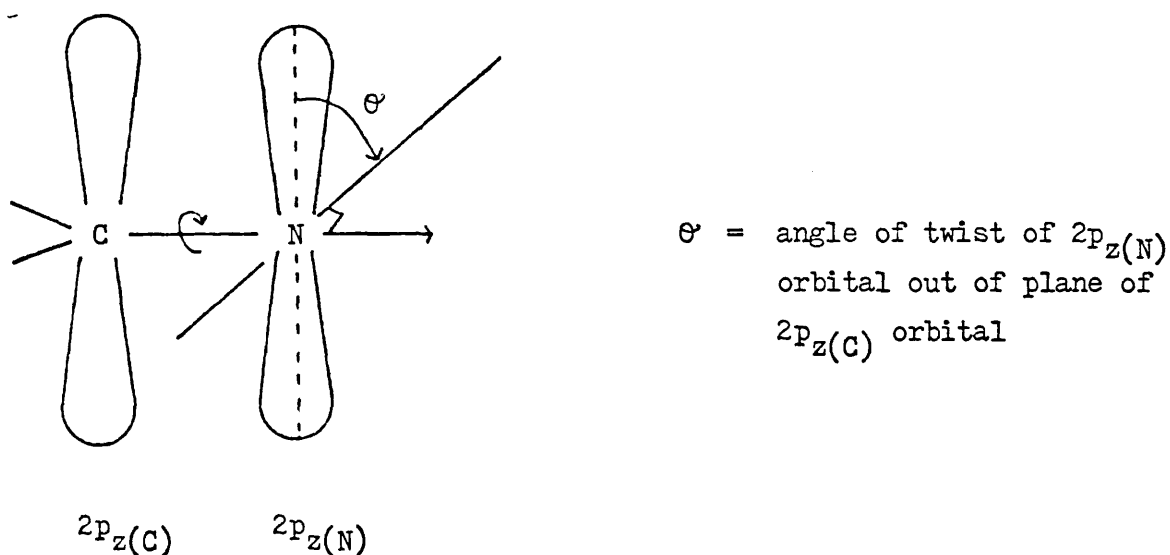


Fig. 45. - Showing the effect of rotation of nitrogen $2p_z$ orbital out of the plane of the carbon $2p_z$ orbital system.

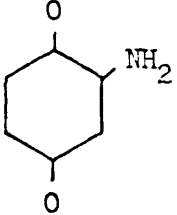
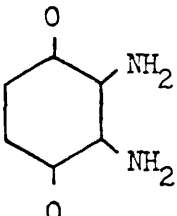
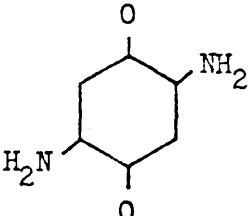
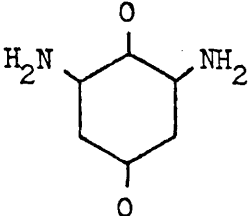
Tables (8) and (9) give the values of Θ calculated from the approach of Sullivan, using equation (38). These show that, generally, when a positive value of a_{NH}^{H} is used Θ has a value in the range $40-55^\circ$, whereas when a negative value of a_{NH}^{H} is used Θ is smaller and, generally, in the range $20-35^\circ$. The latter set of results is predictable when comparing them with those obtained from the approach of Bullock and Howard. In both cases the negative value of a_{NH}^{H} presumes that spin polarisation is the dominant mechanism, but the $\cos^2 \Theta$ factor introduced by Sullivan will reduce the size of the spin polarisation contribution and thus Θ .

In amino-groups where a_{NH}^{H} is very much smaller than a_{N} (e.g. radical XI) the likely cause is the near equivalence of the contributions from spin polarisation and hyperconjugation which largely cancel each other out. In such cases the choice of sign for a_{NH}^{H} would have relatively little effect on the value of Θ obtained from either equation (37) or equation (38).

Although, without definite knowledge of the sign of a_{NH}^{H} in these compounds, the values of Θ in Tables (6), (7), (8) and (9) are inconclusive they do, nevertheless, support the observation that there is significant out of plane movement of the amino-group in aminosemiquinones. Furthermore, it seems likely that spin polarisation is the dominant mechanism and that it is therefore the values of Θ calculated from negative values of a_{NH}^{H} that are relevant. If this is indeed the case then the values of Θ obtained from the approach of Bullock and Howard suggest a situation for the amino-groups close to that of time-averaged free rotation, whereas those obtained from the approach of Sullivan suggest that the amino-groups are undergoing restricted rotation of the order of 30° .

Table (8)

Calculated Values of σ° for Amino-groups in Amino-1,4-semiquinones
 [from eqn. (38)].

Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	σ° ($+a_{NH}^H$)	σ° ($-a_{NH}^H$)
	0.0856	0.1101	0.85	46.22	31.78
	0.0231	0.0119	0.00	52.19	52.19
	0.0964	0.1723	1.00	40.80	28.00
	0.0600	0.0792	0.25	41.76	35.84

(continued)

Table (8) (cont.)

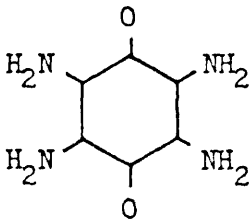
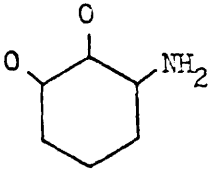
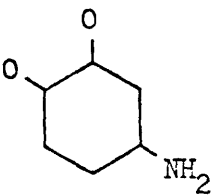
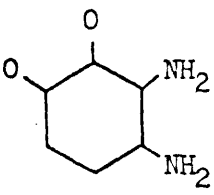
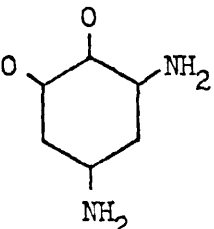
Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	e° ($+a_{NH}^H$)	e° ($-a_{NH}^H$)
	0.0290	0.0366	0.20	44.40	34.34

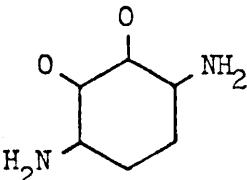
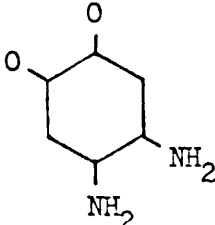
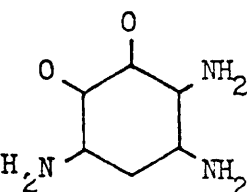
Table (9)

Calculated Values of θ° for Amino-groups in Amino-1,2-semiquinones
 [from eqn. (38)].

Radical Skeleton	ρ_N	$\rho_{C(N)}$	$\left a_{NH}^H \right $	θ° ($+a_{NH}^H$)	θ° ($-a_{NH}^H$)
	0.0900	0.1079	0.70	45.92	34.25
	0.0882	0.1148	3.95	76.18	22.78
	(3) -0.0046	-0.0360	0.68	41.28*	55.60*
	(4) 0.0614	0.0738	1.00	52.18	27.09
	(3) 0.0600	0.0777	0.21	41.59	36.57
	(5) 0.0736	0.1156	1.21	46.77	24.67

(continued)

Table (9) (cont.)

Radical Skeleton	ρ_N	$\rho_C(N)$	$\left a_{NH}^H \right $	θ° ($+a_{NH}^H$)	θ° ($-a_{NH}^H$)
	0.0223	0.0039	0.68	-	13.09
	0.0957	0.1708	0.17	35.77	33.60
	(3) 0.0393	0.0522	0.76	52.22	23.47
	(4) 0.1062	0.1856	2.35	48.00	18.89
	(6) 0.1002	0.1667	1.82	46.68	22.77

* See page 117.

On theoretical grounds, the spin polarisation contribution would be expected to decrease as the amino-group moved out of the molecular plane and overlap between the nitrogen $2p_z$ orbital and the ring $2p_z$ system decreased. Thus, with no allowance for this in their treatment, the values of Θ obtained from the approach of Bullock and Howard are probably too large. Although Sullivan does include a $\cos^2 \Theta$ parameter to allow for this decrease in the spin polarisation contribution, it is, nevertheless, only an approximation.¹⁰⁷ However, bearing in mind the energy barriers to rotation^{46,110,111} (the position of lowest energy is normally coplanarity with the ring) it would seem that a situation of restricted rotation is more probable than one of free rotation and that the equation (38) used by Sullivan is likely to be closer to the truth.

IV.3 Azidosemiquinones

In the azidosemiquinones the nitrogen coupling constant is smaller than that in the corresponding aminosemiquinone. This feature can be explained by a consideration of the orbitals involved in the two systems. As already demonstrated (see Ch. 1, Sec. 5.1), the nitrogen splittings are related to the unpaired electron spin-density at the nitrogen atom, and this is normally present in a $2p_z$ orbital which overlaps with the rest of the conjugated system. In the azido group, however, the $2p_z$ orbital is involved in N-N bonding¹¹² and is therefore not available for overlap with the π -system of the molecule.

Because of the orbital overlap within the azido group¹¹²⁻¹¹⁴, one might expect to observe a splitting from all three nitrogens. It is interesting, therefore, that in these two azidosemiquinones there is no apparent splitting from the second and third nitrogens. The splittings would be expected to decrease with distance from the ring p^π -system, and the splitting from even the first nitrogen is not very great, so any splitting from the second and third nitrogens would be expected to be very small. However, the lines in the spectra of these two compounds (Figs. 42 and 43) are very sharply resolved with a small linewidth, so there is no evidence of even a small coupling from the other two nitrogens.

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