ELECTRON-SPIN RESONANCE SPECTRA OF AROMATIC RADICALS AND RADICAL-IONS

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1. Introduction

ELECTRON-SPIN RESONANCE SPECTROSCOPY is a branch of microwave spectroscopy which is applied specifically to molecules possessing electrons with unpaired spins. It provides the organic chemist with a unique tool for the study of free radicals, and this Review is concerned with some of the phenomena encountered when liquid solutions are examined. Much of the theory is applicable to both aliphatic and aromatic radicals but there have, as yet, been very few studies of aliphatic radicals in solution because of their rather short lifetimes. Consequently most of this Review is concerned with aromatic radical ions, and furthermore is restricted to molecules containing only one unpaired electron.

By far the most impressive result of electron-spin resonance studies has been to demonstrate the value and power of modern valence theory. Conversely, it is scarcely possible to understand a single feature of an electron-resonance spectrum without resort to ideas based on quantum mechanics. It seems certain that the technique will find increasing use in the study of free-radical intermediates in chemical reactions. An elementary knowledge of the factors governing the distribution of an unpaired electron and its interaction with magnetic nuclei is essential if one is to avoid making errors in experimental analysis and assignment. The present Review is written with this in mind, but in particular, it is addressed to the reader who has doubts about the relevance of valence theory to experimental chemistry. Many of the results described in the following pages would be unintelligible without the assistance provided by molecular-orbital or valence-bond theory.

2. Principles of electron-spin resonance

A free electron has a spin S of $\frac{1}{2}$ and can therefore exist in two states of equal energy, said to be degenerate. This degeneracy is only removed by the application of an external magnetic field and two separate levels, characterised by the spin quantum numbers $M_s = -\frac{1}{2}$ or $+\frac{1}{2}$, result. The lower level corresponds to parallel alignment of the electron-spin *magnetic-moment* with the external field; the upper level corresponds to anti-parallel alignment (Fig. 1a). The separation between the levels is equal to $g\beta_e H$, where H is the strength of the applied magnetic field, β_e is the Bohr magneton, and g is a dimensionless quantity having the value 2·0023 for a free electron.

The application of a radio-frequency field of the appropriate frequency (ν) causes the electron spin to change its orientation, and the resulting transition is detected as an absorption of energy from the radio-frequency field. In practice electron-spin resonance spectrometers are operated at a fixed frequency (commonly 9000 Mc./sec.) and the strength of the applied magnetic field is adjusted to the value required for a resonance transition. For this reason it is customary to quote separations between absorption lines in terms of gauss. The resonance condition is therefore $h\nu = g\beta_e H$, and in any particular case the required magnetic field is determined by the value of g. For an unpaired electron in an organic free radical the g-value is always very close to the value for a free electron. In other cases, notably the transition-metal ions which possess d-electrons with unpaired spins, the g-value may be quite different from the free-spin value.[1] We will not be concerned with such cases here.
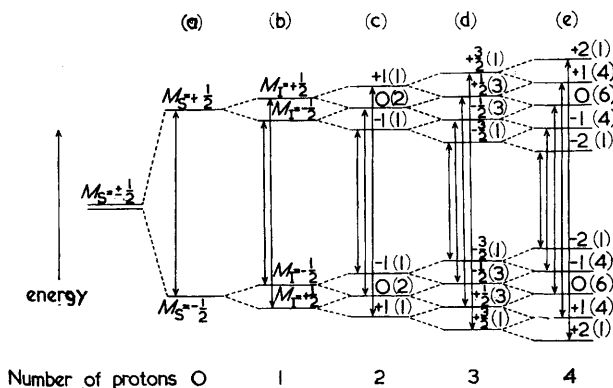

FIG. 1. *Hyperfine energy levels resulting from interaction of an unpaired electron with varying numbers of equivalent protons. Each number in parentheses gives the degeneracy of the level to which it refers. The vertical arrows indicate the allowed electron-spin resonance transitions.*

The feature which makes electron-spin resonance spectra so fascinating is their hyperfine structure, arising from interactions between the unpaired electron and magnetic nuclei in the molecule. For example, the proton nucleus has a spin I of $\frac{1}{2}$ with a resultant magnetic moment which can be aligned either parallel or antiparallel to the electron-spin magnetic moment. In the case of the hydrogen atom, possessing one electron and one proton, there are two possible orientations of the nuclear spin associated with each orientation of the electron spin, making a total of four levels which have different energies in the presence of a magnetic field. These are illustrated in Fig. 1(b). Each of the four levels can be characterised by two quantum numbers, $M_s(\pm\frac{1}{2})$ and $M_I(\pm\frac{1}{2})$, the electron-spin and nuclear-spin quantum numbers, respectively. The allowed electron-spin resonance

[1] Carrington and Longuet-Higgins, *Quart. Rev.*, 1960, **14**, 427.

transitions are those in which the nuclear spin does not change ($\Delta M_s = \pm 1$, $\Delta M_I = 0$) so that the spectrum of the hydrogen atom consists of two absorption lines.[2] These lines are of equal intensity because the energy differences between the levels with same M_s value but different M_I are so small that their populations at room temperature are essentially equal.

By constructing the energy level diagram for a system in which an electron interacts with a number of symmetrically equivalent protons, one can readily deduce the rules which govern the number and intensity of the hyperfine lines. The procedure is to consider the splitting due to each proton in turn. Thus for the case of two equivalent protons we extend our energy level diagram for the hydrogen atom, as shown in Fig. 1(c). Each electron spin level is now split into three sub-levels, the central one being doubly degenerate. For this situation the spectrum would consist of three lines with relative intensities 1:2:1. Obviously we could continue to extend the energy level diagram indefinitely. Fig. 1 goes as far as four equivalent protons, in which case each electron spin level is split into five sub-levels having the degeneracies 1,4,6,4,1. Consequently a radical in which the unpaired electron interacts with just four equivalent protons would show a spectrum consisting of five lines with relative intensities 1:4:6:4:1. An example of this situation is the *p*-benzosemiquinone anion (1);[3] the

(1)
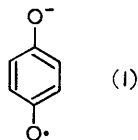
observed spectrum is shown in Fig. 2. Examples of spectra arising from interaction with six and eight equivalent protons are the anions of benzene[14a] and cyclo-octatetraene,[14b] respectively (Fig. 2). It will now be apparent that interaction of the unpaired electron with n equivalent protons gives rise to $(n + 1)$ hyperfine lines whose relative intensities are proportional to the coefficients of a binomial expansion of order n. The lines are equally spaced and the separation between two adjacent lines, measured in gauss, is referred to as the proton hyperfine splitting constant (a_H). (Multiplication by 2·80 converts the splitting constants into frequency units, Mc./sec.) The experimental analysis of a free-radical electron-spin resonance spectrum thus reduces to the problem of determining the hyperfine splitting constant for each type of proton in the molecule. Once these constants have been obtained the whole spectrum can be reconstructed and the reconstruction compared with the experimental pattern.

Two examples should suffice to demonstrate this method of analysis. Consider first the naphthalene negative ion[4] in which the unpaired

[2] Nafe and Nelson, *Phys. Rev.*, 1948, **73**, 718.

[3] Venkataraman and Fraenkel, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.

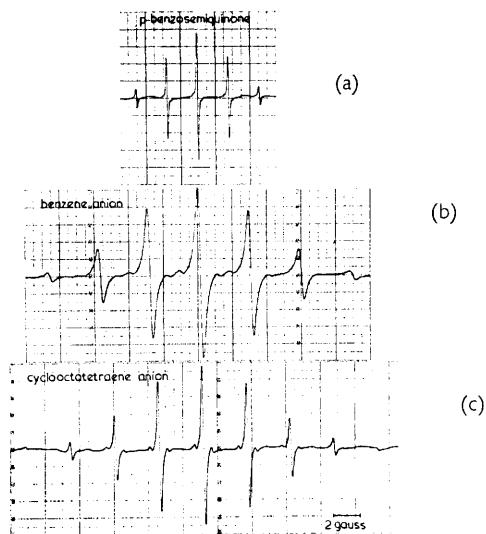[4] Weissman, Townsend, Paul, and Pake, *J. Chem. Phys.*, 1953, **21**, 2227.

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FIG. 2.   *Electron-spin resonance spectra of* (a) *the* p-*benzosemiquinone anion,* (b) *the benzene anion,* (c) *the cyclo-octatetraene anion. The spectra are displayed as the first derivative of absorption with respect to the magnetic field.*
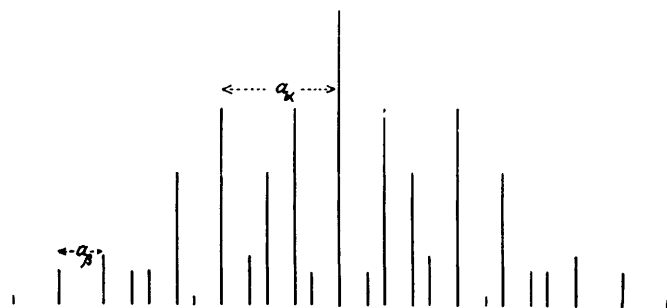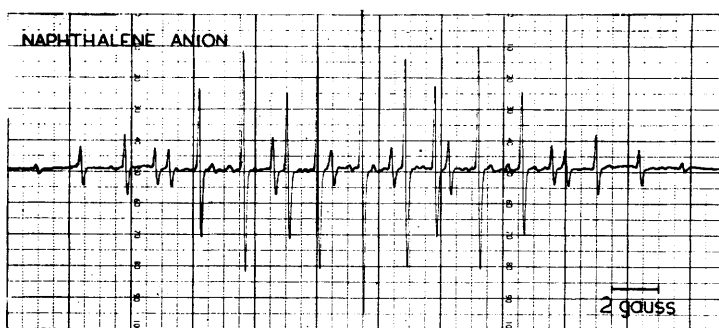

FIG. 3.   *Electron-spin resonance spectrum of the naphthalene anion with a reconstruction indicating the origin of the hyperfine lines.*

electron moves in a molecular π-orbital and is able to interact with the eight ring-protons. These can be divided into two sets, four α-protons and four β-protons, and our problem is to determine the two splitting constants. The reconstruction of the spectrum is shown in Fig. 3. The four α-protons alone would give five lines with relative intensities 1:4:6:4:1, but each of these lines is further split by the β-protons into a quintet with a similar intensity distribution. Hence the complete spectrum consists of twenty-five lines and the two splitting constants are 4·90 and 1·83 gauss respectively.[5]

A second example is the pyrazine anion,[6] containing two equivalent nitrogen atoms and four equivalent ring-protons. The ^{14}N nucleus also has a spin but in this case $I = 1$, rather than $\frac{1}{2}$, and there are thus three quantised orientations of the nucleus, with respect to the electron spin, characterised by the quantum numbers $M_I = +1$, 0, $- 1$. Interaction of an unpaired electron with one nitrogen nucleus therefore gives rise to three equally spaced, equally intense, hyperfine lines, and it is readily seen that interaction with two equivalent nitrogens will produce five lines with relative intensities 1:2:3:2:1. In the case of the pyrazine anion each of these lines is further split into a quintet by the four ring-protons. Hence we again observe a twenty-five line spectrum (Fig. 4),
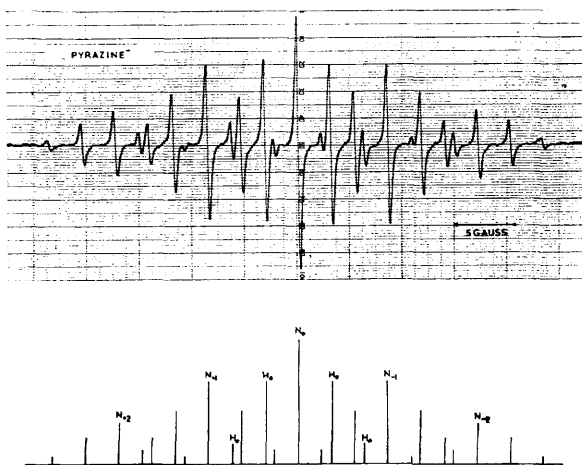

FIG. 4. *Electron-spin resonance spectrum of the pyrazine anion with a reconstruction indicating the origin of the hyperfine lines.*

[5] Carrington, Dravnieks, and Symons, *J.*, 1959, 947.
[6] Carrington and Veiga, *Mol. Phys.*, 1962, **5**, 21; Ward, *J. Amer. Chem. Soc.*, 1962, **84**, 332; McDowell, Paulus, and Rowlands, *Proc. Chem. Soc.*, 1962, 60; Henning and de Waard, *J. Chem. Phys.*, 1961, **35**, 2258.

defined by two splitting constants which are $a_N = 7 \cdot 22$ gauss and $a_H = 2 \cdot 66$ gauss.

We have shown how the spectra can be constructed once the hyperfine-splitting constants are known. In practice, of course, the problem is to determine the splitting constants from the observed spectra. This process is best described as one of intelligent guesswork, or trial and error. The spectra illustrated in Figs. 3 and 4 are relatively simple and, being completely resolved, are easily analysed. Other spectra may be much more complex, with lines overlapping, resulting in distorted intensities. In these cases it may be necessary actually to reconstruct line shapes,[7] although detailed examination of the wings of the spectrum will usually prove to be profitable.

3. The origin of proton hyperfine-structure

In organic free radicals there are two quite separate ways by which the unpaired electron can interact with a magnetic nucleus to produce hyperfine structure in the electron-spin resonance spectrum. The first mechanism is simply the dipole-dipole interaction between the electronic and nuclear magnetic moments, the magnitude of this interaction being inversely proportional to the cube of the distance between the electron and the nucleus, and also depending on the relative orientation of the two spins. If the radical can be studied in a single crystal this *anisotropy* can be measured directly, and the results agree very well with theoretical estimates of the dipole-dipole interaction.[8] If, however, the radical is in liquid solution, its orientation with respect to the external magnetic field changes rapidly and randomly because of the Brownian motion, and under these conditions the dipolar interaction has an average value of zero.[9]

The second mechanism for hyperfine interaction, and one which does not average to zero when the molecule is tumbling, is the Fermi contact interaction.[10] For this to occur there must be a finite unpaired-electron density at the nucleus in question. Electrons in pure p, d, or f orbitals have no density at the nucleus so it is necessary for the unpaired electron to have a certain amount of s-orbital character. It is, however, by no means obvious how this necessary condition can be fulfilled in a π-electron radical, where the unpaired electron moves in an orbital which has a node in the molecular plane. The answer to this problem was obtained by several authors[11] but the most complete investigations are those of McConnell

[7] Glarum and Snyder, *J. Chem. Phys.*, 1961, **36**, 2989.

[8] (a) McConnell and Strathdee, *Mol. Phys.*, 1959, **2**, 129; (b) Ghosh and Whiffen, *ibid.*, p. 285.

[9] Weissman, *J. Chem. Phys.*, 1954, **22**, 1378; Weissman and Banfill, *J. Amer. Chem. Soc.*, 1953, **75**, 2534.

[10] Fermi, *Z. Physik*, 1930, **60**, 320.

[11] (a) McConnell, *J. Chem. Phys.*, 1956, **24**, 764; (b) Bersohn, *ibid.*, p. 1066; (c) Weissman, *ibid.*, 1956, **25**, 890; (d) Jarrett, *ibid.*, p. 1289.

and Chesnut.[12] We will examine the detailed theory in due course, but for the moment we give a simple qualitative picture only.

Consider a $>\dot{C}H$ fragment of an aromatic system, in isolation from the rest of the molecule. A C–H σ-bonding orbital is formed by 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 $2p_\pi$-orbital whose axis is perpendicular to the trigonal plane. This arrangement can be represented diagrammatically (2 and 3), where the directions of the arrows

(2)   (3)
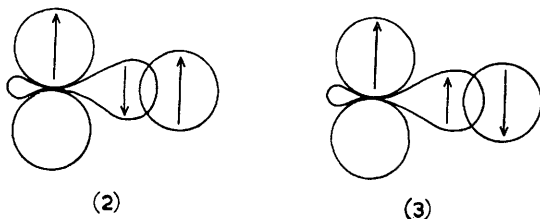
represent the electron-spin orientations. Clearly there are two possible arrangements, as shown, and both are equally important in the approximation of perfect pairing. However, there is a tendency for the carbon sp^2-electron to orient its spin parallel to that of the $2p_\pi$-electron, so that the second arrangement (3) is slightly preferred. The result is that there are small unpaired-spin densities in the carbon sp^2 and hydrogen $1s$-orbitals, the latter giving rise to the isotropic hyperfine structure, characteristic of π-electron radicals. Note that we have used the term "*spin density*"; we shall see why in section 6.

One might expect the effect described above to be rather small, and indeed it is. For unit unpaired-electron density on the carbon atom the proton hyperfine splitting is found to be about 23 gauss, compared with a 500 gauss splitting for the hydrogen atom itself. In aromatic radicals the unpaired-electron density on a particular carbon atom is usually much smaller than unity. McConnell[11] suggested the relationship $a_H = Q\rho$, where ρ is the unpaired-electron density at a given carbon atom, a_H is the hyperfine splitting due to the adjacent ring proton, and Q is a constant, usually taken to have a value between 22·5 and 30 gauss. The theoretical foundations of this relationship have been very thoroughly examined[12,13] and a vast number of experimental studies have confirmed its usefulness and applicability. In essence, it forms the bridge between experimental and theoretical studies, for a_H is something one can measure from the spectrum, and ρ can be calculated from valence theory.

The relationship holds for all π-electron radicals, both aromatic and aliphatic. For example, the benzene negative ion shows a seven-line

[12] McConnell and Chesnut, *J. Chem. Phys.*, 1958, **28**, 107; McConnell, *ibid.*, p. 1188; Brovetto and Ferroni, *Nuovo Cim.*, 1957, **5**, 142.
[13] McLachlan, Dearman, and Lefebvre, *J. Chem. Phys.*, 1960, **33**, 65; Aono, *Prog. Theor. Phys.*, 1959, **21**, 779.

spectrum (Fig. 2) with a spacing of 3·75 gauss so that $Q = 6 \times 3·75 = 22·5$ gauss; the methyl radical,[15] with unit unpaired-electron density on the carbon atom, gives four lines with a spacing of 25 ± 2 gauss.

4. Some properties of aromatic hydrocarbons

We have seen in the previous section that the magnitudes of the ring-proton hyperfine-splitting constants depend upon the distribution of the unpaired electron over the molecular framework. The measurement of electron-spin resonance spectra therefore provides a sensitive test of the theories of electron distribution, especially molecular-orbital theory. Conversely, we may expect the theory to be of considerable assistance in the analysis of complex hyperfine-patterns.

The Hückel molecular orbital theory of aromatic hydrocarbons has been described very thoroughly elsewhere[16,17] and we will do no more than summarise the results that are important for our purposes:

(1) It is assumed that the π-electrons can be treated independently of the C–C and C–H σ-bonding electrons.

(2) The π-electrons occupy molecular orbitals (ψ) which can be expressed as linear combinations of carbon $2p_\pi$-atomic orbitals (ϕ_n). Thus each molecular orbital has the form $\psi = \Sigma_n c_n \phi_n$, where the summation is over the n carbon atoms in the molecule.

(3) The energies of the molecular orbitals ψ and the values of the atomic orbital coefficients c_n are obtained by use of the variation principle. The energies are expressed in terms of parameters α and β, α being the Coulomb integral for a carbon $2p_\pi$-electron and β the C–C resonance integral.

(4) The ground state of the molecule is constructed by assigning the electrons to the lowest available molecular orbitals, with the restriction that not more than two electrons may be placed in the same orbital.

In order to interpret the electron-spin resonance spectra of aromatic radicals it is necessary to identify the molecular orbital containing the unpaired electron, and hence to calculate the unpaired-electron density at each carbon atom. If the required molecular orbital is $\psi = c_1\phi_1 + c_2\phi_2 + \ldots$, then the density ρ_1 at atom 1 is given by $c_1{}^2$, ρ_2 is given by $c_2{}^2$, and so on.

An aromatic hydrocarbon is called "alternant" if one can put stars against some of the atoms in such a way that each starred atom is bonded

    [14] (a) Tuttle and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 5342; (b) Strauss and Katz, *J. Chem. Phys.*, 1960, **32**, 1873.
   [15] Cole, Pritchard, Davidson, and McConnell, *Mol. Phys.*, 1958, **1**, 406.
    [16] Coulson, "Valence", Oxford University Press, Oxford, 2nd edn., 1961.
    [17] Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley and Sons, Inc., New York, 1961.

only to unstarred atoms, and *vice versa*.[18] The additional adjectives "even" or "odd" refer to the number of conjugated carbon atoms. Naphthalene (4) is an example of the former and benzyl (5) of the latter. The above procedure is impossible if there are any odd-membered rings in the molecule; hydrocarbons such as azulene (6) are therefore non-alternant.

(4)   (5)   (6) (non-alternant)
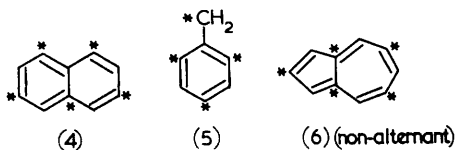
Most of the electron-spin resonance studies of aromatic systems have been concerned with radical anions and cations of even-alternant hydrocarbons. An important theoretical property of such molecules is that for every bonding orbital with energy $\alpha + x\beta$ (x positive) there exists a corresponding antibonding orbital of energy $\alpha - x\beta$. The coefficient of any atomic orbital has the same magnitude in these two molecular orbitals, but not necessarily the same sign.

This property can be verified by studying the spectra of the positive and negative ions of a given hydrocarbon and comparing the proton hyperfine-splitting constants. In the positive ion the unpaired electron occupies the bonding orbital of highest energy, whilst in the negative ion the extra electron occupies the lowest energy antibonding orbital. Since these orbitals are related in the manner just described and since the unpaired-electron densities are obtained simply by squaring the appropriate atomic-orbital coefficients, one would expect the spectra of the two ions to be very similar. These conclusions were first reached and verified by Weissman, de Boer, and Conradi[19] for the cases of anthracene and perylene. Fig. 5 summarises the results described by several authors for a variety of even-alternant hydrocarbon ions. The proton hyperfine-splitting constants a_H are plotted against the corresponding Hückel unpaired-electron densities ρ, the straight line indicating the theoretical relationship $a_H = Q\rho$ with a value of Q of 30 gauss. Thus the plot both confirms the similarity between the anions and cations of the same hydrocarbon and shows the measure of absolute agreement between theoretical and experimental splitting constants. It will be noticed that the hyperfine-splitting constants for the positive ions tend to be rather larger than those for corresponding positions in the negative ions. These differences are now well understood[20] and are due to the slight dependence of Q on the total charge density at a particular position.

The "pairing-property" of the molecular orbitals still holds for odd-

[18] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947 *A*, **192**, 16.
[19] Weissman, de Boer, and Conradi, *J. Chem. Phys.*, 1957, **26**, 963.
[20] Colpa and Bolton, *Mol. Phys.*, to be published.

alternant hydrocarbons but in these cases there is an additional non-bonding orbital. The distribution of an unpaired electron in this non-bonding orbital is easily calculated and molecular-orbital theory predicts that the unpaired-electron density on every alternate carbon atom (*e.g.* the unstarred atoms in the benzyl radical) should be zero. There are very
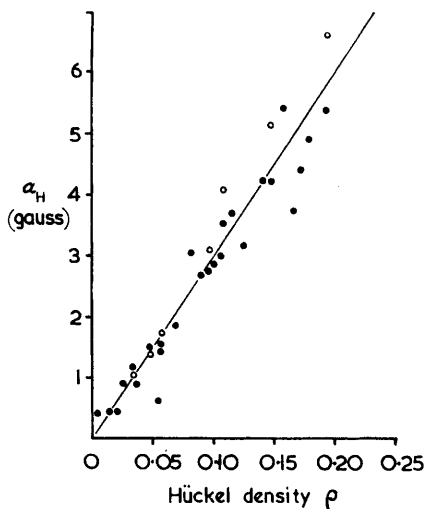

FIG. 5. *Experimental proton hyperfine-splitting constants plotted against Hückel unpaired-electron densities. The open circles refer to positive ions; closed circles refer to negative ions. The graph incorporates the results for the positive ions of anthracene, naphthacene, perylene, and coronene, and the negative ions of benzene, cyclo-octatetraene, naphthalene, anthracene, naphthacene, pentacene, perylene, coronene, phenanthrene, and biphenyl.*

few experimental opportunities for testing this result. Those molecules which have been studied give splitting constants which are in rather poor agreement with the simple theory and lead us to an extremely important concept which is the subject of section 6.

5. Derivatives of benzene

A considerable number of studies have been devoted to radical-ions derived from compounds which can be regarded as derivatives of benzene. These include alkyl-, cyano-, and nitro-substituted benzene anions, *ortho-* and *para*-benzosemiquinone ions, nitrogen heterocyclic anions and amino-benzene cations. The results can be understood in terms of the benzene molecular orbitals, in the following way.

The six carbon $2p_\pi$ atomic orbitals can be combined to form six molecular orbitals, three bonding and three antibonding. The relative energies of these are shown in Fig. 6 and it will be noticed that the highest bonding and lowest antibonding orbitals occur in degenerate pairs. Hence in the

benzene negative-ion the unpaired electron is equally distributed between the two degenerate antibonding orbitals. The distribution of the electron in the separate orbitals is shown in Fig. 6, the two orbitals being classified as "symmetric" or "antisymmetric" according to their behaviour on reflection through a plane perpendicular to the ring, and passing through opposite atoms. The average electron-density at each carbon atom is $\frac{1}{6}$ and the spectrum of the benzene negative ion[14] consists of seven lines (intensities 1:6:15:20:15:6:1) with spacing 3·75 gauss, as we have already shown (Fig. 2).
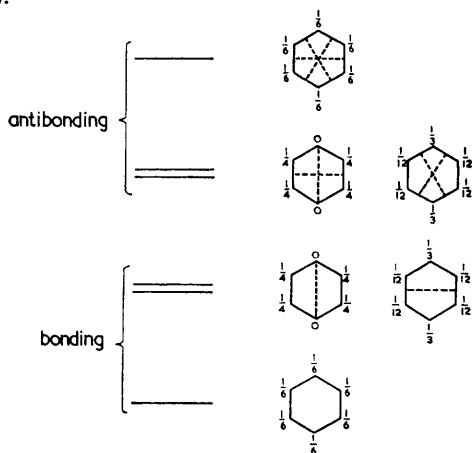

FIG. 6.   The electron distribution in the molecular orbitals of benzene. The dotted lines give the positions of the π-orbital nodes.

For substituted benzene negative-ions which have lower than three-fold symmetry the orbital degeneracy is removed and, provided the perturbation due to the substituent is not too large, the unpaired electron distribution corresponds rather closely to that in one or other of the two orbitals shown in Fig. 6. The simplest cases to consider are those in which the perturbation can be regarded as being purely inductive. If the substituent is electron-repelling the unpaired electron will occupy the antisymmetric orbital, thereby avoiding the substituent, and the spectrum will consist of a 1:4:6:4:1 quintet, with spacing approximately 5·5 gauss, these lines arising from the *ortho* and *meta* ring-protons. The *para* ring-proton and any magnetic nuclei in the substituent should give only very small splittings.

If however the substituent attracts electrons the unpaired electron will occupy the symmetric orbital, since it then has a maximum density ($\frac{1}{3}$) at the substituent position. In this case the spectrum will be rather more complicated but should be characterised by a large doublet-splitting (approximately 8 gauss) from the *para* ring-proton, with further smaller splittings from the *ortho* and *meta* protons. As we shall see these conclusions, which apply to mono- or *para*-disubstituted benzenes, are in excellent accord

with experiment. But before we examine the experimental evidence, let us apply the same reasoning to *meta*- and *ortho*-derivatives. For *meta*-disubstituted benzene negative ions in which the substituent is electron-attracting, the electron should occupy the antisymmetric orbital which has maximum densities ($\frac{1}{4}$) at the substituent positions. If the substituent repels electrons the unpaired electron should occupy the symmetric orbital, having minimum densities ($\frac{1}{12}$) at the substituent positions. The same sort of argument leads us to conclude that in *ortho*-disubstituted anions the unpaired electron will occupy the antisymmetric or the symmetric orbital depending on whether the substituents attract or repel electrons, respectively.

We are now in a position to review the experimental results. The above conclusions are directly applicable to substituents whose effect is mainly inductive and the arguments require only slight modification for substituents which provide or accept π-electrons.

(i) **Methyl derivatives.**—The anions of toluene and the xylenes can be prepared by reduction of the hydrocarbons with potassium in 1,2-di-methoxyethane; they are quite stable in solution at $-70°$c. The proton hyperfine splitting constants[14,21] are as shown in (7)—(9):

(7)   (8)   (9)
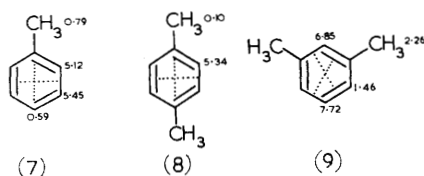
The dotted lines indicate the approximate positions of the π-orbital nodes. The spectrum of the toluene anion[21a] is shown in Fig. 7 and the reader who
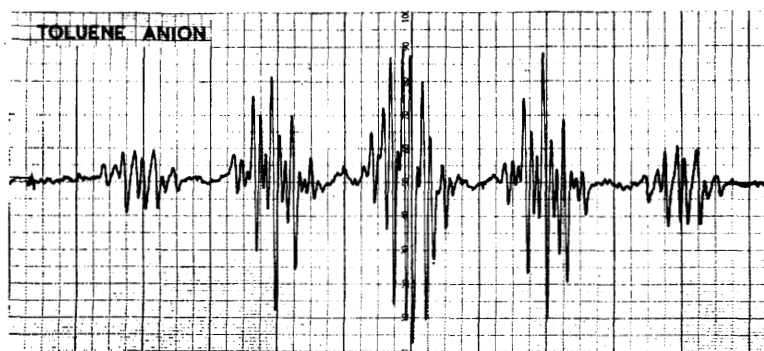

Fig. 7.   *Electron-spin resonance spectrum of the toluene anion.*

[21] (*a*) Bolton and Carrington, *Mol. Phys.*, 1961, **4**, 497; (*b*) Tuttle, *J. Amer. Chem. Soc.*, 1962, **84**, 2839.

seeks experience in the analysis of electron-spin resonance spectra should find this spectrum interesting. The splitting constants are in accord with our expectations, especially for toluene and *p*-xylene. The results for *m*-xylene (9) reflect the small changes in electron distribution due to the effect of the methyl groups. The distribution given in Fig. 6 is only a first (but rather good) approximation; however, particularly when the electron occupies the symmetric orbital, we shall expect to find some modification of the distribution.

It has not so far proved possible to prepare the anions of the more highly methyl-substituted benzenes.[21a]

(ii) **Nitrogen heterocyclic anions.**—Only two simple nitrogen heterocyclic anions have been studied, namely those derived from pyrazine[6] and pyridazine.[22] The splitting constants are as shown in (10) and (11).

(10) Pyrazine   (11) Pyridazine
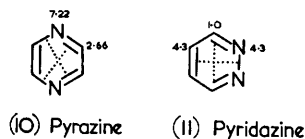
Again these results are reasonably close to the predictions of simple theory, and the agreement can be improved by carrying out molecular-orbital calculations which take explicit account of the inductive effect of the nitrogen atoms.

Several attempts to prepare the anion of pyridine have been made and have[6,23] instead given rise to the spectrum of the 4,4'-bipyridyl anion, formed as a result of dimerisation and dehydrogenation. In a particularly careful study Ward[23] has confirmed the assignment of the proton hyperfine splitting constants by deuterium substitution, a very useful technique which will be discussed later. Attempts to study the anion of pyrimidine[22] also indicate that dimerisation occurs and, rather surprisingly, *s*-triazine[22] does not appear to be reduced at all by alkali metals. Nitrogen heterocyclic molecules with the naphthalene or anthracene framework can be readily reduced, however, and the spectra of several such radical-anions have been recorded.[6,24]

It should be noted at this point that the reductions can either be carried out chemically, by using alkali metals,[25] or electrolytically[26]—reduction occurring at the surface of a mercury pool cathode. The electrolytic technique, first developed by Geske and Maki,[26] is extremely elegant and has been used extensively; it is restricted to molecules which are rather easily reduced but otherwise has considerable advantages over the chemical methods.

[22] Carrington and Veiga, unpublished results.
[23] Ward, *J. Amer. Chem. Soc.*, 1961, **83**, 3623.
[24] Hausser, Häbich, and Franzer, *Z. Naturforsch.*, 1961, *A*, **16**, 836.
[25] Lipkin, Paul, Townsend, and Weissman, *Science*, 1953, **117**, 534.
[26] Geske and Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

Another class of radical-ions can be derived from nitrogen heterocyclic molecules. If pyrazine is dissolved in concentrated sulphuric acid and treated with zinc dust, the doubly protonated monocation (12) is produced.[27] This radical cation possesses seven π-electrons and gives a spectrum similar to that of the pyrazine anion, but with additional structure from the protons bonded to the nitrogen atoms. Similar radical-cations derived from phenazine and 4,4'-bipyridyl[27,24] have also been studied.

(12)
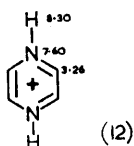
(iii) **Cyanobenzene anions.**—The cyanide group possesses a filled π bonding orbital and an empty antibonding orbital, both of which are able to combine with the π-orbitals of benzene. Provided the orbital mixing is not too large, arguments analogous to those outlined above can be used to determine the orbital of the unpaired electron. Thus in the case of the benzonitrile anion, the vacant low-lying orbital of the cyanide group will interact to depress the energy of the symmetric benzene antibonding-orbital, but it will not interact with the antisymmetric orbital. Hence in this case, and also in that of the terephthalonitrile anion, the unpaired-electron distribution will be approximately that of the symmetric benzene orbital. In the phthalonitrile anion, however, the antisymmetric orbital should have the lower energy. The measured splitting constants[28] are as shown in (13)—(15); they are in reasonable agreement with these conclu-

(13)   (14)   (15)
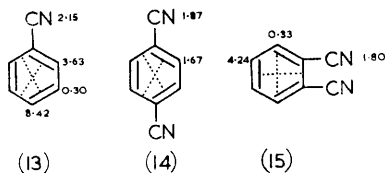
sions. Certainly some delocalisation of the electron onto the cyanide group does occur and again, calculations which take account of the π-orbital mixing[28] give splitting constants in better agreement with those measured.

(iv) **Semiquinone anions.**—Semiquinone anions, formed by reduction of the quinone or oxidation of the quinol, are extremely stable in alkaline solution[29] and have been studied extensively by electron-spin resonance

[27] Bolton, Carrington, and Veiga, *Mol. Phys.*, 1962, **5**, 465.
[28] Carrington and Todd, *Mol. Phys.*, 1963, to be published; Rieger and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2795.
[29] Michaelis, *J. Biol. Chem.*, 1931, **92**, 211.

spectroscopy. The results obtained have stimulated a great deal of work on the theory of hyperfine interactions, hyperconjugation, and relaxation processes. More recently it has been found that doubly-protonated semi-quinone cations are often quite stable in concentrated sulphuric acid.[30]

The simplest semiquinones are the *ortho-* and *para*-benzosemiquinones and the hyperfine-splitting constants obtained[3,30b,31] are as shown in (16)—(18).

(16)   (17)   (18)
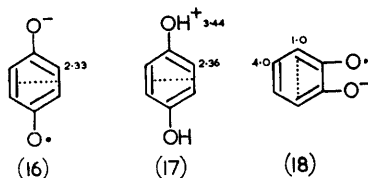
It is clear that, despite the conjugation of oxygen p_π-orbitals with the ring system, the unpaired-electron distribution still bears a fairly close resemblance to the distribution predicted by unmodified Hückel theory. One can regard each of these ion-radicals as a benzene positive ion perturbed by two O^- (or OH) substituents, and adopt the criterion that the most stable electron-configuration will be that in which there is maximum positive charge at the positions of the electron-releasing substituents. Hence, in contrast to the other radical-anions considered so far, the orbital of the unpaired electron is correlated with one of the degenerate *bonding*-orbitals of benzene.

Many authors have carried out molecular-orbital calculations which include modified Coulomb and resonance integrals for the oxygen atom and the carbon-oxygen bond and the results are usually in satisfactory agreement with experiment.[32] Similarly the naphtho- and anthra-semiquinones have been the subject of extensive experimental and theoretical study.[33]

· (v) **Amino-benzene cations.**—The *p*-phenylenediamine cation[34] and the corresponding *N*-tetramethyl derivative[35] (Wurster's Blue cation) can again be regarded as examples of the benzene positive ion stabilised by electron-releasing substituents. The experimental results are as shown in (19) and (20).

[30] (a) Land and Porter, *Proc. Chem. Soc.*, 1960, 84; (b) Bolton and Carrington, *ibid.*, 1961, 385.
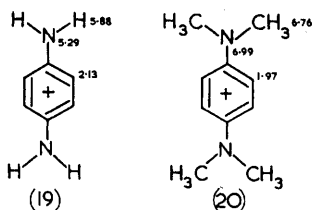
[31] Hoskins, *J. Chem. Phys.*, 1955, **23**, 1975, 2461.

[32] Vincow and Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333.

[33] Wertz and Vivo, *J. Chem. Phys.*, 1956, **24**, 479; Adams, Blois, and Sands, *ibid.*, 1958, **28**, 774.

[34] Melchior and Maki, *J. Chem. Phys.*, 1961, **34**, 471.

[35] Bolton, Carrington, and Veiga, *Mol. Phys.*, 1962, **5**, 615; Weissman, *J. Chem. Phys.*, 1954, **22**, 1135; Tuttle, *ibid.*, 1959, **30**, 331; Hausser, *Z. Naturforsch.*, 1959, *A*, **14**, 425.

(19)   (20)

(vi) Alkylbenzene anions.—We have already referred to the results obtained from methyl-substituted benzenes. A particularly interesting point emerges from the study of a series of monoalkylbenzene anions.[36] The hyperfine-splitting constants are as shown in (21)—(24).

(21)   (22)   (23)   (24)
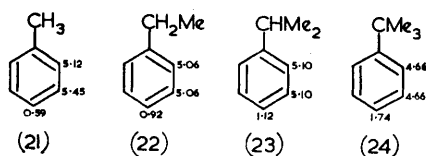
We see that from toluene to t-butylbenzene the splitting from the *para* ring-proton increases and is accompanied by corresponding decreases in splittings from the *ortho-* and *meta*-protons, so that the total hyperfine splitting remains effectively constant at about 22—23 gauss. Now we have already seen that the unpaired electron should occupy the antisymmetric orbital and the results are indeed consistent with this observation. But if the difference in energy between the occupied antisymmetric orbital and the vacant symmetric orbital is small, an important new effect must be considered. The normal approximation made in quantum chemistry is that one can separate those parts of the molecular energy which depend on electron co-ordinates from those which depend on nuclear co-ordinates (Born–Oppenheimer approximation). The electron distributions given in Fig. 6 refer to the nuclei in fixed positions at the corners of a regular hexagon. However, the nuclei are not fixed but are vibrating, and if this is taken into account the proper wave-functions lead to electron distributions which are, in fact, "mixtures" of those illustrated. Now the importance of this "vibronic coupling" of the antisymmetric and symmetric states decreases as the energy separation between the states increases. The fairly large *para*-proton splitting in the t-butyl benzene anion indicates considerable mixing of the two states and the implication of the results obtained is that as we go from methyl- to t-butyl-benzene the perturbation of the benzene orbitals becomes smaller so that they are more nearly degenerate. Quantitative estimates of the effect support this conclusion.

It will be appreciated that when the energy separation involved becomes comparable with kT, it is possible for the higher vacant orbital to be

[36] Bolton, Carrington, Forman, and Orgel, *Mol. Phys.*, 1962, **5**, 43.

significantly occupied thermally at ordinary temperatures. If such an effect is important the hyperfine-splitting constants ought to be temperature-dependent, and very recently a small temperature-dependence has been observed[37] for both the toluene and t-butylbenzene anions. The thermal effect should not, however, be confused with the vibronic effect, which would persist even at absolute zero.

(vii) **Other derivatives.**—It will by now be apparent that, because of the orbital degeneracy of the benzene anion, the electron-spin resonance spectra of monosubstituted benzene anions are very sensitive to the nature of the substituent; small changes in the substituent can lead to drastic changes in the appearance of the spectrum. As an example[38] we can compare the $-CMe_3$, $-SiMe_3$, and $-GeMe_3$ derivatives of benzene. The proton hyperfine-splitting constants, obtained from the spectra of
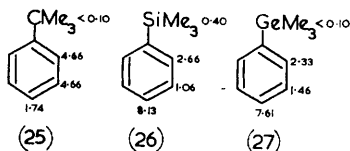
the anions, are as shown in (25)—(27). We have already observed that the t-butyl group repels electrons and hence the unpaired electron occupies the antisymmetric orbital. However, the above splitting constants show that in the silicon and germanium derivatives the symmetric orbital has the lower energy, indicating that the $SiMe_3$ and $GeMe_3$ groups are relatively electron-attracting in this system, although one cannot say whether the main effect is inductive or mesomeric. The larger methyl splitting in the silicon compound certainly indicates more effective π-bonding between the silicon d-orbitals and the ring, as compared with the germanium compound.

It is clear that in the case of *para*-disubstituted benzene anions where the two substituents are different, the orbital of the unpaired electron will be determined by the stronger of the two perturbations. For example, the unpaired electron in the toluene anion occupies the antisymmetric orbital but in the *p*-toluronitrile anion[28] the symmetric orbital has the lower energy. In principle one can balance one group against another and, indeed, it is even possible to obtain an "accidental" degenerate or near-degenerate ground state by appropriate choice of substituents.

The results described in this section should leave the reader in no doubt as to the value of molecular orbital theory, even in its simplest form. The differences between different derivatives can be understood quite naturally in terms of the orbital degeneracy of the benzene anion and the effects of small perturbations. It is difficult to see how purely qualitative arguments

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[37] Tuttle, *J. Amer. Chem. Soc.*, 1962, **84**, 1492; Bolton, unpublished results.
[38] Bedford, Bolton, Carrington, and Prince, *Trans. Faraday Soc.*, 1962, **59**, 53.

or even the deepest intuition could explain, for example, the completely different spectra obtained from the ions of t-butylbenzene and trimethylsilylbenzene.

(viii) **Nitro-derivatives.**—The nitrobenzene derivatives have been left until last because they really have to be treated apart from the rest. The hyperfine-splitting constants of the anions show that the unpaired electron is often largely located on the nitro-groups, so that any discussion in terms of the benzene orbitals is inappropriate. Aromatic nitro-compounds are readily reduced and a number of them have been studied by Maki and Geske,[39] using electrolytic reduction, and also by Ward[40] using alkali-metal reductions. In some cases quite different spectra are obtained according to the method of reduction used, as indicated by the results in (28)—(34).

(a) *Electrolytic reduction:*

(28)   (29)   (30)   (31)
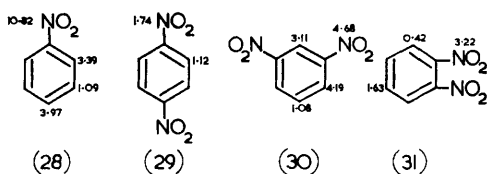
(b) *Alkali-metal reduction:*

(32)   (33)   (34)
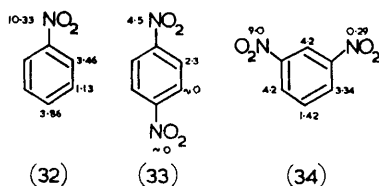
There is now an increasing amount of evidence to show that splitting constants are sometimes sensitive to solvent changes. However, the very large differences between the spectra of, for example, the *m*-dinitrobenzene anion prepared by the two different methods must be due to strong interaction with the alkali-metal cation. Ward[40] suggests that there may be near-orbital degeneracy in the anion and that co-ordination of the alkali-metal cation (sodium, in this case) to one of the nitro-groups causes an inversion of the orbitals with a consequent large change in unpaired-electron distribution. In support of this conclusion additional hyperfine structure from the sodium-23 nucleus is observed, indicating

[39] Maki and Geske, *J. Chem. Phys.*, 1960, 33, 825.
[40] Ward, *J. Amer. Chem. Soc.*, 1961, 83, 1296; *J. Chem. Phys.*, 1962, 36, 1405.

ion-pair formation, a phenomenon which was first observed and interpreted by Adam and Weissman.[41]

Maki and Geske[42] have also studied a series of *para*-substituted nitrobenzene anions and have measured the effects of different substituents on the unpaired-electron distribution in the ring.

6.   Negative spin densities

Nearly all of the results which we have considered so far can be understood in terms of simple Hückel molecular-orbital theory, but there are a number of important exceptions to this. Let us consider two examples. The first is the perinaphthenyl free radical, formed by air-oxidation of a solution of perinaphthene in carbon tetrachloride.[43] This is an odd-alternant hydrocarbon radical, so that the unpaired electron should occupy a non-bonding molecular orbital with the distribution shown in (35). We would therefore expect to find a seven-line spectrum with an

(35)   (36)
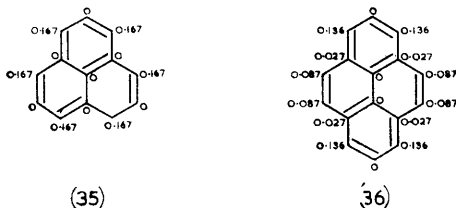
overall width of at most 25—30 gauss. In fact the observed spectrum[43] is 49 gauss wide and consists of a septet (spacing 7·3 gauss), each member of which is split into a 1:3:3:1 quartet (spacing 2·2 gauss). Obviously the extra splitting arises from the three equivalent ring protons which should be in nodal positions. A second example is the pyrene negative-ion for which the Hückel unpaired-electron densities are shown in (36). Again there should be no hyperfine-interaction with the two terminal protons but, in fact, a splitting of 1·09 gauss is observed.[44]

In order to understand these and similar results we must go a little deeper into the theory and discuss the results in terms of spin densities[12] which, unlike the unpaired-electron densities so far defined, have both magnitude and sign. The spin density at a carbon atom is obtained by adding the spins of all the electrons at the atom. If there is an excess of α- over β-spins the spin density is positive, and if not, it is negative.

We will return to the above examples a little later but first consider a simpler case, namely, the allyl radical. We first use valence-bond theory and then re-examine the problem in terms of molecular-orbital theory.
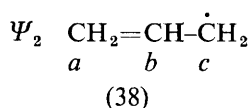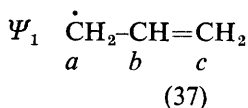
[41] Adam and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.
[42] Maki and Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.
[43] Sogo, Nakazaki, and Calvin, *J. Chem. Phys.*, 1957, **26**, 1343.
[44] Hoijtink, Townsend, and Weissman, *J. Chem. Phys.*, 1960, **34**, 507.

The ground state of the allyl radical can be regarded as a resonance hybrid of the two structures, shown in (37) and (38):

$$\Psi_1 \quad \overset{\bullet}{C}H_2\text{–}CH\text{=}CH_2 \qquad\qquad \Psi_2 \quad CH_2\text{=}CH\text{–}\overset{\bullet}{C}H_2$$
$$ a \quad\; b \quad\; c \qquad\qquad\qquad\quad a \quad\; b \quad\; c$$
$$(37) \qquad\qquad\qquad\qquad\qquad (38)$$

We can write the valence-bond wave functions which represent these two structures, the first being

$$\Psi_1 = \frac{1}{\sqrt{12}} \begin{vmatrix} a^\alpha(1) & a^\alpha(2) & a^\alpha(3) \\ b^\beta(1) & b^\beta(2) & b^\beta(3) \\ c^\alpha(1) & c^\alpha(2) & c^\alpha(3) \end{vmatrix} - \frac{1}{\sqrt{12}} \begin{vmatrix} a^\alpha(1) & a^\alpha(2) & a^\alpha(3) \\ b^\alpha(1) & b^\alpha(2) & b^\alpha(3) \\ c^\beta(1) & c^\beta(2) & c^\beta(3) \end{vmatrix}$$

which is more usually abbreviated to

$$\Psi_1 = \frac{1}{\sqrt{3!}} \left\| a(1)b(2)c(3) \right\| \times (\alpha\beta\alpha - \alpha\alpha\beta) \frac{1}{\sqrt{2}}$$

a, b and c are the three carbon $2p_\pi$-orbitals; 1, 2 and 3 are the electrons which can each have either α- or β-spin.

A brief word or two is needed about this wave function.[45] The two determinants that arise are called Slater determinants; they express the wave function in a compact form automatically including the Pauli exclusion principle which demands that the wave function must be anti-symmetric with respect to interchange of any pair of electrons.

In a similar manner, the wave function for the second resonance hybrid can be written, in abbreviated form,

$$\Psi_2 = \frac{1}{\sqrt{3!}} \left\| a(1)b(2)c(3) \right\| \times (\alpha\beta\alpha - \beta\alpha\alpha) \frac{1}{\sqrt{2}}$$

The difference between the two wave functions is that in Ψ_1 the electrons in orbitals b and c form a bond and so must have opposite spins ($\alpha\beta$ or $\beta\alpha$), whereas in Ψ_2 the bond is between a and b.

Now the true wave function Φ for the ground state is an equal mixture of Ψ_1 and Ψ_2 and can be written,

$$\Phi = \frac{1}{\sqrt{3}}(\Psi_1 + \Psi_2) = \frac{1}{\sqrt{6}}(2\alpha\beta\alpha - \alpha\alpha\beta - \beta\alpha\alpha) \times \left\| a(1)b(2)c(3) \right\|$$

$\left(\Psi_1 \text{ and } \Psi_2 \text{ are not orthogonal, hence the factor } \dfrac{1}{\sqrt{3}} \right)$

[45] Stewart, *Ann. Reports*, 1961, **58**, 8.

We now sum to obtain the total spin in each atomic orbital, with the following results:

$$\text{For } a, \text{ spin} = \frac{4}{6}\alpha + \frac{1}{6}\alpha + \frac{1}{6}\beta = \frac{2}{3}\alpha$$

$$b, \text{ spin} = \frac{4}{6}\beta + \frac{1}{6}\alpha + \frac{1}{6}\alpha = \frac{1}{3}\beta$$

$$c, \text{ spin} = \frac{4}{6}\alpha + \frac{1}{6}\beta + \frac{1}{6}\alpha = \frac{2}{3}\alpha$$

Thus we see that each terminal carbon atom has $\frac{2}{3}\alpha$ spin but the centre atom has $\frac{1}{3}\beta$ spin; the latter is referred to as a negative spin density.

Now let us examine the same problem using molecular-orbital theory. If we carry out a Hückel calculation we obtain the energies and the corresponding molecular orbitals as,

$$E_1 = \alpha + \sqrt{2}\beta \qquad \psi_1 = \frac{1}{2}(a + \sqrt{2}b + c)$$

$$E_2 = \alpha \qquad \psi_2 = \frac{1}{\sqrt{2}}(a - c)$$

$$E_3 = \alpha - \sqrt{2}\beta \qquad \psi_3 = \frac{1}{2}(a - \sqrt{2}b + c)$$

where in this case α and β are the Coulomb and resonance integrals as before. (The use of α and β in this context, and also to denote the two spin states of an electron, is perhaps confusing, but nevertheless standard practice.) Since there are three electrons, the unpaired electron will occupy the non-bonding orbital ψ_2 and the unpaired-electron densities will be $\frac{1}{2}$, 0, $\frac{1}{2}$ in the atomic orbitals a, b and c, respectively. As before, a more complete way of expressing the ground state is as a Slater determinant,

$$\Psi_1 = \frac{1}{\sqrt{3!}} \left\| \psi_1(1)\, \psi_1(2)\, \psi_2(3) \right\| \alpha\beta\alpha$$

This description of the ground state is, however, inadequate because it does not take account of the spatial correlation between electrons of opposite spin. This effect is known to be important in neutral radicals and it is possible to obtain a more accurate wave function for the ground state by mixing Ψ_1 with appropriate excited-state configurations. Some of these excited configurations (for example, the one with an electron in each molecular orbital) give unpaired spins in the molecular orbitals ψ_1 and ψ_3, and these orbitals do not have nodes on the central carbon atom. The details of the calculation are complicated and we will not explore them here. The essentials are, in summary, that mixing of excited states with Ψ_1 leads to an excess of electrons with β-spin on the central atom.

By returning to the results described at the beginning of this section, a valence-bond calculation[46] for perinaphthenyl with $Q = 22.5$ gauss leads to splitting constants of 3·96 and 7·22 gauss, and a molecular-orbital calculation[44] for the pyrene anion, including excited configurations, gives a splitting constant of 1·05 gauss for the terminal protons, in excellent agreement with experiment. The corresponding spin densities, which are zero in the Hückel calculation, are now found to be negative.

It is possible to measure the sign of a spin density directly, by nuclear magnetic resonance spectroscopy.[47] The protons in an aromatic free radical experience a very large local field due to the unpaired electron and if the nuclear magnetic resonance spectrum is measured at very low temperatures large chemical shifts are observed. The direction of the shift depends upon the sign of the spin density at the hydrogen nucleus, which in turn depends upon the sign at the adjacent carbon atom. Now the proton magnetic resonance spectrum of the pyrene anion has been measured at 4°K; three resonance lines are observed, corresponding to the three types of ring proton.[48] Two of these lines occur on the high-field side of the normal values observed in the pyrene molecule, whilst the other line, which is half as intense, is found on the low field side. The last line corresponds to the two equivalent terminal protons. The magnitudes of the chemical shifts are fairly closely proportional to the hyperfine-splitting constants obtained from the electron-spin resonance spectrum, and show clearly that the spin density at the terminal position is of opposite sign to that at the other two ring positions. In order to predict the actual direction of the shift one must delve more deeply into the origin of the hyperfine inter-action, as we shall do in the next section.

In conclusion one may say that negative spin-densities are most likely to occur when simple molecular-orbital theory predicts electron densities which are zero or very small. This is especially the case for odd-alternant radicals, and in these cases it is often necessary to improve the molecular wave function, either by including excited-state configurations, or by self-consistent field methods.[49]

7.   Ring-proton hyperfine structure

We are now in a position to return to the problem which was left somewhat unsatisfactorily in section 3. How does an unpaired electron, moving in a molecular orbital compounded of carbon $2p_\pi$ orbitals, cause unpaired spin to appear at a ring proton?

Quantitative answers to this question have been obtained by using valence-bond theory[11] but we will follow Weissman's exposition[11c] based on molecular-orbital theory, which is perhaps slightly easier to grasp. We again consider the $>\dot{C}$—H fragment and examine the electron

[46] McConnell and Dearman, *J. Chem. Phys.*, 1958, **28**, 51.
[47] Gutowsky, Kusumoto, Brown, and Anderson, *J. Chem. Phys.*, 1959, **30**, 860.
[48] Anderson, Zandstra, and Tuttle, *J. Chem. Phys.*, 1960, **33**, 1591.
[49] McLachlan, *Mol. Phys.*, 1960, **3**, 233.

configuration $(\sigma_B)^2\pi^1$, where two electrons are placed in the C–H σ-bonding orbital (σ_B) and one electron in the carbon π-orbital. We write the proper wave function corresponding to this configuration as a Slater determinant in abbreviated form,

$$\Phi_1 = \frac{1}{\sqrt{6}} \left\| \sigma_B\,(1)\ \sigma_B\,(2)\ \pi\,(3) \right\| \alpha\beta\alpha$$

Now if this were a completely satisfactory representation of the ground state there would be no isotropic hyperfine interaction; in order to obtain such interaction we must improve the wave function by mixing it with appropriate excited configurations. In particular we seek configurations leading to unpaired spin in a σ-orbital. Consider the electron configuration $(\sigma_B)^1(\pi)^1(\sigma_A)^1$ in which an electron has been promoted into the C—H σ-antibonding orbital (σ_A). Now that we have three orbitals and three electrons there are no longer any restrictions on the electron spins; a configuration in which all three electrons have α-spin, say, is certainly possible. However this state cannot be mixed with Φ_1, for we are restricted to wave functions in which only two electrons have the same spin. There are three such functions, which we may write

$$D_1 = \frac{1}{\sqrt{6}} \left\| \sigma_B(1)\sigma_A(2)\pi(3) \right\| \alpha\alpha\beta$$

$$D_2 = \frac{1}{\sqrt{6}} \left\| \sigma_B(1)\sigma_A(2)\pi(3) \right\| \alpha\beta\alpha$$

$$D_3 = \frac{1}{\sqrt{6}} \left\| \sigma_B(1)\sigma_A(2)\pi(3) \right\| \beta\alpha\alpha$$

At this point we should digress briefly to enumerate some of the rules for constructing spin wave functions. When there is only one electron to consider, only one state can be formed, with $S = \frac{1}{2}$, the allowed values of the spin quantum number M_s being $\pm \frac{1}{2}$. Thus the spin wave functions are simply

$$\alpha \ldots \ldots M_s = +\frac{1}{2} \text{ and } \beta \ldots \ldots M_s = -\frac{1}{2}$$

Two electrons in different orbitals can be combined to form either a singlet spin-state ($S = 0$) in which the electrons have their spins paired, or a triplet spin-state ($S = 1$) having three components characterised by spin quantum numbers $M_s = +1, 0, -1$. The wave functions are

$$\frac{1}{\sqrt{2}} \Big\{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \Big\} \qquad \text{for } S = 0$$

$$\frac{1}{\sqrt{2}} \Big\{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \Big\} \qquad M_s = 0$$

$$\alpha(1)\alpha(2) \qquad\qquad\qquad M_s = +1 \quad \text{for } S = 1$$

$$\beta(1)\beta(2) \qquad\qquad\qquad M_s = -1$$

Now, three electrons in different orbitals can be combined to form two doublet spin states ($S = \frac{1}{2}$) or one quartet state ($S = \frac{3}{2}$). The permissible wave functions which arise are

$$\alpha\alpha\alpha \qquad\qquad M_s = +\frac{3}{2}$$

$$\frac{1}{\sqrt{3}}\left\{\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha\right\} \qquad M_s = +\frac{1}{2}$$

$$\frac{1}{\sqrt{3}}\left\{\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta\right\} \qquad M_s = -\frac{1}{2} \qquad S = \frac{3}{2}$$

$$\beta\beta\beta \qquad\qquad M_s = -\frac{3}{2}$$

$$\frac{1}{\sqrt{6}}\left\{2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha\right\} \qquad M_s = +\frac{1}{2}$$

$$\frac{1}{\sqrt{6}}\left\{2\beta\beta\alpha - \beta\alpha\beta - \alpha\beta\beta\right\} \qquad M_s = -\frac{1}{2} \qquad S = \frac{1}{2}$$

$$\frac{1}{\sqrt{2}}\left\{\alpha\beta\alpha - \beta\alpha\alpha\right\} \qquad M_s = +\frac{1}{2}$$

$$\frac{1}{\sqrt{2}}\left\{\beta\alpha\beta - \alpha\beta\beta\right\} \qquad M_s = -\frac{1}{2} \qquad S = \frac{1}{2}$$

We can now return to the determinantal wave functions, seeking those linear combinations of the three which are components of a doublet spin-state having $M_s = +\frac{1}{2}$. Inspection of the spin wave functions above shows that the two possible combinations are

$$\Phi_2 = \frac{1}{\sqrt{6}}\left\{2D_1 - D_2 - D_3\right\}, \quad \Phi_3 = \frac{1}{\sqrt{2}}\left\{D_2 - D_3\right\}$$

It will be noticed that Φ_3 can be thought of as a combination of the singlet state $(\sigma_B)(\sigma_A)$ with π, so that its inclusion will not lead to unpaired spin in the σ-orbitals. The desired function is, in fact, Φ_2, which does indeed give some unpaired spin in the σ-orbitals.

Hence the improved wave function for the $>\overset{\cdot}{C}H$ fragment may be written

$$\Psi = \Phi_1 + \lambda\,\Phi_2$$

where the admixture coefficient λ is best obtained by perturbation theory. The term in the Hamiltonian operator which brings about the mixing of Φ_1 and Φ_2 is that representing the electrostatic repulsion between electrons.

One very important additional result, which was made clear in section 3, emerges from the above treatment; it is that a π-electron with spin α on the carbon atom induces a little unpaired β-spin at the proton nucleus,

and for this reason the isotropic hyperfine-splitting constant is negative. Now the positions and intensities of the hyperfine lines in a solution spectrum depend only upon the magnitude of the isotropic hyperfine-splitting constant and not upon its sign. But the sign can be determined by studying the angular variation of a single-crystal spectrum and the negative sign for the $>\dot{C}H$ system has been confirmed.[8b] Nuclear magnetic resonance methods have also been used to verify this point.[47]

8.   Methyl-proton hyperfine structure and hyperconjugation

We have come across a number of examples of aromatic radicals containing substituent methyl groups[50] and noted that hyperfine structure from the methyl protons is observed. Indeed, a substituent methyl group often gives a hyperfine splitting slightly larger than that observed for a ring proton at a position of similar spin density. An excellent example is the ethyl radical $CH_3 \cdot \dot{C}H_2$, detected in electron-irradiated liquid ethane.[51] The two hydrogens on the trigonal carbon atom show a splitting of 22·5 gauss whilst the three attached to the adjacent tetrahedral carbon give a 27·1 gauss splitting.

A number of theoretical treatments of the effect have been given,[52] most of which involve the concept of hyperconjugation. It is clear that hyperconjugation would lead to an isotropic methyl-proton hyperfine structure. For, consider the molecular orbital treatment of the methyl group[53] in which the three hydrogen atoms are treated as a single group. If the three hydrogen 1s-orbitals are ϕ_1, ϕ_2, and ϕ_3, then three linear combinations of them can be formed. The first is $\phi_1 + \phi_2 + \phi_3$ which is symmetrical about an axis containing the C–CH_3 bond. The other two combinations are $\phi_1 - \frac{1}{2}(\phi_2 + \phi_3)$ and $\phi_2 - \phi_3$ which have π symmetry and can combine with suitable $2p_\pi$ atomic orbitals on the methyl carbon, one of which can combine with the aromatic π system. Thus an unpaired electron moving in an aromatic π-orbital can be delocalised directly into an "H_3 group-orbital", which is itself formed from hydrogen 1s-orbitals. This, as we have seen, is just the sort of situation which would lead to isotropic hyperfine structure in the electron-spin resonance spectrum. Moreover, theoretical estimates of the magnitude of such delocalisation are encouragingly close to what is required to explain the observed methyl splittings.

Despite this there are some unsatisfactory features of the interpretation. Hyperconjugation, as understood by the organic chemist, involves electron delocalisation from the methyl group into the ring. Such delocalisation

[50] Venkataraman, *J. Chem. Phys.*, 1955, **23**, 588.
[51] Fessenden and Schuler, *J. Chem. Phys.*, 1960, **33**, 935.
[52] (*a*) McLachlan, *Mol. Phys.*, 1958, **1**, 233; (*b*) Bersohn, *J. Chem. Phys.*, 1956, **24**, 1066; (*c*) Chesnut, *ibid.*, 1958, **29**, 43.
[53] Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Coulson and Crawford, *J.*, 1953, 2052.

appears less likely when the aromatic π system already has an extra electron, as in the negative ions. Certainly one might expect hyperconjugation to be a more important mechanism for hyperfine interactions in aromatic positive ions, and evidence in favour of this suggestion has been given.[54]

The alternative to hyperconjugation is some form of indirect spin-exchange polarisation[52a] similar to that which occurs for aromatic $>$CH protons, but the theory of such a mechanism has not yet been adequately formulated. Until this has been done, one is inclined to accept the observation of methyl hyperfine structure as evidence for hyperconjugation, but not with complete confidence. Perhaps a number of mechanisms, including that of hyperconjugation, are involved.

9.   Hyperfine structure from other nuclei

Most of our discussion so far has been concerned with proton hyperfine structure. We have referred to a number of systems in which nitrogen-14 hyperfine structure is observed, and the rules for the analysis of such structure were given in section 2. These rules, of course, apply to other nuclei having spin 1 and the deuterium nucleus is an important example. Deuterium substitution can often be used to resolve ambiguities[55,56] in the assignment of proton hyperfine splitting constants, in the following way. Suppose we have a free radical containing two types of proton, p and q, with two protons of each type. The spectrum will be determined by two hyperfine splitting constants and one might obtain the sort of pattern shown in Fig. 8(a). Now we can easily obtain the two splitting constants but we do not know whether the larger constant refers to protons p or q. The problem can be solved by replacing, say, the protons q by deuterons,
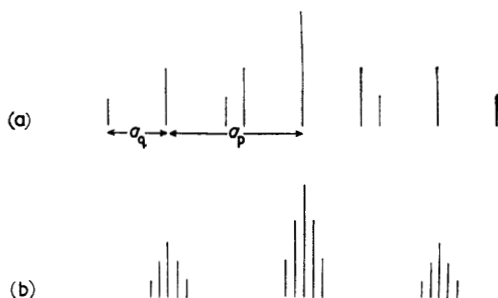
Fig. 8.   (a) *Hyperfine pattern for a radical containing two protons, with splitting* a_p, *and two protons, with splitting* a_q.

(b) *Corresponding hyperfine pattern when the q-protons are replaced by deuterons.*

[54] Bolton, Carrington, and McLachlan, *Mol. Phys.*, 1962, **5**, 31; Brivati, Hulme, and Symons, *Proc. Chem. Soc.*, 1961, 384.

[55] Venkataraman and Fraenkel, *J. Chem. Phys.*, 1956, **22**, 737.

[56] Tuttle, Ward, and Weissman, *J. Chem. Phys.*, 1956, **25**, 189; Weissman, Tuttle, and de Boer, *J. Phys. Chem.* 1957, **61**, 28.

when the pattern shown in Fig. 8b will be obtained. Two changes in the spectrum have occurred. First, the deuterium nucleus has a spin of 1 so that interaction with two equivalent deuterons gives five lines with relative intensities 1:2:3:2:1. Thus the triplet structure due to the two q protons has been replaced by a quintet structure. The second change is due to the fact that the constant Q relating the hyperfine splitting to the spin density includes, among other factors, the nuclear g factor g_I. For protons g_I is equal to 5·5855 but for deuterons it is only 0·8574. Consequently the quintet hyperfine splitting is smaller than the original proton triplet splitting by a factor of 0·8574/5·5855 $\simeq$ 2/13.

Examples of the use of isotopic substitution are to be found in the work of Tuttle, Ward, and Weissman on the naphthalene anion,[56] and Ward[23] on the 4,4′-bipyridyl anion.

It is frequently possible to observe hyperfine lines due to carbon-13, which has a natural abundance of 1·1%. The nuclear spin is $\frac{1}{2}$ so that each carbon-13 nucleus gives a doublet splitting, but these additional lines are naturally much weaker than proton hyperfine components. The spectrum of the cyclo-octatetraene anion shown in Fig. 2 shows additional weak lines due to carbon-13. Since there are eight carbon atoms in the molecule, approximately 8% of all molecules will contain one carbon-13 atom so that the spectrum consists of nine proton hyperfine lines, each of which is accompanied by two satellites twenty-five times less intense.

Carbon-13 hyperfine splitting constants have been measured in a large number of aromatic free-radicals.[58] The spectrum of the naphthalene anion in Fig. 3, for example, shows additional weak lines due to carbon-13 which have been analysed. The weak doublet satellites in the spectrum of the benzene anion[57] (Fig. 2) are also due to carbon-13. The theory of such splitting has been investigated in detail by several authors[59] and it is found theoretically, and observed experimentally, that the magnitude of the splitting depends not only on the π-spin density at the carbon atom in question but also on the densities at adjacent atoms. Karplus and Fraenkel's explanation[59] is as follows. Consider the aromatic fragment (39), where

$$\rho_1\ \underset{\rho_3 C}{\overset{C}{\diagdown}} \underset{}{\overset{\rho_2}{\diagup}} C-H$$

(39)
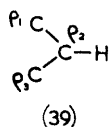
$\rho_1, \rho_2,$ and ρ_3 are the spin densities on the three carbon atoms, and examine the possibility of hyperfine splitting due to a carbon-13 nucleus at position 2. We have already seen that the C–H σ-bonding electrons are polarised by the spin density ρ_2, leaving some unpaired spin in the hydrogen 1s-

[57] Carrington and Bolton, unpublished work.
[58] Tuttle and Weissman, *J. Chem. Phys.*, 1957, **25**, 190; Strauss and Fraenkel, *ibid.*, 1961, **35**, 1738; Reitz, Dravnieks, and Wertz, *ibid.*, 1960, **33**, 1880; Weissman and Sowden, *J. Amer. Chem. Soc.*, 1953, **75**, 503.
[59] Karplus and Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

orbital which leads to proton hyperfine structure. The same effect naturally leads to unpaired spin in the carbon sp^2 hybrid orbital, so that one contribution to isotropic carbon hyperfine structure is immediately apparent. However, it is also possible for the unpaired spin on atoms 1, 2, and 3 to polarise the C–C σ-bonding electrons, and even for the spin density ρ_2 to polarise the $1s$-electrons of carbon atom 2. All of these contributions are significant, but they are not necessarily of the same sign, so that some cancellation usually occurs. In consequence each example must be examined separately, and in cases where this has been done[60] the agreement between experiment and theory is remarkably good.

In view of these results for carbon-13 splittings, one might also expect to find nitrogen-14 splittings in nitrogen heterocyclic anions to be sensitive to spin densities on adjacent atoms. This does not seem to be the case however. One can calculate the unpaired-electron distribution by using molecular-orbital theory, with a Coulomb parameter for nitrogen adjusted to give the best agreement between theoretical and experimental ring-proton splittings. The nitrogen splitting then seems to be proportional to the calculated unpaired-electron density on the nitrogen.[60] Theoretical estimates[61] of the contributions to the splitting from spin densities on adjacent atoms indicate that they should be small. The situation is complicated, however, and more experimental and theoretical work is desirable.

10.   Line widths and shapes

In any observation of an electron-spin resonance line there are three main features of interest. Usually one is concerned with its position and intensity relative to other lines in the spectrum and everything that has been discussed, so far, relates to these details. However, one should also be interested in the shape and width of the line. There is often important information concealed in these features, sometimes relevant to the interests of the chemist.

The shape of the resonance lines from a free radical in solution depends upon a number of factors which we shall discuss, but it usually approximates to either Lorentzian or Gaussian. In Fig. 9 we show these line shapes
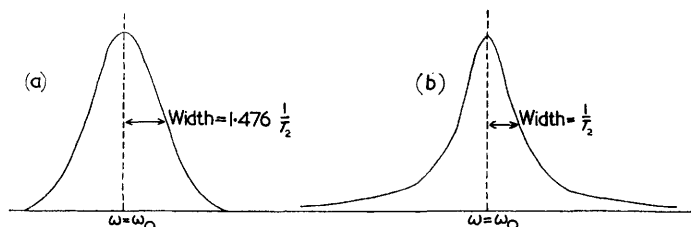

FIG. 9.   (a) *Gaussian line shape.*
            (b) *Lorentzian line shape.*

[60] Carrington and Veiga, *Mol. Phys.*, 1962, **5**, 285.
[61] Veiga, unpublished results.

as plots of absorption intensity $[g(\omega-\omega_0)]$ against frequency (ω). The equations for the line shapes are,

Lorentzian: $g(\omega-\omega_0) = \dfrac{T_2}{1 + (\omega-\omega_0)^2 T_2{}^2}$, width at half-height $= 1/T_2$

Gaussian: $g(\omega-\omega_0) = \dfrac{T_2}{\pi}.e^{-(\omega-\omega_0)^2 T_2{}^2/\pi}$

width at half-height $= (\pi \log_e 2)^{\frac{1}{2}}/T_2$

T_2, which has the dimensions of a time, is called the line-width parameter and is the quantity which we can determine experimentally from the width at half-height.

We must therefore enquire about the factors which contribute to $1/T_2$, and as we shall see, these can be divided into two categories. To anticipate our further discussion slightly, use is made of the approximate relationship[62]

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{1}{T_2'}.$$

T_1 is called the electron spin-lattice relaxation time, whilst T_2' is the transverse relaxation time. Various processes occurring in solutions can contribute to either T_1 or T_2', or both. The nature of these processes is our present concern and we will deal first with spin-lattice relaxation.

Suppose we have a solution of free radicals surrounded by an external magnetic field. At any given instant some of the unpaired electrons will have α-spin and some β-spin but, even in the absence of an applied microwave field, a particular electron will not remain in one spin orientation for very long. There are a number of factors which can cause the electron spin to change quite rapidly and this process is known as relaxation. Obviously when we attempt to measure an electron-spin resonance absorption line, what we observe will be in some way determined by this relaxation.

The problem can be formulated quantitatively with the aid of some quite simple mathematics.[63] We consider an assembly of unpaired electrons, each of which can exist in one of two spin states (α or β). In the absence of any applied field the populations of the two states are equal, since they are of equal energy. We now apply a steady magnetic field so that the energies of the states are no longer equal. Their populations will now be different and we must enquire as to how long it takes for the new populations to reach their equilibrium values.

[62] Bloembergen, Purcell, and Pound, *Phys. Rev.*, 1948, **73**, 679.
[63] Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959.

Let n_α and n_β be the number of electrons per unit volume in the α and the β state respectively. We want to determine the difference in populations $n = n_\beta - n_\alpha$, as a function of time.

Suppose that $W_{\beta\alpha}$ and $W_{\alpha\beta}$ are the probabilities per unit time of
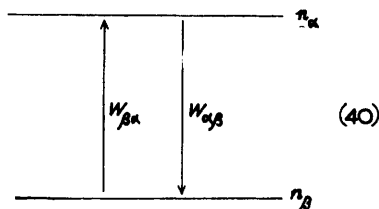
upward and downward transitions respectively (40). At equilibrium the total number of upward and downward transitions must be equal so that

$$n_\alpha W_{\alpha\beta} = n_\beta W_{\beta\alpha} \tag{1}$$

Since, because of the Boltzmann factor, n_β is slightly greater than n_α, an upward transition decreases the difference n by 2 whilst a downward transition increases n by 2. Hence

$$\mathrm{d}n/\mathrm{d}t = -2n_\beta W_{\beta\alpha} + 2n_\alpha W_{\alpha\beta} \tag{2}$$

If we now write the mean of $W_{\beta\alpha}$ and $W_{\alpha\beta}$ as W, equation (2) becomes

$$\mathrm{d}n/\mathrm{d}t = -2W(n - n_{\mathrm{eq}}) \tag{3}$$

where n_{eq} is the equilibrium value of the excess number n. We now define a time T_1 equal to $1/2W$, and therefore the solution of equation (3) may be written

$$n - n_{\mathrm{eq}} = (n - n_{\mathrm{eq}})_0 e^{t/T_1}$$

Hence the difference between the initial excess population and its equilibrium value is reduced by a factor e after time T_1. The spin-lattice relaxation time T_1 is thus a measure of the rate at which the spin system approaches thermal equilibrium.

When a microwave field is applied to the system it induces upward and downward transitions with equal probability and we observe a resonance absorption line only because n_β is greater than n_α. The microwave field forces the spin system to approach a situation in which the levels are more-equally populated and this is only counterbalanced by the spin-lattice relaxation. Even so, spin-lattice relaxation times in aromatic free radicals are rather long so that it is not difficult to equalise the populations of the levels by using high microwave powers. Under these conditions the absorption signal decreases eventually to zero and the spectrum is said to be "saturated". Usually one tries to avoid this situation.

As we have seen, processes which induce transitions between the two levels contribute to T_1. However there are other effects occurring in

solution which actually change the energies of the levels so that the energy separation between them varies with time. In other words, the horizontal lines in our simple two-level energy diagram (40) represent *average* energies. Obviously, fluctuations in the positions of the levels will affect the width of our resonance line and such contributions to the width are characterised by T_2'.

We will not go into the details of the processes which can contribute to T_1 and T_2' but merely list some of those which are important for organic free radicals in solution, as follows:

(i) the interactions between the spins of electrons on different molecules (contributing to both T_1 and T_2'),

(ii) electron exchange (discussed later),

(iii) spin-orbit coupling (contributing to T_1 and apparently important in ions with degenerate ground states,[64] *e.g.* the benzene anion),

(iv) nuclear hyperfine and *g*-value anisotropy (affecting T_1 and T_2').[65]

Before leaving this part of the subject it should be pointed out that, in general, one is concerned with transitions between levels which arise from the interaction of the unpaired electron with magnetic nuclei. Thus processes which affect either the electron-spin or the nuclear-spin levels, or both, will contribute to the observed line widths.

Finally we discuss certain rate processes which can have extremely specific effects on the shape of the electron-spin resonance spectrum. These include inter- and intra-molecular electron transfer and rotational isomerisation. One of the first applications of electron-spin resonance spectroscopy to the study of rate processes arose from the observations of Ward and Weissman[66] that the resolution of the spectrum of the naphthalene anion deteriorates in the presence of excess of naphthalene. The reason is that the electron-transfer reaction $N + N^- \rightleftharpoons N^- + N$, is quite rapid at ordinary temperatures. When the time spent by the electron on one molecule becomes comparable with the inverse frequency separation between the hyperfine components (approximately 10^{-7} sec.), the hyperfine lines are broadened, and as the rate of electron transfer increases still further all hyperfine structure is lost and finally a single "exchange-narrowed" line is obtained. It follows that if one knows the hyperfine splitting (in Mc./sec.) the rate of electron transfer can be estimated from the line widths, and Ward and Weissman[66] were indeed able to estimate the bimolecular rate constant for the above reaction. In the case of intramolecular electron transfer the situation is rather different and is

[64] Townsend and Weissman, *J. Chem. Phys.*, 1960, **32**, 309; McConnell, *ibid.*, 1961, **34**, 13; McConnell and McLachlan, *ibid.*, 1961, **34**, 1; Hobey and McLachlan, *ibid.*, 1960, **33**, 1695.

[65] McConnell, *J. Chem. Phys.*, 1956, **25**, 709; Kivelson, *ibid.*, 1960, **33**, 1094; Stephen and Fraenkel, *ibid.*, 1960, **32**, 1435; Carrington and Longuet-Higgins, *Mol. Phys.*, 1962, **5**, 447.
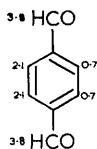
[66] Ward and Weissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3612.

nicely illustrated by the work of Weissman[67] on the paracyclophane (41) anions.
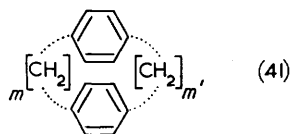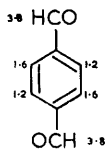

When m or $m' \leq 2$ the electron jumps rapidly from one benzene ring to the other and nine lines of spacing 2·7 gauss are observed, corresponding to hyperfine interaction with the eight ring-protons. However when m or $m' \geq 3$ the rate of electron transfer is slow and the spectrum consists of five lines with spacing 5·5 gauss, due to interaction with the four protons of one ring only. Note that in the slow transfer system the hyperfine splitting is twice as large as when the electron transfer is rapid, as it should be. From these experiments it is possible to assign upper and lower limits to the rate of electron transfer. A molecule in which the hyperfine splitting and the electron-transfer rate were comparable would show anomalous line-width effects, probably temperature-dependent, and in these circumstances it is possible to determine the rate quite accurately.

Rather similar theoretical considerations are involved in the study of rotational isomerisation. The first relevant observations were made by Maki[68] who noted that the spectrum of the terephthalaldehyde anion consists of a superposition of the spectra of both the *cis-* and the *trans-*isomer. The hyperfine-splitting constants can be assigned as shown in (42) and (43).

Our interest is centred on the ring-proton splittings and we will ignore the additional aldehyde-proton triplet-splitting, which does not vary from one isomer to the other. So far as the rate of isomerisation is concerned, there are three cases to consider. When the rate is slow compared with the hyperfine splitting (*i.e.* $< 6 \times 10^6$ sec.$^{-1}$) the experimental pattern should consist of a superposition of the spectra of both isomers, as observed. When the rate is fast, a simple quintet hyperfine pattern would be observed, with a splitting of 1·4 gauss, the average of the extreme ring-proton splittings. However, when the rate is comparable with the hyperfine

[67] Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 6462.
[68] Maki, *J. Chem. Phys.*, 1961, **35**, 761.

splittings, a complex pattern of lines with varying widths will be observed.[69] These effects are found in the spectra of the durosemiquinone cation[70] and the naphthazarin semiquinone cation.[71] In the latter case the temperature-dependence of the shape of the spectrum has been measured and the potential barrier to rotation derived.[71]

[69] Carrington, *Mol. Phys.*, 1962, **5**, 425.
[70] Bolton and Carrington, *Mol. Phys.*, 1962, **5**, 161.
[71] Bolton, Carrington, and Todd, *Mol. Phys.*, 1963, to be published.