Electron Spin Resonance Studies of the Triplet State

By Colin Thomson
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ST ANDREWS,
ST ANDREWS, FIFE, SCOTLAND

1 Introduction

Electron spin resonance (e.s.r.) spectroscopy has proved to be of immense value to the Chemist in the study of the electronic structure and properties of transition-metal ions[1] and free radicals,[2] and one might expect this technique also to be of use in the study of the ground or excited triplet states of molecules. Owing, however, to experimental difficulties, it was 1958 before Hutchison and Mangum[3] first detected the naphthalene triplet state by e.s.r., but since that time it has become apparent that e.s.r. can yield very detailed information concerning the electronic structure of the triplet state: information which supplements that obtained by conventional spectroscopic techniques.

The experimental study of photoexcited triplet states by optical means has been thoroughly reviewed,[4] and the present Review is concerned with the study of organic triplet states by e.s.r.

Of more recent origin is the study of molecules with a triplet ground state. Such states have considerable importance in organic chemistry and e.s.r. is a valuable tool in their study. The electronic spin interactions within the triplet state are examples of 'weak interactions'[5] and their measurement and theoretical calculation constitute sensitive tests of approximate molecular wave functions.

2 The Phosphorescence of Aromatic Molecules

Many aromatic molecules dissolved in rigid glassy solvents at low temperatures exhibit phosphorescence upon irradiation with ultraviolet light.[4] The lifetime τ_P varies from a few milliseconds to *ca.* 30 sec., and this phenomenon was attributed by Lewis and Kasha[6] to the radiative decay from the lowest excited triplet state of the molecule (T) to the ground state S_0. The triplet state is populated *via* a radiationless transition from the lowest excited singlet state S_1, into which the molecule reverts following the initial excitation. The situation is summarised in Figure 1.

The triplet state is paramagnetic, as Lewis, Calvin and Kasha showed by susceptibility measurements,[7] and should therefore be detectable by e.s.r. After considerable effort, Hutchison and Mangum[3] succeeded in observing the naphtha-

---

[1] A. Carrington and H. C. Longuet-Higgins, *Quart. Rev.*, 1960, **14**, 427.
[2] A. Carrington, *Quart. Rev.*, 1963, 17, 67; J. R. Morton, *Chem. Rev.*, 1964, **64**. 453.
[3] C. A. Hutchison, jun., and B. W. Mangum, *J. Chem. Phys.*, 1958, **29**, 952; 1961, **34**, 908.
[4] S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 1966, **66**, 199.
[5] M. Karplus, *Rev. Mod. Phys.*, 1960, **32**, 455.
[6] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[7] G. N. Lewis, M. Calvin, and M. Kasha, *J. Chem. Phys*, 1949, **17**, 804.

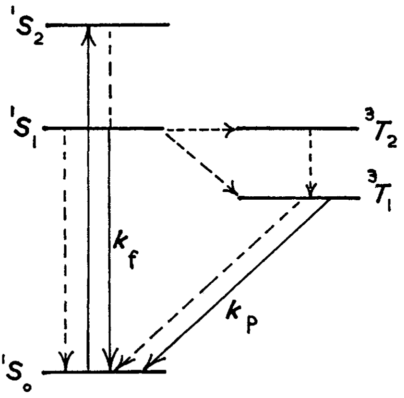


Figure 1 *Excitation and decay of aromatic triplet states. Dashed lines denote non-radiative processes. Transitions denoted* k_f *and* k_p *are the radiative fluorescence and phosphorescence transitions with typical lifetimes of* ca. 10^{-8} *sec. and several seconds respectively*

lene triplet in 1958. The interpretation of the e.s.r. observations necessitates an understanding of the quantum mechanical description of the magnetic interactions between the two unpaired electrons and an external magnetic field to which we now turn.

3 Quantum Mechanical Description of the Triplet State

The triplet-state wave function and energy levels are the eigenfunctions and eigenvalues of the total molecular Hamiltonian operator $\mathscr{H}$, which can be written as a sum of a spin-independent part $\mathscr{H}_0$ and a spin-dependent part $\mathscr{H}_s$.

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_s \tag{1}$$

The usual electronic problem of quantum chemistry is that of finding those wave functions $\psi_{k,s,m}$ which are simultaneously eigenfunctions of $\mathscr{H}_0$ and of the total spin operator $\hat{S}^2$ and its component $\hat{S}_z$.

$$\begin{aligned} \mathscr{H}_0\Psi_{k,s,m} &= E_k\Psi_{k,s,m} \\ \hat{S}^2\Psi_{k,s,m} &= S(S+1)\hbar^2\Psi_{k,s,m} \\ \hat{S}_z\Psi_{k,s,m} &= m_z\hbar\Psi_{k,s,m} \end{aligned} \tag{2}$$

For a triplet state, $S = S_1 + S_2 = 1$, and m_z can take the values $-1,0,1$.

In phenomena involving the interaction of the electron and nuclear spins with external electromagnetic fields, $\mathscr{H}_s$ has to be included with the results that the eigenfunctions $\psi_{k,s,m}$ are no longer eigenfunctions of $\mathscr{H}$. $\mathscr{H}_s$ causes mixing between singlets and triplet states and lifts the triplet spin degeneracy, and the eigenvalues and eigenfunctions must be found by diagonalisation of the matrix of $\mathscr{H}$ using the $\psi_{k,s,m}$ as basis functions.

$\mathscr{H}_s$ is a sum of two parts, the spin–orbit interaction $\mathscr{H}_{so}$ and the dipolar spin–spin interaction $\mathscr{H}_{ss}$. These interactions have the explicit form[8]

---

[8] H. F. Hameka, 'Advanced Quantum Chemistry', Addison-Wesley, New York, 1965.

$$\mathcal{H}_{so} = \sum_i (\hat{S}_i \,.\, \vec{A}_i) \tag{3}$$

where

$$\vec{A}_i = \frac{e}{mc}\left\{\vec{H}_i + \frac{1}{2mc}\,[\vec{F}_i \times \vec{P}_i] + \frac{e}{mc}\sum_{j \neq i} \frac{(\vec{P}_j - \frac{1}{2}\vec{P}_i) \times \vec{r}_{ij}}{r_{ij}^3}\right\} \tag{4}$$

and

$$\mathcal{H}_{ss} = \frac{e^2}{2m^2c^2} \sum_i \sum_{j \neq i} \left\{\frac{\hat{S}_i \,.\, \hat{S}_j}{r_{ij}^3} - \frac{3(\vec{r}_j \,.\, \hat{S}_j)\,(\vec{r}_i \,.\, \hat{S}_i)}{r_{ij}^5}\right\} \tag{5}$$

In these equations, the summation is over all the electrons, $\vec{H}_i$ and $\vec{F}_i$ are the magnetic and electric field strengths at the position of electron i, due both to external fields and to the nuclei, and the other symbols have their usual meaning. Since $\mathcal{H}_s \ll \mathcal{H}_0$ the effect of $\mathcal{H}_s$ on the zeroth-order eigenfunctions and energies $\psi_{k,s,m}$ and E_k can be found by perturbation theory if the zeroth order functions $\psi_{k,s,m}$ are known.

In the triplet state, the eigenfunctions of $\mathcal{H}_0$, ${}^3\psi_{k,s,m}$, can be written as products of a spatial part and the appropriate spin function. The spin functions for a single electron are α and β and are eigenfunctions of $\hat{S}_z$ with eigenvalues m_z of $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ respectively, and of $\hat{S}^2$ with eigenvalue $S(S+1)\hbar^2 = \frac{3}{4}\hbar^2$.

In the case of two unpaired electrons coupled to give $S = 1$, the appropriate spin functions are

$$\begin{aligned} {}^3\zeta_1 &= \alpha(1)\,\alpha(2) &&\equiv |\,1\rangle \\ {}^3\zeta_0 &= \frac{1}{\sqrt{2}}\left\{\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)\right\} &&\equiv |\,0\rangle \\ {}^3\zeta_{-1} &= \beta(1)\,\beta(2) &&\equiv |\,-1\rangle \end{aligned} \tag{6}$$

where we have written the value of $2S + 1$ as superscript and the m_z value as subscript. The usual Dirac notation for these states is given on the right-hand side. The three triplet functions with a common spatial part combined with the above spin functions are degenerate in the absence of $\mathcal{H}_s$, and correspond to pure spin states. Since the Pauli principle states that the total wave function must be antisymmetric, the above symmetric spin functions must be multiplied by an *antisymmetric* spatial part.

The perturbation $\mathcal{H}_{so}$ causes a mixing between singlet and triplet states and therefore a relaxation of the selection rules for $T \rightarrow S_0$ and $S_1 \rightarrow T$ transitions.[4] $\mathcal{H}_{ss}$ on the other hand does not mix singlets and triplets, but both $\mathcal{H}_{so}$ and $\mathcal{H}_{ss}$ lift the degeneracy of the triplet state. From the point of view of e.s.r., $\mathcal{H}_{ss}$ is the most important perturbation* and we henceforth discuss this term alone, referring to the small effects of $\mathcal{H}_{so}$ in Section 15C. Although singlets and triplets are mixed by $\mathcal{H}_s$ it is meaningful to describe the states as predominantly singlet or triplet.

---

*This is true for organic triplet states, but in other systems such as transition-metal ions, spin–orbit effects can be comparable with or greater than spin–spin effects.

4 The Effect of an External Magnetic Field

For an atom with spherical symmetry, a magnetic field lifts the triplet degeneracy so that the possible energy levels in the absence of $\mathscr{H}_{ss}$ and $\mathscr{H}_{so}$ are the eigenfunctions and eigenvalues of

$$\mathscr{H} = g\beta\hat{S}_z\vec{H}_z \tag{7}$$

as in the free-radical case but where $\hat{S}_z$ can have eigenvalues 0, ± 1, *i.e.*,

$$E_1 = g\beta H_z \quad E_0 = 0 \quad E_{-1} = -g\beta H_z \tag{8}$$

Transitions between the triplet sub-levels are subject to the selection rule $\triangle m_z = 1$, and occur at values of the magnetic field H_z which satisfied the resonance condition

$$h\nu = g\beta\vec{H}_z \tag{9}$$

where ν is the microwave frequency. Therefore resonance occurs at the same field value as for free radicals. The transition corresponding to $\triangle m_z = 2$ is strictly forbidden because of the high symmetry. However, in the case of molecules when $\mathscr{H}_{ss}$ is included, the reduced symmetry results in quite a different splitting which we shall examine in detail in Section 6.

5 Semi-classical Picture of Spin–Spin Interaction[9]

The two unpaired electrons with spin $S = \frac{1}{2}$, each have magnetic moment $\vec{\mu} = g\beta\hat{S}$ and the interaction $\mathscr{H}_{ss}$ is equivalent to the classical interaction between two magnetic moments μ_1 and μ_2, with interaction energy,

$$E_{ss} = \mu_1\mu_2 \left\langle \frac{1 - 3\cos^2\phi}{r_{12}^3} \right\rangle \tag{10}$$

r_{12} is the distance between the magnetic moments and ϕ is the angle between the direction of the magnetic moments and the vector $\vec{r}_{12}$. The angular brackets denote an average over the distribution of the two electrons. For an atom, $<\cos^2\phi> = \frac{1}{3}$ and therefore $E_{ss} = 0$ and the triplet degeneracy remains.

In the molecular case we no longer have spherical symmetry, but only one or more symmetry axes. In the absence of an external field, the interaction energy between the spins will be different in different directions: the spin will be coupled to the molecular framework, and this is equivalent to quantisation of the spin along the molecular axes due to a local magnetic field within the molecule. This field is of the order of 2000 gauss and the energy levels of the system are then determined by this molecular field.

In planar aromatic molecules, the z-axis perpendicular to the aromatic plane is always a symmetry axis, and may be a three- or six-fold symmetry axis in molecules like coronene. In this case the x and y axes are equivalent and quantisation of spins can occur along the z-axis or in the x–y plane. The former situation will be doubly degenerate since the situations with $m_z = \pm 1$ will be physically

---

[9] J. H. van der Waals and M. S. de Groot, *J. Chim. phys.*, 1964, 1643.

indistinguishable but quantisation in the plane (corresponding to $m_z = 0$) will have a different energy. In this case the spin–spin interaction will result in one doubly degenerate level and one single level (Figure 2*a*).

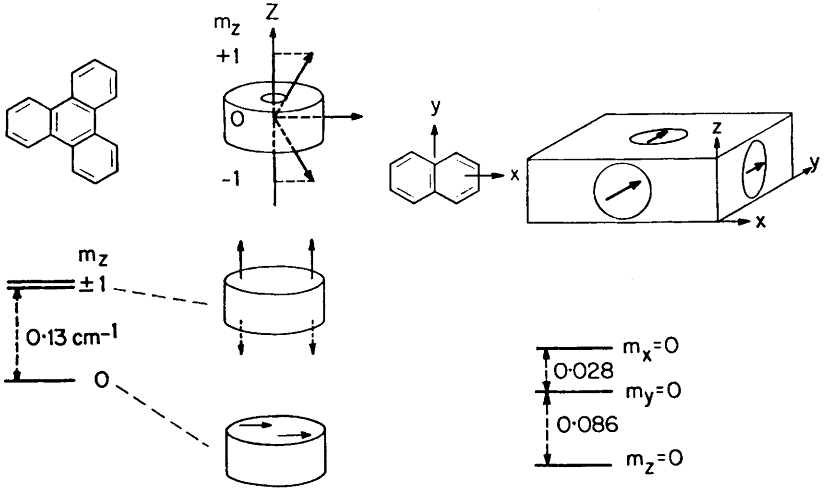


Figure 2 *Zero-field splitting of the triplet spin sub-levels by dipolar interaction*
(*a*) Triphenylene (*b*) Naphthalene

[Reproduced, with permission, from J. H. van der Waals and M. S. de Groot, *J. Chim. phys.*, 1964, 1643]

In molecules of lower symmetry, one can show that the triplet degeneracy is lifted completely and there are three levels even in zero-field corresponding to quantisation of the spin along one of the three symmetry axes of the molecule (Figure 2*b*).[9] One might expect that the e.s.r. signal will give information concerning the symmetry of the triplet state. If an external magnetic field H_0 is applied which is small compared with $\mathscr{H}_{ss}$, the spins will still be predominantly coupled to the molecular axes, but if H_0 is very large, the spins will be quantised along H_0. In the usual e.s.r. experiment, $H_0 = ca.$ 3000 G and is thus a competition between the molecular axes and the external field for the spin quantisation. The result is that the triplet energy levels are strongly dependent on the angle between H_0 and the molecular symmetry axes.[3,9,10]

For an assembly of randomly oriented molecules, there will be a wide range of possible energy levels and the resonance fields will occur over several hundred gauss for transitions at constant microwave frequency. Thus the resonance will be highly *anisotropic* and the resulting broad lines difficult to detect. This fact was responsible for the earlier failures in the search for triplet state e.s.r. signals.

---

[10] C. A. Hutchison, jun., *Rec. Chem. Progr.*, 1963, **24**, 105.

6 Quantum Mechanical Treatment of Triplet State Energy Levels in the Presence of H_0 and $\mathcal{H}_{ss}$

In the presence of $\mathcal{H}_{ss}$ and an external field the Hamiltonian becomes[10]

$$\mathcal{H} = \beta \vec{H}_0 \cdot g \cdot \hat{S} + \mathcal{H}_{ss} = \beta \vec{H}_0 \cdot g \cdot \hat{S} + \hat{S} \cdot \mathcal{T} \cdot \hat{S} \tag{11}$$

where, since $\hat{S}$ and H_0 are vectors, the interaction may be written in tensor form and g and $\mathcal{T}$ are the g and spin–spin interaction tensors. However, the tensors can always be transformed to an axis system in which they are diagonal. Furthermore, the g-tensor is usually nearly isotropic and in this case, and henceforth, we denote its isotropic value by g and the diagonal elements of the tensor by T_{ii}, in which case

$$\mathcal{H} = g\beta \vec{H}_0 \cdot \hat{S} + T_{xx}\hat{S}_x^2 + T_{yy}\hat{S}_y^2 + T_{zz}\hat{S}_z^2 \tag{12}$$

and the terms $g\beta\hat{S} \cdot \vec{H}_0$ and $\mathcal{H}_{ss}$ are comparable in magnitude.

The zero-field splitting of the levels is due to $\mathcal{H}_{ss}$ and the splitting depends on the orientation of the spins and on their spatial distribution. The zero-field energy levels and wavefunctions are found by diagonalisation of the matrix of $\mathcal{H}_{ss}$ with respect to the zeroth order basis functions ${}^3\zeta_0$, ${}^3\zeta \pm 1$.

It is convenient to rearrange $\mathcal{H}_{ss}$ so that spatial and spin parts are separated. This is a straightforward expansion and if the axes are chosen so as to diagonalise the tensor $\mathcal{T}$, one can show that[11]

$$\mathcal{H}_{ss} = -g^2\beta^2 \sum_{j>i} \left\{ \frac{3}{2} \frac{(x_{ij}^2 - y_{ij}^2)}{r_{ij}^5} (\hat{S}_{ix}\hat{S}_{jx} - \hat{S}_{iy}\hat{S}_{jy}) + \frac{1}{2} \frac{(3z_{ij}^2 - r_{ij}^2)}{r_{ij}^5} (3\hat{S}_{iz}\hat{S}_{jz} - \hat{S}_i \cdot \hat{S}_j) \right\} \tag{13}$$

Since the total wave function is written as a product, the principal values of the tensor in the situation where $\mathcal{H}_{ss}$ is diagonalised will involve integrals of the antisymmetric spatial part of the wave function with the above co-ordinate operators. Van Vleck and McLachlan[12] have shown that the matrix elements of $\mathcal{H}_{ss}$ are equivalent to those of the spin Hamiltonian operator

$$\mathcal{H}_s = D(\hat{S}_z^2 - \tfrac{1}{3}\hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{14}$$

where $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ are the components of the total spin $\hat{S} = \hat{S}_1 + \hat{S}_2$. This form is the most useful for describing experimental results since these are the result of transitions between spin levels and the separations between these levels enables one to measure the zero-field splitting (Z.F.S.) parameters D and E.[9,10]

The zero-field splitting of the levels is easily found by use of eqn. (14) with $H_0 = 0$. In molecules with a three- or six-fold symmetry axis, $E = 0$ and the eigenvalues of $\mathcal{H} = D(\hat{S}_z^2 - \tfrac{1}{3}\hat{S}^2)$ are

$$E_{1,\pm 1} = \tfrac{1}{3}D;\ E_{1,0} = -\tfrac{2}{3}D \tag{15}$$

---

[11] S. A. Boorstein and M. Gouterman, *J. Chem. Phys.*, 1963, **39**, 2443.

[12] J. H. van Vleck, *Rev. Mod. Phys.*, 1951, **23**, 213; A. D. McLachlan, *Mol. Phys.*, 1963, **6**, 441.

in agreement with the semi-classical picture of Section 5. For $E \neq 0$, there are off-diagonal elements of $\mathscr{H}_s$ between the basis functions $|1>$, $|0>$, and $|-1>$, and the 3×3 matrix is then (16) and there are three non-degenerate levels with

$$\begin{bmatrix} \frac{1}{3}D & O & E \\ O & -\frac{2}{3}D & O \\ E & O & \frac{1}{3}D \end{bmatrix} \tag{16}$$

$$E_1 = \tfrac{1}{3}D + E,\ E_2 = \tfrac{1}{3}D - E,\ E_3 = -\tfrac{2}{3}D \tag{17}$$

This splitting is illustrated in Figure 2*b*. The effect of an external field $\vec{H}_0$ is shown in Figure 3 for the case of $\vec{H}_0$ along two of the three principal axes of the naphthalene molecule. For $\vec{H}_0$ parallel to the $\vec{y}$-axis, the energy-level diagram is shown in heavy lines in Figure 3, and for H_0 parallel to z the energy levels are denoted by the light lines.[10] This behaviour is predicted from the above spin Hamiltonian and this accurately describes the experimental results in single crystals. In the limit of very strong fields the wave functions of the states are the pure spin functions but at 3000 G the $|1>$ and $|-1>$ states are strongly mixed.

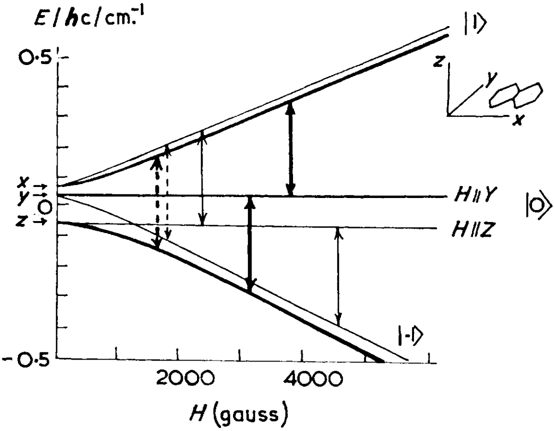


Figure 3 *Energies of the triplet state sub-levels of naphthalene as a function of the external field H_0*
Heavy lines: $\vec{H}_0$ parallel to y-axis
Light lines: $\vec{H}_0$ parallel to z-axis
Arrows correspond to e.s.r. transitions with $\nu = 9650$ Mc./sec.

The quantum of radiofrequency energy is indicated in the diagram and it is clear that for $\triangle m_z = 1$ transitions (the high field region) one obtains two possible transitions at very different resonance fields, and these fields are different for each of the three orientations above. Thus the e.s.r. spectrum is highly anisotropic and the exact field strengths depend critically on the angle between H_0 and the molecular axes.

However, in the molecular case van der Waals and de Groot[13] have shown that there is a finite probability for observing $\triangle m_z = 2$ (low field) transitions, with an intensity of *ca.* 1 to 2% of the $\triangle m_z = 1$ transitions, and these transitions are much more isotropic than the high-field transitions, as is clear from Figure 3.

7 E.S.R. Spectra in Randomly Oriented Samples

For glassy samples where the triplets are randomly oriented, each triplet state has its molecular axis system at different angles θ, ϕ to the direction of $\overline{H}_0$ (z-direction in the laboratory frame; Figure 4). The energy levels are determined by θ and ϕ and are obtained by expanding the expression for $g\beta\hat{S} \,.\, \overrightarrow{H}$ and diagonalising $\mathscr{H} = g\beta\hat{S}.\overrightarrow{H} + \mathscr{H}_{ss}$ with the triplet basis functions. The general analysis by Kottis and Lefebvre, following earlier work by van der Waals, can be summarised as follows.[13,14]

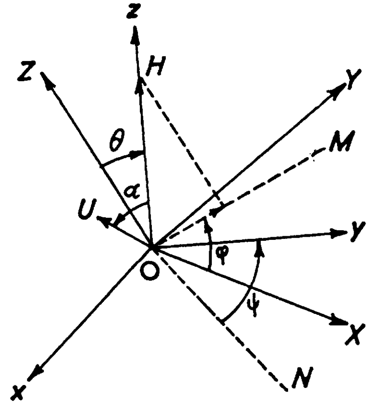


Figure 4 *Reference systems,* Oxyz *in the laboratory,* 0XYZ *in the molecule.* ON *is the intersection between the* xOy *and* XOY *planes,* OM *the projection of* Oz *in the* XOY *plane.* U *is a unitary vector in the* xOz *plane, along the direction of the oscillating field,* H *is the static magnetic field,* α *the angle between the two fields*
[Reproduced, with permission, from P. Kottis and R. Lefebvre, *J. Chem. Phys.*, 1963, **39**, 393]

If we use the basis functions (these are more convenient for reasons of symmetry):

$$\begin{aligned} T_x &= 2^{-\frac{1}{2}} \,\{\beta(1)\,\beta(2) - \alpha(1)\,\alpha(2)\} \\ T_y &= 2i^{-\frac{1}{2}} \{\beta(1)\,\beta(2) + \alpha(1)\,\alpha(2)\} \\ T_z &= 2^{-\frac{1}{2}} \,\{\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)\} \end{aligned} \tag{18}$$

and rewrite

$$\mathscr{H} = g\beta\hat{S} \,.\, \overrightarrow{H}_0 - \{X\hat{S}_x^2 + Y\hat{S}_y^2 + Z\hat{S}_z^2\} \tag{19}$$

---

[13] J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, 1959, **2**, 333; 1960, **3**, 190.
[14] Ph. Kottis and R. Lefebvre, *J. Chem. Phys.*, 1963, **39**, 393; 1964, **41**, 379.

where X, Y, and Z are the principal values of the coupling tensor, then

$$X = \tfrac{1}{3}D + E\,;\; Y = \tfrac{1}{3}D - E;\; Z = -\tfrac{2}{3}D \qquad X + Y + Z = 0 \tag{20}$$

In this case, the energy levels are the solutions of the cubic equation

$$E^3 - E[(g\beta H_0)^2 - (XY + XZ + YZ)] + (g\beta H_0)^2\,[X\sin^2\theta\cos^2\phi + Y\sin^2\theta\sin^2\phi + Z\cos^2\theta] - XYZ = 0 \tag{21}$$

The condition for resonance is that two of the roots be separated by $\delta = h\nu$ and this condition is

$$X\sin^2\theta + Y\sin^2\theta\sin^2\phi + Z\cos^2\theta = XYZ(g\beta H_0)^{-2} \mp 3^{-\frac{3}{2}}\,[(g\beta H_0)^{-2}(\delta^2 + XY + XZ + YZ) - 1]\,[(4g\beta H_0)^2 - \delta^2 - 4(XY + XZ + YZ)]^{\frac{1}{2}} \tag{22}$$

which can be written

$$f(\theta, \phi) = F(H_0, \delta) \tag{23}$$

For a given molecule, the solution can be illustrated graphically, and is given in Figure 5, for the case of naphthalene[3] which has values of $X = 0{\cdot}0197$ cm.$^{-1}$, $Y = 0{\cdot}0471$ cm.$^{-1}$, $Z = -0{\cdot}0669$ cm.$^{-1}$, $g = 2{\cdot}0030$. The function $F(H_0, \delta)$ is plotted with these values and if a line parallel to the H_0 axis is drawn at an ordinate equal to the value of $f(\theta, \phi)$, the abscissae give the allowed resonance fields.

It is clear that the observed behaviour is predicted by the construction. There are in general three resonance fields for every θ, ϕ; two at high field ($\triangle m_z = 1$) and one at low field ($\triangle m_z = 2$) and the low-field one is very much less anisotropic.

The largest value of $f(\theta, \phi)$ is Z and thus the largest resonance field possible in the low-field region occurs at $H_z{}^1 = 1648$ for $C_{10}H_8$, whereas the minimum field H_m occurs when $F(H_0, \delta)$ ceases to be real, *i.e.*,

$$\begin{aligned} H_m &= (2g\beta)^{-1}\,[\delta^2 + 4(XY + XZ + YZ)]^{\frac{1}{2}} \\ &= (2g\beta)^{-1}\,[\delta^2 - 4[D^2/_3 + E^2]\,]^{\frac{1}{2}} \end{aligned} \tag{24}$$

For $C_{10}H_8$, the low-field anisotropy is *ca.* 121 G and a peak can be seen at this value in random samples. The largest signals occur when the resonance field is stationary, *i.e.*, $\mathrm{d}H_0 = 0$ where

$$\mathrm{d}H_0 = \frac{\mathrm{d}f}{F'(H_0, \delta)} \tag{25}$$

and this occurs (1) when $F'(H_0, \delta) \rightarrow \infty$ which is the case for $H_0 = H_m$, and (2) when $\mathrm{d}f = 0$ which is the case for H_0 along one of the three principal axes of the molecule. These are the CANONICAL ORIENTATIONS and for these values there are again three possible fields which we label $H_x{}^1 H_y{}^1 H_z{}^1$ in the $\triangle m_z = 2$ region, and $H_x{}^2 H_y{}^2 H_z{}^2$, and $H_x{}^3 H_y{}^3\, H_z{}^3$ in the $\triangle m_z = 1$ region.

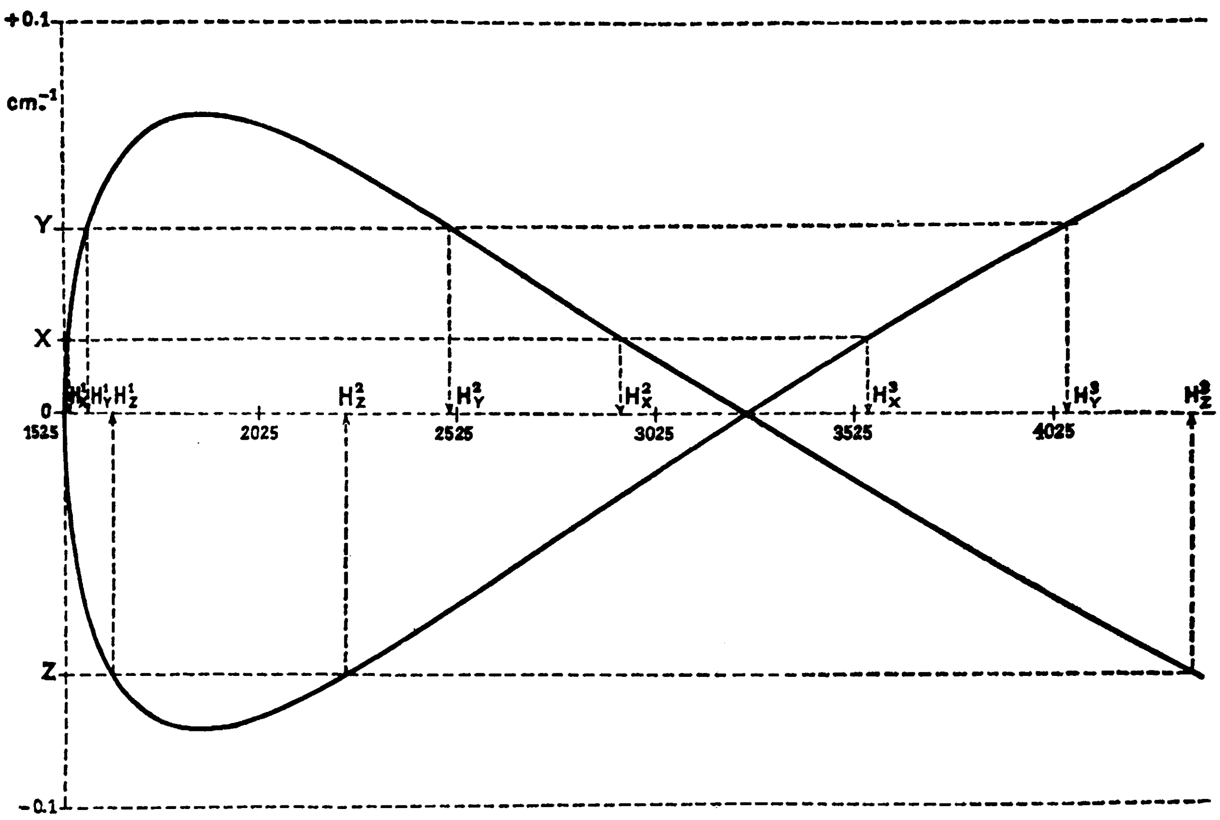


Figure 5 *The function* $F(\vec{H}_0, \delta)$ *for naphthalene at* 9279 *Mc./sec. The axis system used by Kottis and Lefebvre has the x and y axes interchanged from those used in Figure* 3 [Reproduced, with permission, from P. Kottis and R. Lefebvre, *J. Chem. Phys.*, 1963, 39, 393]

It has been shown that when one averages the resonance fields over all the molecules the distribution of resonance fields is that shown in Figure 6.[14] There are thus maxima (peaks) in random samples at the canonical fields and H_m, the latter being the most intense. For molecules of higher symmetry $H_x{}^1$ and $H_y{}^1$

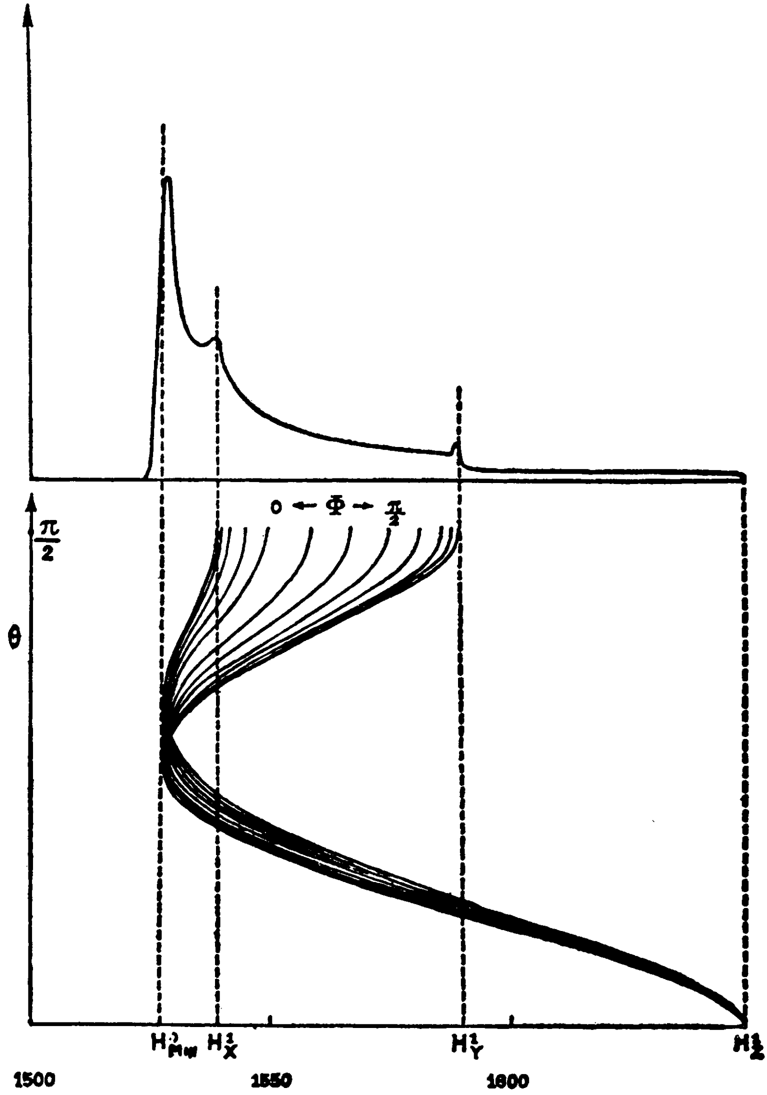


Figure 6 *Distribution of resonance fields in the* $\Delta m_Z = 2$ *region for naphthalene at* $\nu = 9279$ *Mc./sec.*
[Reproduced, with permission, from P. Kottis and R. Lefebvre, *J. Chem. Phys.*, 1963, **39**, 393]

merge into a single peak and H_z^1 disappears, hence the structure of the spectra in random samples will enable one to deduce the triplet symmetry.

The $\triangle m_z = 1$ region gives similar structure from the canonical peaks in random samples, and it is possible to relate the resonance peak positions to X, Y, and Z and hence obtain the Z.F.S. (zero field splitting) parameters in randomly oriented samples. The gross features of the spectra of random samples can also be predicted from the experimental results on single crystals.

8 Experimental Methods in the Study of Triplet States

A. Single Crystals.—For the study of oriented triplet states,[3,10] the molecule is incorporated into a material with which it will form a substitutional solid solution and a single crystal grown. The concentration of guest molecules should be *ca.* 10^{-2}—10^{-3}M (pure crystals of the host do not show phosphorescence owing to rapid exciton transfer effects). If the crystal is a true substitutional solid solution, the guest molecules will be in known orientations in the lattice if the crystal structure of the host is known. The crystals are mounted so that they can be rotated about their principal axes, or the magnet can be rotated and the crystal held fixed. In this way, the variation of the resonance with the angle between $\vec{H}_0$ and the molecular axes can be determined.

Crystals are cooled to 77°K and irradiated with ultraviolet light in the singlet absorption band after suitable focusing of the light through ports in the side of the cavity. The characteristic phosphorescence decay time can be measured from the decay of the e.s.r. signal after the radiation is cut off. With mixed crystals, energy transfer effects can be studied.

The disadvantage is that suitable host crystals for the molecule of interest are difficult to find.

B. Rigid Glasses.—The zero-field splitting parameters can fortunately be obtained from the use of random samples.[9,13] In this technique, the molecule is dissolved in a solvent which freezes to a clear transparent glass at 77°K. The most commonly used is ether–isopentane–alcohol, (E.P.A.) but many other solvents have been described by Smith, Smith, and McGlynn.[15] E.P.A. is relatively stable and easily prepared but most glasses are not stable over a wide temperature range.

C. Plastics.—The incorporation of the organic molecule into a plastic[16] has the advantage of stability over a wide temperature range and in this case the molecule is dissolved in monomer, the polymerisation is carried out, and the sample irradiated. Variations in lifetimes and *Z.F.S.* parameters with temperature can then be determined.

D. The Cavity Arrangements.—The observation of the e.s.r. signals in single crystals can be carried out with the conventional e.s.r. system with the radio-

---

[15] F. Smith, J. Smith, and S. P. McGlynn, *Rev. Sci. Instr.*, 1962, **33**, 1367.
[16] C. Thomson, *J. Chem. Phys.*, 1964, **41**, 1.

frequency field $\vec{H}_{rf}$ perpendicular to $\vec{H}_0$. This arrangement also can be used to observe the $\triangle m_z = 1$ transitions in random samples. However, in the special arrangement with $\vec{H}$ parallel to H_0, additional features of the spectra and the canonical peaks at low field are more readily seen and this is to be preferred to the conventional arrangement for studies of $\triangle m_z = 2$ lines in random samples, since D and E can be obtained directly. For H_{rf} perpendicular to $\vec{H}_0$, low-field measurements give H_m which is related to $D^* = (D^2 + 3E^2)^{\frac{1}{2}}$ and D and E cannot be determined separately. The experimental results in single-crystal studies are usually fitted to the spin Hamiltonian so that the experimental and predicted spectra agree. For random samples, computer simulation of the spectra is carried out.

9 Experimental Investigations of Triplet States of Aromatic Molecules by E.S.R.

The triplet states of aromatic molecules can be divided into two types.[4] In aromatic hydrocarbons, the lowest unfilled and highest filled M.O.'s are π-type and the lowest triplet state is always of the ($\pi \rightarrow \pi^*$) type in which an electron is promoted to an excited π^* orbital. With the introduction of heteroatoms with lone pairs, there is also the other possibility that the lowest triplet state is an ($n \rightarrow \pi^*$) type with the electron promoted from a lone-pair, non-bonding orbital n on the heteroatom. The nature of the lowest triplet state depends on the molecule; in general ($n \rightarrow \pi^*$) states have short ($< 0{\cdot}1$ sec.) phosphorescence lifetimes whereas ($\pi \rightarrow \pi^*$) have lifetimes $> 0{\cdot}1$ sec. Only ($\pi \rightarrow \pi^*$) triplet states have been detected by e.s.r. and in this section we consider only this type of triplet.

A. E.S.R. of Aromatic Molecules in Single Crystals.—The full power of the e.s.r. method is available for the case of oriented molecules in single crystals, and in this case the observed spectra allow one to determine the g-tensor components and those of the spin–spin interaction tensor. The principal values of the latter X, Y, Z are related to D and E (eqn. 20).

Despite the limitations discussed above, a large number of aromatic molecules have been studied in the four host crystals, durene, biphenyl, fluorene, and benzophenone.

(i) *Aromatic hydrocarbons.* The pioneering work of Hutchison and Mangum,[3] and subsequent studies by their group,[17] remain the classic experiments on oriented triplet states. The results are given in Table 1. Naphthalene and its deuterated derivatives have been the most extensively studied in durene, biphenyl, and fluorene. The observed spectra in these matrices show that matrix effects on D and E are small. The results accurately fit the spin Hamiltonian and show that the host molecules are well oriented and that spin–spin interaction is the dominant perturbation.

In the case of naphthalene[17] or phenanthrene in biphenyl, and pyrene in

---

[17] N. Hirota, C. A. Hutchison, jun., and P. Palmer, *J. Chem. Phys.*, 1964, **40**, 3717; R. W. Brandon, R. E. Gerkin, and C. A. Hutchison, jun., *ibid.*, 1962, **37**, 447.

Table 1 *E.s.r. results in single crystals: aromatic compounds*

Molecule	*Host crystal*	D/hc (cm.$^{-1}$)	E/hc (cm.$^{-1}$)	*Ref.*
Naphthalene	Durene	+0·10119	−0·01411	3, 10, 17
„	Biphenyl	+0·0994	−0·0154	10
		+0·09921	−0·01548	17
[$^2H_8$]Naphthalene	Durene	±0·1010	∓0·0134	10
Phenanthrene	Biphenyl	±0·10043	±0·04658	17
Pyrene	Fluorene	±0·0810	±0·0182	18
		±0·0806	±0·0182	*b*
Quinoxaline	Durene	±0·1007	∓0·0182	*a*
Quinoline	Durene	±0·1030	∓0·0162	19
Isoquinoline	Durene	±0·1004	∓0·0117	19
Phenoxazine	Biphenyl	±0·1247	±0·0119	48

[a] J. S. Vincent and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 3088; [b] O. H. Griffith, *J. Phys. Chem.*, 1965, **69**, 1429.

biphenyl,[18] four resonance lines ($\Delta m_z = 1$) are found for each orientation, since in these systems there are two inequivalent lattice sites for the $C_{10}H_8$ molecules in which the planes of two such molecules are mutually perpendicular. The simple two-line pattern discussed above has so far not been found in practice because of the more common feature of inequivalent lattice sites.

In the cases of quinoline and isoquinoline, eight peaks are found for each orientation,[19] because in this case the principal axes of the molecular spin–spin tensor do not coincide with the durene axes, so there are two magnetically inequivalent orientations of quinoline in each of the two lattice sites in durene. The effect of temperature on the D and E values is small but measurable.

The decay of the phosphorescence and that of the e.s.r. signal, as measured by the lifetimes τ_p and τ_p^R are found to be exponential and the two sets of values are in good agreement. For instance, $C_{10}H_8$ in durene has $\tau_p^R = 2{\cdot}1 \pm 0{\cdot}1$ sec. compared with $\tau_p = 2{\cdot}6 + 0{\cdot}2$ sec. The substitution of deuterium in the molecule increases both τ_p and the signal intensity, and τ_p approaches the true radiative lifetime which is often much larger than the observed decay time. The single-crystal results at 77°K give only the relative signs of D and E, and

---

[18] S. W. Charles, P. H. H. Fischer, and C. A. McDowell, *Mol. Phys.*, 1965, **9**, 517.
[19] J. S. Vincent and A. H. Maki, *J. Chem. Phys.*, 1965, **42**, 865.

measurements at 4°K and 1°K are necessary to obtain the absolute signs.[20]

These studies have furnished very detailed information and there is hope that other host crystals will be found which will extend the applicability of the method.

B. E.S.R. of Aromatic Molecules in Rigid Glasses.—The study of triplets in glasses greatly extended the utility of the method. The earlier workers observed $\triangle m_z = 2$ transitions, and with H_{rf} perpendicular to H_0, only H_{min} was observed. However, the use of H_{rf} parallel to H_0 does result in characteristic structure in this region from which D and E can be determined. The use of fully deuterated molecules has also helped in detecting these weak peaks since line-broadening is less.

The observation of $\triangle m_z = 1$ transitions has superseded this work and D and E have now been measured for a large variety of molecules (Table 2).

Table 2 *E.s.r. results in glasses and plastics: aromatic hydrocarbons*

Molecule	D/hc (cm.$^{-1}$)	E/hc (cm.$^{-1}$)	D^*/hc (cm.$^{-1}$)	*Ref.*
Benzene	0·156	0	0·156	13
	0·159	0	0·159	22
Naphthalene	—	—	0·1048	13
	—	—	0·1049	22
	—	—	0·1063	16
[$^2H_8$]Naphthalene	0·10046	−0·01536	0·1008	*a*
Anthracene	—	—	0·077	22
[$^2H_{10}$]Anthracene	0·0724	0·0081	0·0737	*a*
	—	—	0·1335	22
Phenanthrene	0·100	0·047	0·129	23
	—	—	0·129	*b*
	—	—	0·1336	16
[$^2H_{10}$]Phenanthrene	0·1050	0·046	0·1321	*c*
Pyrene	—	—	0·093	23
	—	—	0·0929	22
Chrysene	—	—	0·1052	22
	—	—	0·103	*b*
	0·095	$\lvert 0·025 \rvert$	0·104	23

---

[20] A. W. Hornig and J. S. Hyde, *Mol. Phys.*, 1963, **6**, 33.

Table 2—*continued*

Molecule	D/hc (cm.$^{-1}$)	E/hc (cm.$^{-1}$)	D^*/hc (cm.$^{-1}$)	*Ref.*
1,2-Benzanthracene	0·079	|0·014|	0·083	23
1,2:5,6-Dibenzanthracene	0·090	|0·025|	0·100	23
1,2-Benzopyrene	0·090	|0·023|	0·098	23
3,4-Benzopyrene	—	—	0·0758	22
Triphenylene	0·1353	0	0·1353	22
	0·134	0	0·134	13
	0·1360	0	0·1360	16
	0·1338	0	0·1338	*a*
Coronene	0·096	0	0·096	13
	0·0971	0	0·0971	22
	0·0983	0	0·0983	16
	0·093	0	0·093	*b*
1,12-Benzoperylene	—	—	0·0718	16
Biphenyl	0·1092	0·0036	0·1094	*d*
	—	—	0·1130	22
	—	—	0·1111	16
Terphenyl	—	—	0·0961	22
Fluorene	0·1075	0·0033	0·1092	*d*
	—	—	0·1096	22
	—	—	0·1088	16
Fluoroanthene	—	—	0·076	*b*
	—	—	0·0817	16
Toluene	—	—	0·171	21
Acenaphthene	—	—	0·1029	16
Triptycene	0·135 (77°K)	0	0·135	21
Decacylene	0·057	0	0·057	41

Table 2—*continued*

Molecule	D/hc (cm.$^{-1}$)	E/hc (cm.$^{-1}$)	D^*/hc (cm.$^{-1}$)	*Ref.*
[Decacylene]$^{2-}$	0·021	0	0·021	41
1,3,5 Triphenyl-benzene	0·111	0	0·111	13
[Triphenylbenzene]$^{2-}$	0·042	0	0·042	41

[a] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41,** 1763; [b] G. von Foerster, *Z. Naturforsch.*, 1963, **189,** 620; [c] M. S. de Groot and J. H. van der Waals, *Physica*, 1963, **29,** 1128; [d] S. Siegel and H. Judeikis, *J. Phys. Chem.*, 1966, **70,** 2201.

(i) *Aromatic hydrocarbons.* The appearance of $\triangle m_z = 2$ peaks with H_{rf} parallel to H_0 reflects the symmetry of the state and in molecules of D_{6h} symmetry, two peaks are observed and this has been found for coronene, triphenylene, and triphenylbenzene (Figure 7).[13] Benzene does not give the two-peak pattern, showing conclusively that the lowest triplet state no longer has hexagonal symmetry.[21] This surprising result had been suggested in early phosphorescence studies and the e.s.r. results showed this fact unequivocally.

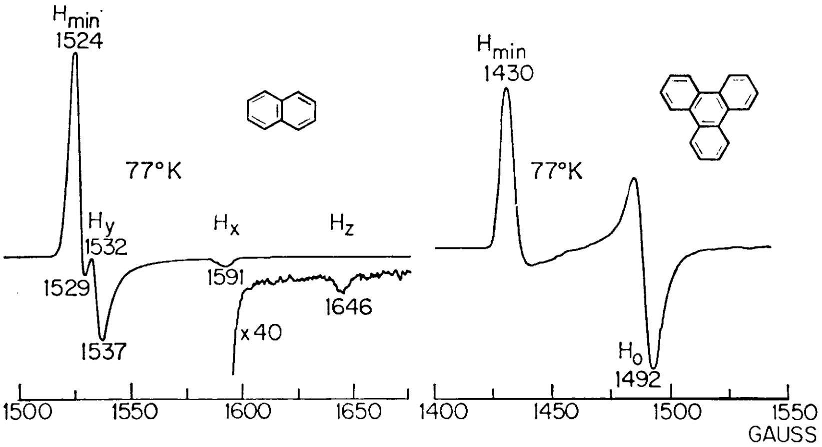


Figure 7 $\Delta m_z = 2$ *Transitions in glassy samples*

(*a*) Naphthalene (*b*) Triphenylene

[Reproduced, with permission, from J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, 1960, **3,** 190]

The spectrum of benzene and the methylbenzenes and the decay times $\tau_{\mathrm{p}}{}^{\mathrm{R}}$

---

[21] M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, 1963, **6,** 545; M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *ibid.*, 1965, **10,** 91.

are very temperature-dependent. These effects have been interpreted in terms of the non-equivalence of the possible conformational isomers and these effects could hardly have been investigated except by e.s.r.[21]

For those molecules which have been studied in glasses and in single crystals, observed values of D and E and D^* are in good agreement. The line-widths have been correlated with the carbon–hydrogen ratios and indicate that hyperfine broadening predominates.[22] Hyperfine interactions are not usually resolved in glasses.

Measurements on the $\triangle m_z = 1$ peaks, give D and E directly and have been carried out for a large number of hydrocarbons, most recently by Brinen and Orloff.[23] A typical spectrum (deuteriophenanthrene) is shown in Figure 8.

(ii) *Aromatic heterocycles and substituted hydrocarbons.*[24] Generally speaking (Table 1), substituents affect E most and D least, but the effects are small, and usually can be attributed to increased delocalisation. However, no systematic study has yet been reported and correlations with spectroscopic evidence might be fruitful.

C. E.S.R. of Aromatic Molecules in Plastics.—The D and E values obtained by this technique[16,25] are in good agreement with the work in single crystals and glasses; slight differences are believed to be due to a stronger matrix effect than is found in the other matrices. Line-widths are always larger in plastics. D has been studied as a function of temperature for coronene and triphenylene[16] but the interpretation given of the slight decrease with T is not unambiguous. The triplet-state lifetimes vary with temperature but also with the nature of host and the previous history of the sample. Further work is needed on these systems.

10 Hyperfine Interactions in Triplet States

Additional structural information is obtained from hyperfine splittings which can be observed in single crystals. The origin of hyperfine interactions (h.f.i.), both anisotropic and isotropic, is now well understood from studies of radicals and has been reviewed.[2] The unpaired spins in triplets give rise to h.f.i. in a similar manner, but unlike the case of free radicals in solution, it is possible to determine the anisotropic h.f.i. if the triplets are oriented. To a very good approximation, the isotropic and anisotropic splittings of a proton in an aromatic C_α–H band are proportional to the spin density ρ_α on the adjacent carbon

$$a_{\mathrm{H}} = \rho_\alpha \mathrm{K} = \rho_\alpha \{A^2\alpha^2 + B^2\beta^2 + C^2\gamma^2\}^{\frac{1}{2}} \qquad (26)$$

where α, β, and γ are direction cosines of $\overrightarrow{H_0}$ with respect to (1) the C–H bond direction (a axis), (2) the normal to the plane (b axis), and (3) the c axis per-

---

[22] B. Smaller, *J. Chem. Phys.*, 1962, **37**, 1578.

[23] J. S. Brinen and M. K. Orloff, *J. Chem. Phys.*, 1966, **45**, 4747; S. Siegel and H. S. Judeikis, *J. Phys. Chem.*, 1966, **70**, 2201.

[24] See refs. 16, 21, and 22.

[25] N. Trublin, R. Santus, and M. Ptak, *Comp. rend.*, 1965, **260**, 1134.

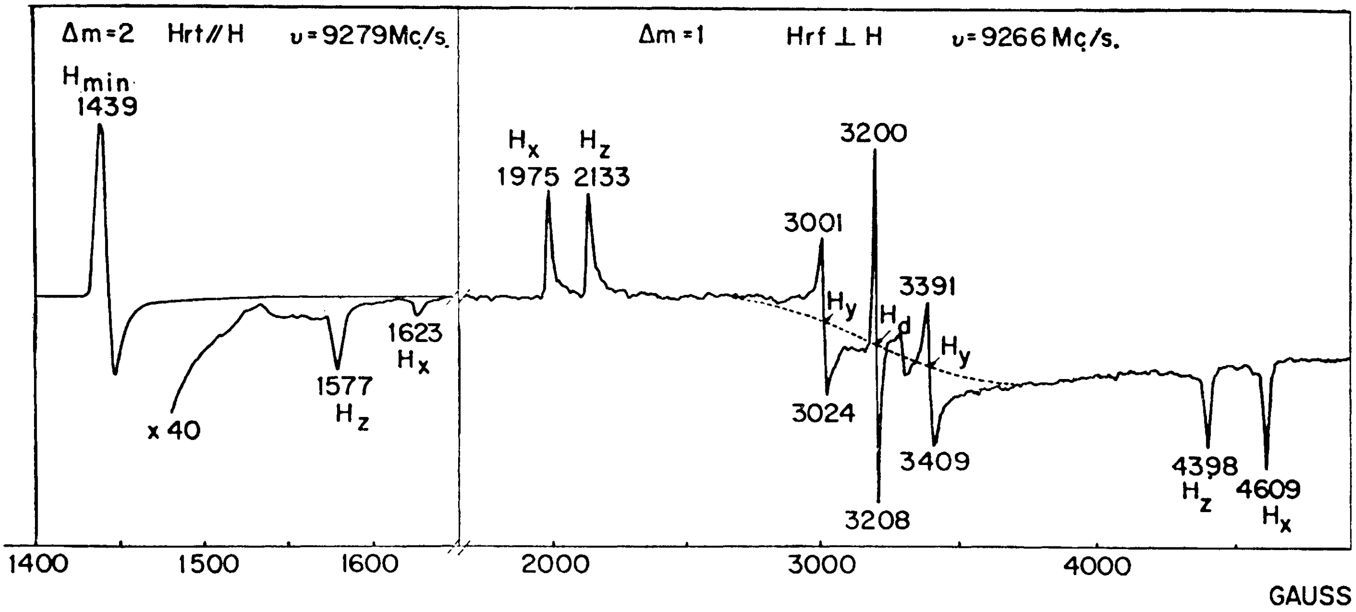


Figure 8 *E.s.r. spectra of deuteriophenanthrene in glassy solution at 77°K*

[Reproduced, with permission, from J. H. van der Waals and M. S. de Groot, *J. Chim. phys.*, 1964, 1643] pendicular to a and b. A, B, and C are the isotropic plus anisotropic h.f.i. per unit spin density on the contiguous carbon atom in the axes a, b, and c respectively.

Measurements of the hyperfine splittings give A^a, B^a, and C^a since the isotropic splitting A^i for C–H is *ca.* −63 Mc./sec. The results show that $A^a = 30$, $B^a = -61$ and $C^a = -92$ Mc./sec. The spectra can be rationalised in terms of these values. The most detailed measurements have been made on naphthalene, deuterionaphthalene, and phenanthrene.

We can regard the naphthalene molecule as a collection of eight C–H fragments (Figure 9) of which there are two types which are structurally inequivalent, the α and β fragments. If H_0 is applied along the x (long) axis of the molecules,

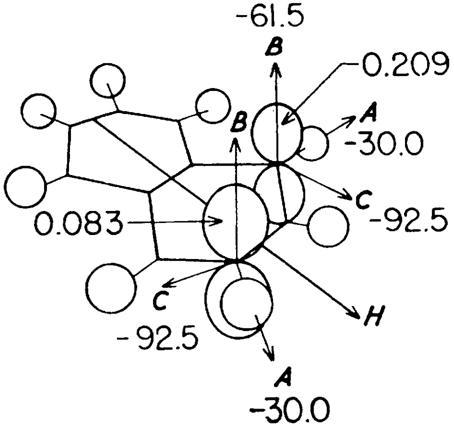


Figure 9 *Hyperfine interactions in naphthalene in terms of the interaction with α and β* C–H *fragments*
[Reproduced, with permission, from C. A. Hutchison, jun., *Rec. Chem. Progr.*, 1963, **24**, 105]

then this direction is parallel to the c axis of the α protons (which have the largest spin density on the adjacent carbon atom) but at the same time H_0 is close to the a axis for the β fragments. Since these directions are those for largest h.f.i. for α protons and smallest h.f.i. for β protons, the hyperfine pattern is one of five lines from the four α-protons ($a_{\alpha H}$) each split into five from the smaller β-splitting ($a_{\beta H}$). The five-line pattern is observed at 77°K but $a_{\beta H}$ is unresolved, though some additional structure is observed at 4°K. For H_0 parallel to the z axis, all protons will appear equivalent and only a single broad line is observed. For H_0 parallel to the y axis, a single peak with some structure is observed as is predicted from the values of A^a, B^a, and C^a for the protons involved.

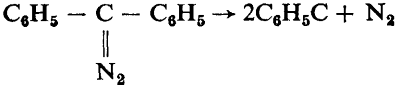
Detailed analysis of the h.f.i. gives the spin densities on the carbon atoms and these can be correlated with theoretical calculations, and the results confirm the symmetry of the triplet state.

No hyperfine structure has been observed for oriented pyrene since here the spin densities are low and there are several similar coupling constants, but it has been observed in oriented quinoxaline, quinoline, and isoquinoline[19] where similar information has been obtained.

11 E.S.R. Spectra of Ground-state Triplets

There are a number of interesting molecules[26,27,28] which have a triplet ground state (as opposed to the triplet excited state of an aromatic molecule) and in recent years the chemistry of carbenes and nitrenes have shown that derivatives of methylene CH_2 and nitrene NH react as though they were in a triplet ground state, and this has been confirmed by e.s.r.

We define a ground-state triplet as one which gives an e.s.r. spectrum which fits the usual spin Hamiltonian with $S = 1$, but whose e.s.r. signal is stable at 77°K for several hours in contrast to excited states which decay in seconds. The ground-state triplet states of substituted methylenes have been studied both in rigid glasses and in single crystals,[29] and are produced by photolysis of the particular precursor diazo-compound at 77°K, *i.e.*,



$$C_6H_5 - \underset{\underset{N_2}{\|}}{C} - C_6H_5 \rightarrow 2C_6H_5C + N_2$$

$\triangle m_z = 1$ and $\triangle m_z = 2$ transitions can be observed, although not all possible transitions are always detected. The triplets are stable to *ca.* 130°K and in contrast to aromatic triplets, D is usually $>0{\cdot}1$ cm.$^{-1}$. The origin of this large value is discussed in Section 16C.

A tabulation of some of the results, representing the various types, is given in Table 3 and considerable structural information has been obtained. Diphenylmethylene is almost linear but with mutually perpendicular phenyl rings, since $E \neq 0$.[30] Phenylmethylene has been studied but not $:CH_2$ itself. The e.s.r. results for pentaphenylcyclopentadienyl confirm the prediction of a triplet ground state by molecular orbital theory.[31]

The derivatives of NH, the nitrenes, have also been extensively studied and are similar to the methylenes.[32] The observed Z.F.S. correlate with the π-electron spin densities in phenyl-substituted nitrenes,[33] since only one of the two π orbitals

---

[26] W. Kirmse, 'Carbene Chemistry', Academic Press, New York, 1964.

[27] A. M. Trozzolo, R. W. Murray, and E. Wassermann, *J. Amer. Chem. Soc.*, 1962, **84**, 4990.

[28] R. W. Murray, A. M. Trozzolo, E. Wasserman, and R. M. R. Cramer, *J. Amer. Chem. Soc.*, 1962, **84**, 3213.

[29] R. N. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, jun., B. E. Kohler, and R. Silbey, *J. Chem. Phys.*, 1965, **43**, 2006.

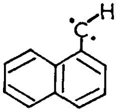
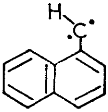
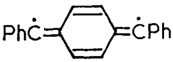
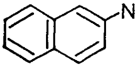
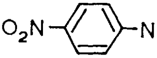
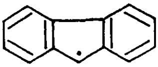
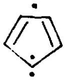
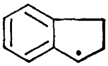
[30] E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 1964, **40**, 2408.

[31] R. Breslow, H. W. Chang, and W. A. Yager, *J. Amer. Chem. Soc.*, 1963, **85**, 2033.

[32] G. Smolinsky, E. Wasserman and W. A. Yager, *J. Amer. Chem. Soc.*, 1962, **84**, 3220; E. Wasserman, G. Smolinsky and W. A. Yager, *ibid.*, 1964, **86**, 3166.

[33] G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, 1963, **35**, 576.

Table 3 *E.s.r. results for ground-state triplets*

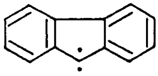
Molecule	*Structure*	*D*/***hc*** (cm.$^{-1}$)	*E*/***hc*** (cm.$^{-1}$)	*Ref.*
CARBENES				
Diphenylmethylene	Ph–C–Ph	0·401	0·018	27, 28
		0·4050	0·0186	*a*
Phenylmethylene	Ph–C–H	0·518	0·024	27
Perfluoroalkylmethylenes	R–CH	0·7	0·02 0·04	*b*
Cyanomethylene	H–C–C≡N	0·889	0	37
1,Naphthyl-methylenes	 	0·4555 0·4347	0·0202 0·0208	36 36
DICARBENES				
p-Phenylene-bis (phenyl methylene)		0·0521	0·002	*c*
NITRENES				
Nitrene	NH	1·86	0	*d*
Cyanonitrene	NCN	1·544	0·002	*e*
2-Naphthylnitrene		0·89	0	67
4-Nitrophenylnitrene		0·98	0	67
n-Propylnitrene	Pr^{n}–N	1·607	0·0034	32
MISCELLANEOUS				
Diazomethylene	CNN	1·153	0·002	*e*
Dicyanomethylene	NCCCN	1·002	0·002	*e*
Fluorenylidene		0·4078	0·0283	*f*, 27
Cyclopentadienylidene		0·4089	0·0120	34
Indenylidene		0·3777	0·0160	34
Propargylene	H–C–$\dot{\text{C}}$ CH	0·6276	0	38

[a] R. W. Brandon, G. Closs, and C. A. Hutchison, jun., *J. Chem. Phys.*, 1962, **37,** 1878; [b] E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, 1965, **87**, 4974; [c] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Amer. Chem. Soc.*, 1963, **85**, 2526; [d] R. N. Dixon, *Canad. J. Chem.*, 1959, **37,** 1171; [e] E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, 1965, **87,** 2075; [f] E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 1964, **40,** 2408.

involved conjugates with the ring. The other $2p\pi$ orbital on the nitrogen is in the molecular plane.

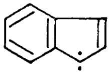
A rather different type are the triplets of fluorenylidene (1), cyclopentadienylidene (2), and indenylidene (3),[34] the first of which has also been studied in single crystals.

(1)



(2)

(3)



D values of *ca.* 0·4 cm.$^{-1}$ are observed, owing to the occurrence of one unpaired electron in a $2p\pi$ orbital and the other in a σ orbital on the same centre. The bonds to the bivalent carbon are bent, and this has been found to be the case in the methylene derivatives from ^{13}C studies.[35] In the case of naphthylmethylenes two distinct geometrical isomers are observed from a single diazo-precursor, thus confirming the non-linear character.[36]

Several more complicated ground-state triplets such as cyanomethylenes,[37] propargylene derivatives,[38] the species CNN, NCN, and NCCCN,[39] and several dicarbenes and dinitrenes where the spins are *ca.* 6 Å apart,[40] have been studied.

Finally, aromatic hydrocarbons with three- or six-fold symmetry axes may form dinegative ions with triplet ground states and triphenylene and decacyclene dianions are examples of this type with low values of *D* owing to stronger electron correlation.[41]

12 Studies of Energy Transfer

Of considerable importance is the use of e.s.r. to study the problems of energy transfer from excited triplet states. This problem has been studied for many years by optical methods but, once more, additional information is obtained by use of e.s.r.

The effect of excitation transfer within the triplet state is typified by the examples of benzene, the methylbenzenes, and the molecules triptycene and tribenzotriptycene; in the last the three aromatic rings are not conjugated with one another.[21]

As mentioned in Section 9B (i), the benzene spectrum indicates that the molecule no longer has hexagonal symmetry. This implies that there are two configurations I and II with two different bond lengths and different energies in

---

[34] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Amer. Chem. Soc.*, 1964, **86**, 2304.

[35] E. Wasserman, *J. Chem. Phys.*, 1965, **42**, 3739.

[36] A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, 1965, **87**, 129.

[37] K. A. Bernheim, R. J. Kempf, P. W. Humer, and P. S. Skell, *J. Chem. Phys.*, 1964, **41**, 1156.

[38] R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, 1965, **43**, 196.

[39] E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, 1965, **87**, 2075.

[40] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Amer. Chem. Soc.*, 1963, **85**, 2526.

[41] R. E. Jesse, P. Biloen, R. Prins, J. D. W. van Voorst, and G. J. Hoijtink, *Mol. Phys.*, 1963, **6**, 633.

each of which there are two equivalent conformations. Vibrations of the right symmetry can cause the system to interconvert between the Type I conformations *via* Type II. A theoretical study substantiates this model.[21] The rate of this process compared with characteristic e.s.r. times determines the spectral appearance and accounts for the temperature-dependence. For a very fast interconversion rate, the time-average conformation will have D_{6h} symmetry and in this case one can show that the resonance peak broadens and moves to higher fields as is observed when the temperature is raised. The converse is found for decreasing temperature.

The methylbenzenes, in which the equivalence of the conformational isomers is destroyed, exhibit similar behaviour.

Triptycene and tribenzotriptycene[21] are similar, except now the individual conformations are replaced by excitations in individual π-systems. For rapid excitation transfer, once again D_{6h} symmetry is approached and the observed temperature-dependence gives the rate of transfer of triplet excitation. At 20°K, the excitation is mainly localised but it is delocalised at 77°K.

The second triplet state energy-transfer mechanism is intermolecular. This was first observed by Farmer, Gardner, and McDowell by e.s.r.,[42] who showed that the benzophenone triplet transfers energy to a naphthalene molecule giving the triplet of the latter in a rigid glass. No benzophenone triplet resonance is observed since this is an $(n \rightarrow \pi^*)$ state.

Much more detailed investigations on the mechanism of energy transfer in single crystals have since been carried out by Hutchison's group,[43,44] which have shed some light on triplet-transfer and triplet–triplet annihilation processes, and have shown that the transfer proceeds *via* the crystalline host lattice and that complex-formation does not occur.

Smaller, Avery, and Remko[45] have studied similar problems in glasses of different viscosity and have shown that exchange mechanisms dominate at high η but diffusion processes at low η. Similar work has been done by Siegel and his collaborators.[46]

Finally, it has been shown that energy transfer from the triplet state to the solvent produces free radicals at a rate proportional to the rate of decay of the triplet state, and it is believed to involve a highly excited triplet state.[47] The influence of deuteration of triplet state lifetimes has been extensively studied by Hirota.[48]

13 The Electronic Structure of Triplet States

The correlation of the observed Z.F.S. parameters with the molecular electronic structure is perhaps the most important aspect of this work, since these weak

---

[42] J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 1961, **34**, 1058.

[43] N. Hirota and C. A. Hutchison, jun., *J. Chem. Phys.*, 1964, **42**, 2869.

[44] N. Hirota, *J. Chem. Phys.*, 1965, **43**, 3354.

[45] B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, 1965, **43**, 922.

[46] S. Siegel and H. Judeikis, *J. Chem. Phys.*, 1965, **42**, 3060 and many earlier papers by these authors.

[47] B. Smaller, *Nature*, 1962, **195**, 593.

[48] N. Hirota, *J. Chem. Phys.*, 1967, **46**, 1561.

interactions constitute a very sensitive test of the molecular wave function.[5] Since the triplet wave function must have an antisymmetric spatial part, this means that the unpaired electrons must occupy different spatial orbitals, *i.e.*, they are kept apart by Pauli's principle and approximate wave functions can be used to describe the state with some confidence in this case.[49]

For a $2N$ π-electron aromatic molecule, the ground-state wave function can be approximated by the single Slater determinant based upon doubly occupied M.O.'s $\phi_1 \ldots\ldots \phi_N$.

$${}^1\Phi. = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 \ldots\ldots \phi_N\bar{\phi}_N| \tag{27}$$

The lowest triplet state is described in terms of one-electron excitations from M.O. ϕ_i to an antibonding M.O. ϕ_k ($k = N + 1 \ldots\ldots 2N$), the lowest energy configuration being

$${}^3\Phi.\,(N \rightarrow N + 1) = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 \ldots\ldots \phi_N\phi_{N+1}| \tag{28}$$

for the state with $M_z = +1$ (we restrict our discussion to this component). The exact triplet wave function in general will be a superposition of all possible configurations of the appropriate symmetry, *i.e.*,

$${}^3\Psi = \sum_{i}\sum_{k\neq i} C_{ik}\,\Phi(\mathrm{i} \rightarrow \mathrm{k}) \tag{29}$$

with the dominant term ${}^3\Phi(N \rightarrow N + 1)$

$$\Phi(i \rightarrow k) = |\phi_1\bar{\phi}_1 \ldots\ldots \phi_i \ldots\ldots \phi_N\bar{\phi}_N\phi_k| \tag{30}$$

particularly if the ϕ_i are open-shell S.C.F. orbitals.[50] More complicated wave functions, such as the Unrestricted Hartree–Fock[51] functions, do not appear to be as useful for evaluating the zero-field splittings.

The ground-state triplet states have similar descriptions where, however, the unpaired electrons may now occupy different orthogonal orbitals on the same centre, one of which can conjugate with aromatic rings. It should be emphasised that these orbital descriptions are all approximate but a similar analysis[52] holds for exact wave functions in the calculation of Z.F.S. parameters.

14 Theoretical Calculation of *D* and *E*

The theoretical calculation of D and E involves the evaluation of the expectation value of $\mathscr{H}_{ss}$ (eqn. 5) with the triplet-state wave function. The evaluation of the spin–spin interaction energy can be shown to give the following expressions for D and E

---

[49] J. C. Slater, 'Quantum Theory of Molecules and Solids', McGraw-Hill, New York, 1963, vol. 1.

[50] C. C. J. Roothaan, *Rev. Mod. Phys.*, 1960, **32**, 179.

[51] G. G. Hall and A. T. Amos, *Adv. Atomic and Mol. Phys.*, 1965, **1**, 1; A. T. Amos and L. C. Snyder, *J. Chem. Phys.*, 1965, **43**, 2146.

[52] R. McWeeny, *J. Chem. Phys.*, 1961, **34**, 399; R. McWeeny and Y. Mizuno, *Proc. Roy. Soc.*, 1960, *A*, **259**, 554; R. McWeeny, *J. Chem. Phys.*, 1965, **42**, 1717.

$$\begin{aligned} D &= \frac{3}{4} g^2\beta^2 \left\langle {}^3\Psi \left| \frac{3z_{12}{}^2 - r_{12}{}^2}{r_{12}{}^5} \right| {}^3\Psi \right\rangle \\ E &= \frac{3}{4} g^2\beta^2 \left\langle {}^3\Psi \left| \frac{y_{12}{}^2 - x_{12}{}^2}{r_{12}{}^5} \right| {}^3\Psi \right\rangle \end{aligned} \tag{31}$$

where the expectation value is over the antisymmetric spatial part of the wave function.

We shall not go into a detailed discussion of the evaluation of this expectation value in this Review (for further details consult refs. 51, 53, 54—57), but shall indicate the problems involved and the significance of the results.

It is clear from eqn. (29) that the evaluation of D and E will involve knowledge of the coefficients C_{ik} in the configuration interaction description, and the integrals involving the particular configurations.

The former is a straightforward problem in quantum chemistry and for the latter one can show that these integrals reduce to molecular integrals over M.O.'s of the form

$$\{ab, cd\} = \int\int a(1)b(2) \quad \hat{o} \quad [c(1)d(2) - c(2)d(1)]\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{32}$$

where the operators $\hat{o}$ are those of eqn. (31). The numerators of the operators measure the anisotropy in the two-electron distribution functions, and the denominators reflect its overall size.

If the M.O.'s are expressed in L.C.A.O. form, *i.e.*,

$$a = \sum_{i=1}^{2N} a_i X_i \tag{33}$$

then the problem reduces to evaluation of products of the coefficients a_i and the atomic integrals $\{ij, kl\}$ where now i,j,k,l refer to $2p\pi$ atomic orbitals. Until quite recently, only approximate values of the latter were available, but recent work by Karplus and his co-workers[53] has furnished accurate values of these integrals. The integrals may involve π atomic orbitals on two, three, or four centres for (π–π^*) states, but for methylenes and nitrenes there are also one-centre integrals.

15 Comparison of Experimental and Theoretical Values of *D* and *E*

A. Aromatic Hydrocarbons.—Early work was based on a two-configuration approximation[58] to the triplet state, with wave function

$${}^3\Psi_{\mathrm{L_a}} = \sin\theta\,\Phi(N \rightarrow N+1) + \cos\theta\,\Phi(N-1 \rightarrow N+2) \tag{34}$$

---

[53] I. Shavitt and M. Karplus, *J. Chem. Phys.*, 1965, **43**, 398; C. W. Kern and M. Karplus, *ibid.*, 1965, **43**, 415; M. Godfrey, C. W. Kern, and M. Karplus, *ibid.*, 1965, **44**, 4459.

[54] J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, 1964, **8**, 301.

[55] Y. N. Chiu, *J. Chem. Phys.*, 1963, **39**, 2763, 2749.

[56] C. Thomson, *Mol. Phys.*, 1966, **11**, 197.

[57] J. S. Brinen and M. K. Orloff, *J. Chem. Phys.*, 1966, **45**, 4747.

[58] N. S. Ham and K. Ruedenberg, *J. Chem. Phys.*, 1956, **25**, 13.

θ is the mixing parameter, determined in ref. 58 by energy minimisation, but in Goutermann's earlier work[59] it was treated as a parameter and the optimum value found by comparison with experiment. These early calculations used approximate values of the two-centre integrals and Hückel or Hoffman[60] M.O.'s and neglected three- or four-centre integrals. The results in Table 4, Columns 1 and 2, show that the results were satisfactory for the smaller molecules. Similar calculations were carried out by Chiu.[55]

A more serious criticism of this approach is that the best θ values differ from those values which give the best triplet energy[58] and so these calculations do not really test the quality of the triplet wave function. For higher accuracy, the triplet-state wave function must be obtained by minimisation of the energy, as was shown by van der Waals and de Groot[54] and Thomson.[56] These authors used similar approximations for the integrals, but used rather different wave functions. Van der Waals's calculations and later work by Brinen and Orloff[57] were based on Open Shell S.C.F.–Pariser–Parr-type wave functions, including a semi-empirical treatment of the σ electrons, but employing the zero-differential overlap approximation.

Thomson[56] on the other hand used Hummel and Ruedenberg's[61] wave functions which give very good agreement for triplet-state energy levels. These *include* overlap between nearest neighbours (T.B.M.) or nearest and next-nearest neighbours (I.R.M.) and employ well-tested methods of evaluating electron repulsion and core integrals. Both sets of calculations used extensive configuration interaction which is necessary for accurate work (Table 4, Columns 3,4; 6,7). This work is currently being extended by use of the accurate integral values of Karplus.[53,62]

Agreement with experiment was very good, particular improvements being apparent for the *peri*-condensed molecules. However, the importance of the influence of σ electrons[54] and more accurate integral values[53] need studying in order to obtain values of D and E to within a few per cent. of experimental values. Nevertheless, the calculations using properly energy minimised wave functions do appear to constitute a good test of the wave functions used.[63]

B. Aromatic Heterocycles and Other Molecules.—Very little work has been carried out on other than hydrocarbons, particularly with respect to the use of accurate integrals. Boorstein and Gouterman[64] have carried out similar calculations to those of van der Waals on quinolines and quinoxalines, using more accurate (but still not exact) integrals, but more work is needed in this area. An estimate of (n–π*)-state Z.F.S. parameters has been made by Sternlicht.[65]

[59] See ref. 11 for bibliography of earlier calculations in this approximation.
[60] R. Hoffman, *J. Chem. Phys.*, 1963, **39**, 1397.
[61] R. L. Hummel and K. Ruedenberg, *J. Phys. Chem.*, 1962, **66**, 2334.
[62] C. Thomson, unpublished work.
[63] See however, T. J. Dougherty, T. Vladimiroff, and S. T. Epstein, *J. Chem. Phys.*, 1966, **45**, 1803.
[64] S. A. Boorstein and M. Gouterman, *J. Chem. Phys.*, 1965, **42**, 3070.
[65] H. Sternlicht, *J. Chem. Phys.*, 1963, **38**, 2316.

Table 4 *Theoretical values of D and E for some aromatic hydrocarbons*

	Approximation*													
	1		2		3		4		5		6		7	
Molecule	D	E	D	E	D	E	D	E	D	E	D	E	D	E
Benzene (D_{6h})	0·1519	0	0·1519	0	0·179	0	—	—	—	—				
	0·15333	0	—	—	—	—	0·157	—	—	—				
Naphthalene†	0·1003	−0·0133	0·0958	−0·0211	0·111	−0·028	0·099	−0·024	0·045	0·005	0·088	−0·011	0·100	−0·011
	0·1002	−0·0146	—	—	—	—	0·097	−0·022	—	—				
Anthracene	0·0727	−0·0148	0·0721	−0·0166	0·076	−0·012	0·071	−0·009	0·034	0·012	0·049	−0·002	0·074	0·001
							0·077	−0·011	—	—				
Pyrene	—	—	—	—	—	—	0·084	−0·041	—	—	0·069	0·037	0·080	0·039
Phenanthrene	0·0731	0·0269	0·0851	0·0304	0·115	0·056	0·100	0·048	0·063	0·082	0·082	0·059	0·092	0·051
							0·116	0·039						
1,12-Benzperylene	—	—	—	—	—	—	—	—	—	—	0·042	0·001	0·063	−0·001
Coronene	0·0522	0	0·0608	0	—	—	—	—	—	—				
	0·0546	0	—	—	—	—	—	—	—	—				
Triphenylene	0·0697	0	0·0810	0	—	—	0·134	0	—	—				
	0·0693	0	—	—	—	—	—	—	—	—				

**Approximations used*

1. Reference 11: All two-centre integrals included. Single Gaussian approximation in integral evaluation. Two-configuration wave function (eqn. 34), based on Hückel orbitals.
2. Reference 11: As for 2·but with Hoffmann orbitals.
3. Reference 54: Pariser–Parr approximation in Open-Shell SCF–M.O. calculation including C.I. with all singly and some doubly excited configurations; integrals by direct quadrature.
4. References 54 and 57: As for 4 but only singly excited configurations included; semi-empirical adjustment of nearest-neighbour $(X_iX_j; X_iX_j)$ to take σ-effects into account.
5. Reference 51: Unrestricted Hartree–Fock method; single Gaussian approximations in integral evaluation: Pariser–Parr parameters.
6. Reference 56: Ruedenberg TBM wave functions; single Gaussian approximation to integrals; overlap between nearest neighbours.
7. Reference 56: As in 6 but wave functions (IRM) included nearest and next-nearest neighbour overlap integrals.

†The values of D and E for naphthalene, using Pariser's eight-configuration wave function and accurate values of all two-, three-, and four-centre dipolar integrals are $D = 0{\cdot}1081$, $E = -0{\cdot}0093$ (ref. 53).

C. Ground–state Triplet States.—The calculation of the Z.F.S. parameters in the substituted methylenes and nitrenes has been considered in detail by Higuchi in a series of papers.[66] These calculations, typified by the work on substituted methylenes, have shown that the one-centre terms are the most important and, for reasonable values of the integrals, the calculated D and E are in fair agreement with experiment. D and E mainly depend on the spin density at the methylene carbon.[33] The effect of bond angle on D and E shows that the –C– bond is bent.[66] The exact explanation of the observed angle must, however, await more detailed calculations, including in-plane σ-electrons. Similar calculations on nitrene derivatives have been made.[67] The use of *ab-initio* wave functions will be of great importance in this type of work and Loundsbury[68] has calculated D for NH using one centre *ab-initio* SCF wave functions with encouraging results.

Finally, the influence of spin–orbit interaction has been investigated (eqns. 3 and 4) which was neglected in all the above discussions.[69] This is a second-order effect and it appears likely that for methylenes the contribution to D is *ca.* 10% of the spin–spin interaction. It is expected to be less important in delocalised systems, but quantitative calculations are needed.

16 Miscellaneous Remarks

The Triplet State in Solution.—Very few studies have been carried out on triplet states in solution, since (1) lifetimes are usually too short or (2) the Z.F.S. anisotropy results in lines too broad to observe. Recently, however, Lemaire and his co-workers have described[70] some biradicals which give well-resolved triplet state spectra in solution.

The molecules consist of two nitroxide radical fragments linked *via* a saturated chain.

The e.s.r. spectra depend on the magnitude of the exchange integral J coupling the two unpaired electrons. For $J \ll a_N$, the spectrum is a triplet characteristic of two independent nitroxide groups, but for $J \gg a_N$, five lines are observed separated by $a_N/2$. Each electron interacts with both nitrogen nuclei. For $J = ca.\ a_N$, line-width alternation occurs and Lemaire *et al.* have described biradicals in which J varies from one extreme to the other. By using liquid

---

[66] J. Higuchi, *J. Chem. Phys.*, 1963, **38**, 1237; 1963, **39**, 1847; 3455; 1964, **41**, 2084.

[67] J. A. R. Coope, J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 1965, **42**, 54.

[68] J. B. Loundsbury, *J. Chem. Phys.*, 1965, **42**, 1549.

[69] S. H. Glarum, *J. Chem. Phys.*, 1963, **39**, 3141; S. J. Fogel and H. F. Hameka, *ibid.*, 1965, **42**, 132.

[70] R. M. Dupeyre, H. Lemaire, and A. Rassat, *J. Amer. Chem. Soc.*, 1965, **87**, 3771; R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. chim. France*, 1965, **11**, 3290.

crystals,[71] where the molecules are partly oriented, these workers have been able to observe further splitting of the lines owing to the zero-field splitting in the triplet state. Extensions of this type of work to other systems should be most interesting.

Polarised Light Studies.—Oriented triplet states can be produced by use of polarised light and the influence of the polarised light on the canonical peak intensities has given interesting information on the polarisation of the exciting singlet.[72]

17 Conclusions

I have tried to show that e.s.r. has provided a wealth of important information concerning the electronic structure of the triplet state, together with information of energy-transfer processes and the factors influencing such processes. The detailed information available emphasise the power of the e.s.r. technique and present the theoretical chemist with data which test the available theories of the electronic structure of such states.

I thank Professors D. Kivelson, M. A. El-Sayed, and Y-N. Chiu for many fruitful discussions on this topic.

[71] H. R. Falle, G. R. Luckhurst, H. Lemaire, Y. Marechal, A. Rassat, P. Rey, *Mol. Phys.*, 1966, **11**, 49.

[72] M. A. El-Sayed and S. Siegel, *J. Chem. Phys.*, 1966, **44**, 1416; M. Lhoste, P. Hang and M. Ptak, *ibid.*, p. 648, 654; G. P. Rabold and L. H. Piette, *Photochem. and Photobiol.*, 1966, **5**, 733.