Molecular Deformations Induced by Liquid Crystalline Solvents

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The electron resonance spectrum of the 2-trithienylmethyl radical has been recorded at several temperatures in both the isotropic and nematic phases of 4,4'-dimethoxyazoxybenzene. The temperature dependence of the anisotropic hyperfine splitting constants in the nematic mesophase cannot be explained in terms of the increased alignment of the solute molecules alone. A redistribution of spin density deriving from a solvent induced deformation of the radical seems to be responsible for the observed trend.

Expressions for calculating the hyperfine tensor resulting from the dipolar interaction between a nucleus and an electron contained in a Slater $3p_z$ orbital have been also derived, extending from the McConnell and Strathdee treatment.

INTRODUCTION

The problem of establishing whether the geometry of a nonplanar flexible radical may be altered when going from the isotropic phase to the nematic mesophase of a liquid crystalline solvent has received attention in two recent papers (*1, 2*).

Falle and Luckhurst (*1*) examined the triphenylmethyl radical, studying the temperature dependence of the proton coupling constants in the nematic mesophase of 4,4'-dimethoxyazoxybenzene. By lowering the temperature they found that the *ortho* and *para* splittings decrease initially, pass through a minimum, and finally increase. The explanation of this unusual behavior, which cannot be due only to the increased alignment in the mesophase, was found in the flexible geometry of the radical by proposing that the solute molecules undergo a deformation by the liquid crystalline solvent towards a more planar conformation.

Haustein, Dinse, and Möbius (*2*), by looking at the ESR spectra of the anion radical of tetracyanoquinodimethane, observed a minimum in the ^{13}C hyperfine splitting constants of the cyano group carbons when varying the temperature in the nematic region. They also interpreted this result on the basis of a redistribution of spin density deriving from a flattening of the molecule in the nematic phase.

Since in both cases the variation of the coupling constants was very small and no quantitative determination of the degree of deformation could be made, we have undertaken a similar study on the trithienylmethyl radical, to establish whether the same effect can also be revealed in this case, and to estimate, if possible, to which extent the deviation from planarity is reduced in this radical when dissolved in nematic liquid crystals.

EXPERIMENTAL

The 2-trithienylmethyl radical was prepared by reducing with zinc powder the corresponding perchlorate in degassed solutions as described previously (3, 4).

The ESR spectra were recorded at several temperatures on a JEOL JES-ME-IX Spectrometer equipped with standard variable temperature accessories. The temperature was measured with a chromel-alumel thermocouple placed in the Dewar insert just above the sample.

The values of the hyperfine splitting constants determined at each temperature are the results of at least ten independent measurements. The g factor of 2.00362 was measured taking as a standard the Fremy's salt having an isotropic g factor of 2.00550.

RESULTS AND DISCUSSION

Before proceeding with a discussion of our findings, we first summarize briefly the theoretical aspects of electron resonance in liquid crystals.

In the nematic mesophase of a liquid crystalline solvent the average hyperfine splitting constant differs from the isotropic value and is given by

$$\bar{a} = a + \tfrac{2}{3} \sum_{ij} \mathcal{O}_{ij} A'_{ij}, \qquad [1]$$

where $\mathcal{O}_{ij}$ and A'_{ij} denote the ordering matrix elements and the anisotropic components of the hyperfine tensor, respectively. When the molecule possesses a threefold or higher symmetry axis, Eq. [1] reduces to (5)

$$\bar{a} = a + \mathcal{O}_{33} A'_{33}, \qquad [2]$$

and the problem of interpreting the coupling constants depends on the knowledge of the hyperfine tensor components in the direction of the threefold axis.

Expressions for calculating $\mathbf{A}'$ in π-radicals have been derived by McConnell and Strathdee (6). They calculated the hyperfine tensor resulting from the dipolar interaction between a nucleus Y and an electron contained in a Slater $2p_z$ orbital on a nucleus X, the axis system for the fragment X-Y being that of Fig. 1.

The principal components of the tensor are

$$\begin{aligned}
A'_{11} &= 2\rho P, \\
A'_{22} &= -\rho(P + Q), \\
A'_{33} &= \rho(Q - P),
\end{aligned} \qquad [3]$$

where ρ is the spin density on atom X. The quantities P and Q are related to the internuclear separation R (Å) and to the effective nuclear charge Z for the $2p_z$ orbital on atom X by

$$P = \frac{g\beta\gamma_y}{2\pi R^3} \left\{ 1 - \frac{9}{a^2} + \left(a^3 + 4a^2 + 10a + 17 + \frac{18}{a} + \frac{9}{a^2} \right) \exp(-2a) \right\} \qquad [4]$$

and

$$Q = \frac{g\beta\gamma_y}{2\pi R^3} \left\{ \frac{9}{2a^2} - \left(a^3 + 3a^2 + 6a + 9 + \frac{9}{a} + \frac{9}{2a^2} \right) \exp(-2a) \right\}, \qquad [5]$$

where γ_y is the magnetogyric ratio for nucleus Y (79.056 MHz Å for hydrogen), $a = ZR/2a_0$, and a_0 is the radius of atomic hydrogen, 0.5292 Å.

In the 2-trithienylmethyl the contributions to the hyperfine tensors coming from spin density on the carbon atoms may be calculated using these formulas. Since the radical also contains sulphur atoms, we had to derive similar expressions which could be used
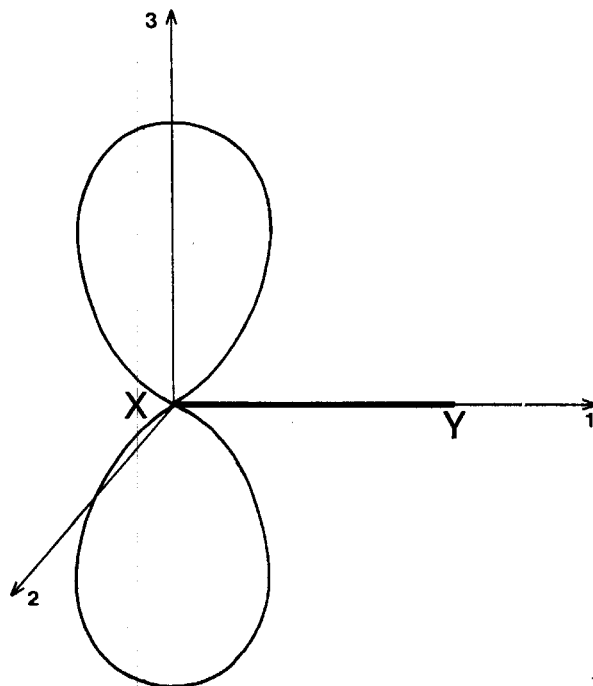

FIG. 1. The coordinate system for the fragment $\dot{X}$-Y.

when the unpaired electron is contained in a Slater $3p_z$ orbital (see Appendix). The principal components of the tensors are still given by formulas [3] where P and Q are now

$$P = \frac{g\beta\gamma_y}{2\pi R^3}\left\{1 - \frac{189}{5a^2} + \frac{1}{5}\left(\frac{64}{729}a^5 + \frac{64}{81}a^4 + \frac{376}{81}a^3 + \frac{184}{9}a^2\right.\right.$$

$$\left.\left. + \frac{68}{3}a + 163 + \frac{252}{a} + \frac{189}{a^2}\right)\exp(-4a/3)\right\},$$ [6]

$$Q = \frac{g\beta\gamma_y}{2\pi R^3}\left\{\frac{189}{10a^2} - \frac{1}{5}\left(\frac{64}{729}a^5 + \frac{160}{243}a^4 + \frac{88}{27}a^3 + \frac{112}{9}a^2\right.\right.$$

$$\left.\left. + \frac{112}{3}a + 84 + \frac{126}{a} + \frac{189}{2a^2}\right)\exp(-4a/3)\right\};$$ [7]

the symbols have the same meaning as in Eqs. [4] and [5].

The electron resonance spectrum of the 2-trithienylmethyl radical may be analyzed in terms of three different splittings due to the hydrogens in positions 3, 4, and 5. The larger coupling constant has been shown by means of deutero substitution (4) to come from the protons in position 3, and the smaller from the protons in position 4. The results of the measurements of the hyperfine splittings made in 4,4′-dimethoxyazoxy-benzene over a wide range of temperatures are collected in Fig. 2. In the isotropic phase

it can be seen that the proton splittings remain constant within the limits of experimental uncertainties. When going to the nematic mesophase, they first increase to a more or less pronounced extent, then, with decreasing temperature, the splitting from proton 4 increases regularly as predicted by Eq. [2] while splittings from both proton 3 and proton 5 initially increase, reach a maximum, and finally stabilize or slightly decrease. This behavior is rather unexpected since protons having large and, hence, negative constants usually experience on alignment a decrease of their splittings since the product $A'_{33} \mathcal{O}_{33}$
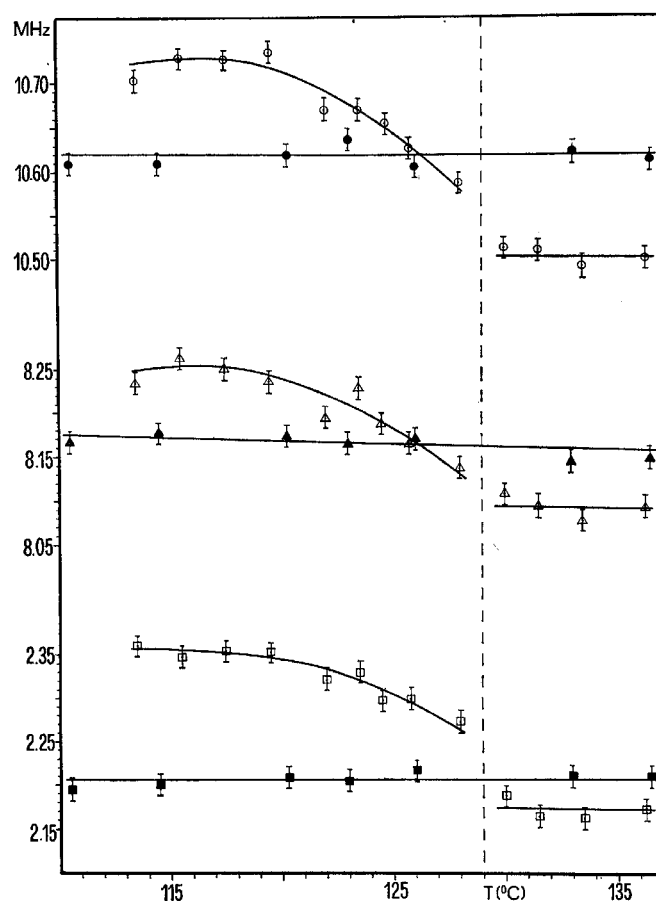

Fig. 2. The temperature dependence of the hyperfine splitting constants of the protons 3, 5, and 4 (starting from the top) of 2-trithienylmethyl in 4,4'-dimethoxyazoxybenzene (empty symbols) and tris-butyl-phosphate (full symbols).

is normally positive. In fact also in this case, as it will be discussed later on, Eq. [2] would predict a regular decrease of the anisotropic splitting if the conformation of the radical remains unchanged.

Consequently, the observed trend should be due to a reassessment of the geometry of the radical with temperature.

Two facts may be responsible of the observed increase of the proton splittings: the reduced vibrations of the thiophene rings which would lead to a smaller average departure from planarity and the increasing order of the nematic mesophase which could induce deformations of the solute molecules favoring a more planar conformation. We should be able to distinguish between these two effects from the ESR spectra recorded in an isotropic solvent in the same temperature range as that for the nematic mesophase.

The coupling constants measured in tris-butyl phosphate (TBP) are also shown in Fig. 2. As they remain, in practice, constant upon reducing the temperature, the most important effect in the nematic region should be the solvent-induced deformation of the molecule.

As a consequence of the increased planarity, the anisotropic hyperfine splittings will be modified in the following ways; the change in spin density will affect both the iso-tropic constants and the components of the hyperfine tensor, and the rotation of the thiophene rings will alter the component of the tensor along the axis perpendicular to the molecular plane and the internuclear distances, and, hence, A' (1). To establish the relative importance of these effects, we tried to calculate A'_{33} for the planar conformation
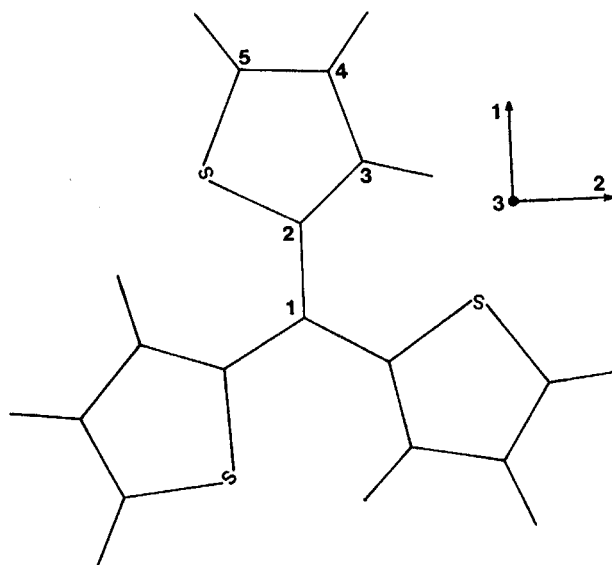

FIG. 3. The formula and axis system for the 2-trithienylmethyl radical.

and for the conformation having the thiophenes rotated by 25° from the molecular plane. The spin densities employed were those given by McLachlan calculations using $h_s = 1.0$ and $k_{cs} = 0.88$, which have been found to reproduce rather well the hyperfine splitting constants in isotropic solvents, when assuming a deviation from planarity of the thiophene rings of 25° and a Q value of -75 MHz (4). The calculations of the tensors have been made considering for each proton of a single thiophene ring the contribution from spin density on the atoms of the given ring and on the central methyl carbon. For the planar conformation, where all the protons lie on the nodal plane of the $2p_z$ and $3p_z$ orbitals, Eqs. [3] were employed, and for the twisted configuration, the contribution from the central carbon was calculated using the equations derived by Derbyshire (7) and reported also in Ref. (1). The effective nuclear charge was set equal to 3.25 and 5.45 for carbon and sulphur, respectively. The structure of the radical and the molecular axis system are shown in Fig. 3. The bond lengths and bond angles (8) used in the calcu-lations are reported in Table 1, and the results relative to the spin densities and to the A'_{33} components of the hyperfine tensors are given in Table 2. For each proton A'_{33} has been calculated to be negative; since also $\mathcal{O}_{33}$ for a planar or nearly planar moelcule is negative (1), the product $A'_{33}\mathcal{O}_{33}$ will always be positive. Moreover, $A'_{33}\mathcal{O}_{33}$ will increase at lower temperature since the degree of alignment increases, and, as a consequence of

TABLE I

BOND LENGTHS (IN Å) AND BOND ANGLES FOR THE
2-TRITHIENYLMETHYL RADICAL

$C_1-C_2 = C_3-C_4 = 1.45$ $C_1-\hat{C}_2-C_3 = 132°$
$C_2-C_3 = C_4-C_5 = 1.35$ $S-\hat{C}_2-C_3 = C_2-\hat{C}_3-C_4 = 112°$
$C_2-S = C_5-S = 1.72$ $C_3-\hat{C}_4-C_5 = 112.5°$
$C-H = 1.085$ $C_4-\hat{C}_5-S = 111.5°$
$C_2-\hat{S}-C_5 = 92°$
$C_4-\hat{C}_3-H_3 = C_3-\hat{C}_4-H_4 = S-\hat{C}_5-H_5 = 119°$

TABLE 2

McLACHLAN SPIN DENSITIES AND A'_{33} COMPONENTS OF THE
ANISOTROPIC HYPERFINE TENSORS IN MHz

	Position					
	3		4		5	
Angle	p	A'_{33}	p	A'_{33}	p	A'_{33}
0°	0.1491	−1.70202	−0.0290	−1.38030	0.1193	−1.01168
25°	0.1392	−0.29428	−0.0283	−1.07599	0.1100	−1.08474

the increased planarity, A'_{33} also becomes larger in magnitude, with the exception of A'_{33} (5) which remains essentially constant.

The anisotropic hyperfine splitting produced by the proton in position 4 is given by the sum of two positive terms both increasing with decreasing temperatures: $A'_{33}\mathcal{O}_{33}$ and the isotropic splitting a_4 which should increase since the negative spin density on the adjacent carbon becomes more negative when reducing the degree of twisting. This prediction agrees with the experimental temperature dependence of the coupling constant of the proton in position 4. The discontinuity at the transition point depends on the sharp increase of the degree of alignment $\mathcal{O}_{33}$ in the nematic mesophase.

For position 3 and 5 the spin density is positive, and, therefore, the isotropic splitting is negative. The anisotropic splitting is then given by two terms having opposite signs; the positive $A'_{33}\mathcal{O}_{33}$ which would lead to a decrease of these splittings with alignment does not counter balance the increase of spin density and hence of a, so that the total effect is an increase of the splittings in the nematic region. This is more evident for the proton in position 3 whose A'_{33} component of the hyperfine tensor in the nonplanar conformation is much smaller then for the proton in position 5. At low temperature the effect of alignment seems instead to prevail and gives rise to the slight decrease of these splittings.

This model explains qualitatively the experimental trends, but we can also try to make an approximate estimate of the degree of deformation induced by the liquid crystals on the 2-trithienlymethyl radical. The degree of twisting of the thiophene rings at a given temperature can be deduced from the knowledge of the isotropic splitting constants in the nematic mesophase and of the calculated spin densities at given rotation angles.

The value of a isotropic may be calculated from the equation $a = \bar{a} - A'_{33}\mathcal{O}_{33}$. The

proton in position 5 is the more suitable for this determination as its A'_{33} component of the hyperfine tensor is, in practice, independent of the conformation.

At 116°C $\bar{a}_5$ is equal to -8.25 MHz, A'_{33} is known from calculations and $\mathscr{O}_{33}$ can be evaluated as -0.17 from the increase in the splitting of the proton in position 4 which is almost completely due to the alignment in the nematic mesophase. Moreover, this value is typical for similar molecules dissolved in the same solvent (*1*). Then the isotropic splitting a_5 may be calculated as -8.43 MHz. The determination of the increase in a due to the squashing of the radical requires also the knowledge of its value in absence of deformation from the liquid crystal. Since the spectra recorded in TBP show no temperature dependence of the proton splittings in the same temperature range, we may
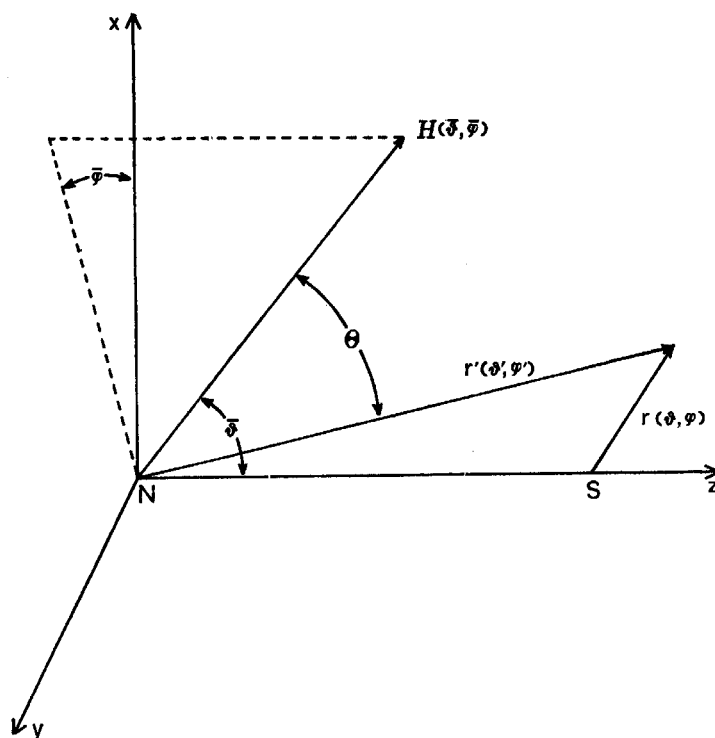

FIG. 4. The axis system for a *N*-*S* fragment with the nucleus *N* on the nodal plane of the $3p_z$ orbital centered on *S*.

assume that this is also the case in 4,4′-dimethoxyazoxybenzene and use the value of -8.09 MHz observed above the nematic-isotropic transition point. The increase in the isotropic hyperfine splitting constant is then 0.34 MHz.

Assuming a rotation angle of 25° for the unperturbed radical, the increase in a_5 of 0.34 MHz may be calculated from McLachlan spin densities to correspond to a reduction of twisting of 7°. This angle is not greatly dependent on the assumed degree of order, since for $\mathscr{O}_{33} = -0.1$ and -0.3, values of 5° and 11°, respectively, may be determined.

APPENDIX

The expressions for calculating the hyperfine tensor resulting from the dipolar interaction between a nucleus *N* and an electron contained in a $3p_\pi$ orbital on a nucleus *S* have been derived following the treatment by McConnell and Strathdee for a $2p_\pi$

orbital and using the same approximations (6). The $3p_\pi$ atomic orbital centered on S with its symmetry axis parallel to the x-axis of Fig. 4 is

$$3p_x = \left(\frac{2K^3}{5\cdot3^8\,\pi}\right)^{1/2} \rho^2 \sin\vartheta \cos\varphi e^{-\rho/3}, \qquad [\text{A-1}]$$

where $K = Z/a_0$ and $\rho = Kr$, Z being the effective nuclear charge.

The dipolar interaction integral is

$$D = \left\langle 3p_x \left| \frac{1}{(r')^3}[1 - 3\cos^2\Theta] \right| 3p_x \right\rangle, \qquad [\text{A-2}]$$

where Θ is the angle between $\mathbf{r}'$ and the external magnetic field $\mathbf{H}$. Substituting [A-1] in [A-2] we obtain

$$D = \frac{2}{5\cdot3^8\,\pi} \int\int\int \frac{1}{(r')^3}[1 - 3\cos^2\Theta]e^{-2\rho/3}\rho^6 \sin^3\vartheta \cos^2\varphi \, d\rho \, d\vartheta \, d\varphi. \qquad [\text{A-3}]$$

To perform the integration is convenient to expand $(1 - 3\cos^2\Theta)$ as an explicit function of the integration variables using the addition theorem for Legendre polynomials and then transform to the polar coordinates ϑ, φ, r centered on atom S using the equations:

$$r'\sin\vartheta' = r\sin\vartheta, \qquad [\text{A-4}]$$

$$r'\cos\vartheta' = r\cos\vartheta + R, \qquad [\text{A-5}]$$

$$r' = |(r^2 + R^2 + 2rR\cos\vartheta)^{1/2}| = (1/K)|(\rho^2 + 4a^2 + 4a\rho\cos\vartheta)^{1/2}|, \qquad [\text{A-6}]$$

where $a = KR/2$.

The integration on the angular variables ϑ and φ is now identical to that given by McConnell and Strathdee and gives

$$D = -\frac{K^3}{5.3^8}\left\{P_{20}(\cos\vartheta)\left[\frac{2}{3a^3}\mathscr{T}_6\Big|_0^{2a} - \frac{1}{5a^5}\mathscr{T}_8\Big|_0^{2a} - \frac{16}{15}\mathscr{T}_3\Big|_{2a}^\infty\right]\right.$$

$$\left. + \cos2\bar{\varphi}P_{22}(\cos\vartheta)\left[\frac{1}{60a^5}\mathscr{T}_8\Big|_0^{2a} + \frac{8}{15}\mathscr{T}_3\Big|_{2a}^\infty\right]\right\}, \qquad [\text{A-7}]$$

indicating with $\mathscr{T}_n\big|_s^t$ the integral

$$\mathscr{T}_n\big|_s^t = \int_s^t \rho^n e^{-2\rho/3} \, d\rho. \qquad [\text{A-8}]$$

The integration on ρ can be easily carried out, with the result

$$D = \{P(1 - 3\cos^2\vartheta) + Q(\cos^2\vartheta - 1)\cos2\bar{\varphi}\}, \qquad [\text{A-9}]$$

where P and Q are defined by the Eqs. [6] and [7].

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