Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: G. R. Luckhurst (1973): Magnetic Resonance Studies of Thermotropic Liquid Crystals, Molecular Crystals and Liquid Crystals, 21:1-2, 125-159

To link to this article: http://dx.doi.org/10.1080/15421407308083316

Molecular Crystals and Liquid Crystals. 1973. Vol. 21, pp. 125–159
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Magnetic Resonance Studies of Thermotropic Liquid Crystals†

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Received November 3, 1972

1. Introduction

It is relevant to begin this review by asking why it should be devoted to a *technique* for investigating the properties of liquid crystals rather than the *properties* themselves. There are a variety of responses to such a question. For example magnetic resonance spectroscopy, unlike many techniques, is able to provide information at the molecular level because the step from a spectrum to a molecular property can usually be taken with complete certainty. Secondly, the technique may be employed to probe both the static and dynamic properties of the system although we shall only be concerned with the static properties. Finally, this branch of spectroscopy may be employed to study a wide range of problems. As an indication of this versatility consider the following aspects of liquid crystals which have been investigated by magnetic resonance: the orientational order in cholesteric, nematic and smectic mesophases; anisotropic solute–solvent interactions in liquid-crystalline solutions; the material constants in continuum theory, the perturbation of the director by several constraints; magnetohydrodynamics in the nematic mesophase; the magnitude and dynamics of thermal fluctuations; the rate and nature of molecular reorientation with respect to the director. It is clearly impossible to describe all of these examples of the applications of magnetic resonance spectroscopy in detail. Instead we shall attempt to concentrate on the physics of just a few applications in order to illustrate the power and potential of the technique in studying liquid crystals.

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† Plenary Lecture presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

In this review we shall be largely concerned with studies employing electron resonance and nuclear magnetic resonance spectroscopy. This should not be taken to imply that other branches of magnetic resonance such as pure quadrupole resonance and Moessbauer spectroscopy are unimportant but simply that their application to the investigation of liquid crystals has yet to mature.

2. Revision

Magnetic resonance is now a well understood branch of spectroscopy and there are a number of texts which describe the basic principles.(1) In addition there are several articles which review the use of liquid crystals as solvents in both nuclear magnetic resonance(2) and electron resonance.(3) There are also two reviews which describe the application of magnetic resonance to the study of liquid crystals.(4,5) Despite this apparent wealth of information it is nonetheless appropriate to consider briefly the form of the spectra which are commonly observed when investigating liquid crystals.

Let us begin by defining the terms fast and slow exchange when applied to magnetic resonance spectroscopy. Consider a situation in which a magnetic nucleus, or electron, may experience one of the two resonance frequencies ω_1 and ω_2 with equal probability. In the absence of exchange between the two environments responsible for these different frequencies the spectrum will contain two lines of equal intensity separated by $\Delta\omega$, $(\omega_1 - \omega_2)$. This situation is described as the slow exchange limit and is observed as long as $\Delta\omega^2\tau^2 > 1$ where τ is the lifetime of the nucleus in either environment. At the other extreme if the lifetime is very short then the nucleus experiences both frequencies many times and so sees their average. The spectrum therefore contains a single line at the mean frequency provided $\Delta\omega^2\tau^2 < 1$ and this is known as the fast exchange limit. The form of the spectrum for intermediate rates of exchange is complicated although a full analysis does provide a means for measuring τ.(1) In the systems with which we shall be concerned the quantity $\Delta\omega$ should be associated with the anisotropic magnetic interactions and τ is then the rotational correlation time. Thus for the dipolar couplings in nuclear magnetic resonance $\Delta\omega$ is about 10^5 Hz and so the correlation time τ must be less than $10^{-6}s$ for $\Delta\omega$ to be averaged by the reorientational diffusion. In contrast the motion must be much faster ($\tau < 10^{-8}s$) to reach the fast exchange limit in electron resonance where, for example, the anisotropy in the hyperfine interaction is typically about 10^7 Hz.

The ability of magnetic resonance to study liquid crystals stems largely from the anisotropy in the magnetic interactions which is averaged to zero when the molecule tumbles isotropically but which is only partially averaged in a liquid crystal. To emphasize this point we shall consider the nuclear magnetic resonance of an idealized nematogen whose molecules contain just two protons situated on the long molecular axis. On its own each proton interacts with the applied magnetic field of the spectrometer and would give a single line at some resonance field B_0. However each nucleus also experiences a magnetic field generated by its neighbour and this may either enhance or detract from the applied field. As a consequence of this interaction between the magnetic dipoles the single line is split into a doublet with a separation

$$\Delta B = D(3\cos^2\theta - 1)/2, \tag{1}$$

where θ is the angle between the interproton vector and the applied field. The dipolar coupling constant D is given by

$$D = 3\gamma\hbar/r^3, \tag{2}$$

where r is the interproton separation.

We shall now use these simple results to discuss the form of the nuclear magnetic resonance spectrum obtained for the isotropic and nematic mesophase of this idealized liquid crystal. In the isotropic phase, provided the molecular reorientation is fast, the dipolar splitting is averaged to zero and so the spectrum contains a single line; this is shown in Fig. 1a. This spectrum may appear unfamiliar but it is simply the first derivative of the more usual absorption spectrum. This particular form of display is employed in electron resonance and wide-line nuclear magnetic resonance as a means of enhancing the sensitivity of the spectrometer. At the other extreme if the motion is quenched, for example by lowering the temperature, then the observed spectrum is a sum of spectra from all orientations:

$$h(B) = \int L(B_r, B, T_2^{-1}) f(\omega)\, d\omega. \tag{3}$$

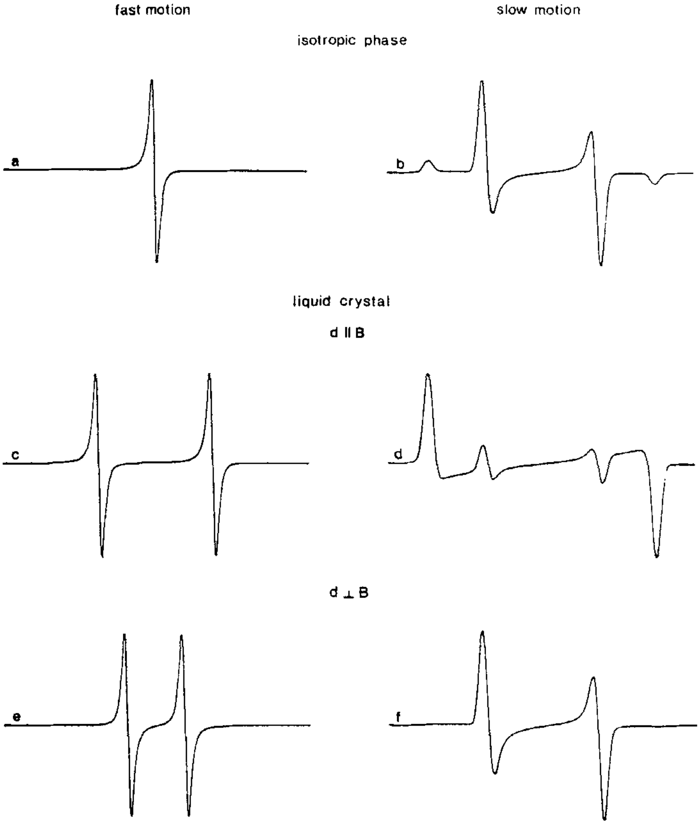

Figure 1. A selection of the nuclear magnetic resonance spectra which might be observed for a nematogen whose molecules contain just two nuclei of spin one half.

Here $L(B_r, B, T_2^{-1})$ is the lineshape which is usually lorenztian and $f(\omega)\,\mathrm{d}\omega$ is the probability of finding the molecule with an orientation between ω and $\omega + \mathrm{d}\omega$. When the molecular distribution is uniform then

$$f(\omega)\,\mathrm{d}\omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi. \tag{4}$$

The form of the spectrum calculated for such a distribution is shown in Fig. 1b and this contains two pairs of extrema separated by approximately D and $D/2$. In other words because of the derivative display spectra from molecules with their interproton vector both parallel and perpendicular to the magnetic field dominate the observed spectrum. The lines separated by $D/2$ are more intense than those with spacing D because there is a greater probability of finding the field perpendicular than parallel to the molecular symmetry axis.

The situation is quite different for the nematic mesophase. Here the magnetic field in the spectrometer will align the director parallel to the field because of the anisotropy in the diamagnetic susceptibility which is magnified by the extensive angular correlation in the mesophase. As a consequence the mesophase is macroscopically anisotropic and so, in the limit of fast exchange, the dipolar splitting is only partially averaged by the molecular reorientation. The spectrum from the mesophase therefore consists of two lines with a separation

$$\overline{\Delta B} = DS, \tag{5}$$

where S is the alignment factor $(3\,\overline{\cos^2\theta - 1})/2$ originally introduced by Zwetkov.⁽⁶⁾ The form of this spectrum is shown in Fig. 1c for S equal to 0.5. Suppose the molecular motion could be quenched while still maintaining the alignment of the director parallel to the magnetic field. The observed polycrystalline spectrum would again be a sum of spectra from all orientations and hence the extrema would still occur at the same positions as for an isotropic distribution. However the probability of finding the field parallel to the interproton vector is now greater than that of finding it perpendicular and so the peaks separated by D will be more intense than those separated by $D/2$. The spectrum shown in Fig. 1d was simulated for such a situation using the anisotropic distribution function:

$$f(\omega)\,\mathrm{d}\omega = \exp\,(a\cos^2\theta)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi, \tag{6}$$

which is consistent with the Maier–Saupe theory of the mesophase.⁽⁷⁾ The value of a (3.485) used in the calculation was chosen to yield an orientational order, S, of 0.5.

If the molecular motion is quenched then rotation of the sample tube will change the orientation of the director with respect to the magnetic field. When the director is orthogonal to the field there is an increase in the probability of finding the interproton vector perpendicular to the field and so the intensity of the inner pair of lines increases at the expense of the outer. In this configuration the probability of finding the interproton vector at an angle θ to the director is still given by the distribution in Eq. (6). However, the probability of finding the interproton vector at an orientation ω with respect to the magnetic field is$^{(8)}$

$$f(\omega)\,\mathrm{d}\omega = \exp\,(a \sin^2\theta \sin^2\phi) \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi. \qquad (7)$$

The spectrum in Fig. 1f was simulated using this angular distribution function; a was again set equal to 3.485.

Even when the molecular motion is fast rotation of the sample tube will change the orientation of the director but this is realigned parallel to the field almost immediately. There are however ways by which the orientation of the director can be changed and we shall discuss these in Secs. 7 and 8. At the moment we are simply concerned with the angular dependence of the magnetic resonance spectrum. Since the rapid motion with respect to the director only partially averages the anisotropic magnetic interactions the dynamic molecule may be thought of as a static species in which the interactions are still anisotropic but cylindrically symmetric tensors.$^{(9)}$ The symmetry axis for these tensors is parallel to the director and so the angular dependence of the dipolar splitting is identical to that in Eq. (1) but with D replaced by the partially averaged quantity $\tilde{D}$;

$$\tilde{D} = DS. \qquad (8)$$

Thus the dipolar splitting $\overline{\Delta B}(\gamma)$ when the director makes an angle γ with the magnetic field is

$$\overline{\Delta B}(\gamma) = \tilde{D}(3 \cos^2 \gamma - 1)/2. \qquad (9)$$

The line separation when the director is orthogonal to the magnetic field is just one half its value when the director is parallel to the field; this situation is shown in Fig. 1e.

The last possibility which we shall consider is, if the director is not uniformly aligned with respect to the magnetic field, the rate of director motion is slow but the rate of molecular reorientation about the director is fast. Under such conditions the observed spectrum is a sum of spectra from all orientations of the director. That is, the spectrum is equivalent to the polycrystalline form encountered previously in which the resonance fields are calculated using partially averaged magnetic interactions. Thus

$$h(B) = \int L(\tilde{B}_r, B, T_2^{-1}) f(\omega)\,\mathrm{d}\omega, \tag{10}$$

where $f(\omega)\,d\omega$ is now the probability of finding the director with an orientation between ω and $\omega + \mathrm{d}\omega$.

In the following sections we shall illustrate the application of the ideas revised in this section to the study of liquid crystals.

3. The Orientational Order

The first study of liquid crystals bymagnetic resonance spectroscopy was the determination of the long range orientational order S in the nematic mesophase of 4,4′-dimethoxyazoxybenzene.(10) As we have seen this parameter may be extracted, from the observed dipolar splitting because the molecular motion is frequently fast in most nematic mesophases. Often, if the number of magnetic nuclei in the molecule is large, the numerous dipolar splittings cannot be adequately resolved and for such systems the orientational order must be determined from the second moment:

$$\langle \Delta B^2 \rangle = \frac{\int_0^\infty (B - \langle B \rangle)^2 h(B)\,\mathrm{d}B}{\int_0^\infty h(B)\,\mathrm{d}B}, \tag{11}$$

of the spectrum $h(B)$.(1) As Weber(11) showed, this second moment is proportional to S^2. There is an alternative method for measuring the order if the molecules constituting the nematogen contain a nucleus, such as ^{14}N or ^{2}D, with a spin equal to or greater than one. By recording the nuclear magnetic resonance spectra of these nuclei it is possible to observe a quadrupole splitting which, like the dipolar splitting, is also proportional to the order.(12) This possibility is attractive because the spectra are usually uncomplicated by other splittings and because many liquid crystals contain nitrogen nuclei. Unfortunately there is a sensitivity problem associated with ^{14}N nuclear magnetic resonance spectra and they have only been reported for 4,4′-dimethoxyazoxybenzene.(13)

All of these alternatives for determining S in a nematic mesophase have been applied to the popular nematogen 4,4′-dimethoxyazoxybenzene and the results for most of these investigations(14) are

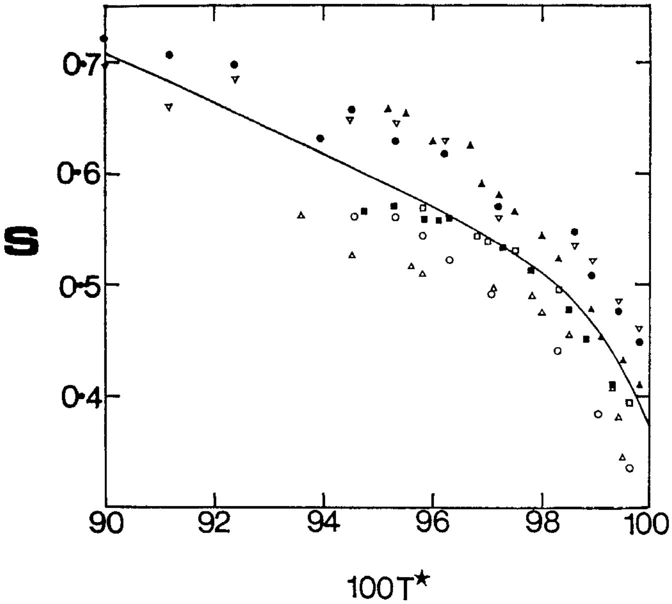

Figure 2. The dependence of the orientational order S for 4,4′-dimethoxyazoxybenzene on the reduced temperature T/T_K. The legend for the various symbols is to be found in Ref. 14.

included in Fig. 2. The large scatter in the values for S is clearly unsatisfactory and can, in part, be attributed to experimental error in the earlier determinations. In addition all of these techniques require an accurate knowledge of the molecular geometry to be able to calculate the order. We can illustrate this point by considering the quadrupole splitting in the deuteron magnetic resonance spectrum of 4,4′-dimethoxyazoxybenzene with deuterons *meta* to the azoxy linkage.(12) The quadrupole splitting is

$$\overline{\Delta B} = 3SQ_{zz}, \tag{12}$$

where Q_{zz} is the component of the quadrupole tensor parallel to the molecular long axis (cf. Eq. (5)). The quadrupole tensor for an aromatic deuteron has cylindrical symmetry about the C—D bond with a component $Q_{\parallel}$ parallel to the symmetry axis. Thus for this example Q_{zz} is related to $Q_{\parallel}$ by

$$Q_{zz} = \frac{(3\cos^2\phi - 1)}{2}\,\frac{(3\cos^2\gamma - 1)}{2}\,Q_{\parallel}, \tag{13}$$

where ϕ is the angle made by the *para* axis with the long axis and γ is the angle between the C—D bond and the *para* axis. This relation is derived by assuming free rotation of the benzene rings about the *para* axis.(12) Unless ϕ is determined by molecular symmetry it has to be estimated with the aid of molecular models; for 4,4′-dimethoxyazoxybenzene it is guessed to be 10°.(15) In an undistorted system γ should be 60° but if this value is used in Eq. (13) the orientational order is found, from the quadrupole splitting of 14.80 gauss, to be 0.280 at 120 °C. This value is unreasonably small since S should be about 0.5 at this temperature. To account for the discrepancy it is suggested that the structure is distorted with γ equal to 57.5°(12) which then yields the more reasonable value of 0.523 for S. This reduction in the angle γ of 2.5° is quite acceptable; indeed distortions of a similar magnitude have been detected by studying the nuclear magnetic resonance spectra of several substituted benzenes dissolved in a liquid-crystal solvent.(16)

Although this analysis of the quadrupole splitting would seem to be realistic is should be noted that there is another interpretation.(17) Even though a molecule of the nematogen is oriented by a cylindrically symmetric potential there is no reason to suppose, as Zwetkov(6) does, that the ordering matrix(2,18) **S** is also cylindrically symmetric. Strictly the low molecular symmetry of the molecule would demand a deviation of **S** from cylindrical symmetry and so the quadrupole splitting should be:

$$\overline{\Delta B} = 3S_{zz}Q_{zz} + 3(S_{xx} - S_{yy})(Q_{xx} - Q_{yy})/2. \tag{14}$$

Here x, y and z are the principal axes for **S** and are determined by reference to molecular models. The equation for $\overline{\Delta B}$ now contains two unknowns even if the principal axes can be obtained unambiguously. However the second moment of the proton spectrum is found to be insensitive to the parameter $(S_{xx} - S_{yy})$ and at 120 °C gives a value for S_{zz} of 0.516. When this is used in conjunction with Eq. (14) for the quadrupole splitting, $(S_{xx} - S_{yy})$ is found to be 0.07,(17) although it remains to be seen if the magnitude of this deviation from cylindrical symmetry is reasonable. In particular it will be interesting to see if this difference of 0.07 is consistent with a uniaxial as opposed to a biaxial state for the mesophase.(19)

Knowledge of the orientational order is important for an understanding of the intermolecular forces responsible for the existence of the liquid-crystalline state. Many of the more tractable statistical theories of the nematic mesophase are based on the molecular field theory⁽²⁰⁾ in which the interaction of a molecule with its neighbours is replaced by a field. In the first of these theories the anisotropic interaction between a pair of rod-like molecules was assumed to be dominated by London dispersion forces.⁽⁷⁾ This theory has since been extended to include all pairwise anisotropic interactions and the pseudo-potential was shown to be⁽¹⁴⁾

$$U(\cos\theta) = \sum_{L(\text{even})} \bar{u}_L \bar{P}_L P_L(\cos\theta), \tag{15}$$

where θ is the angle made by the molecular long axis with the director. The angular dependence of the pseudo-potential is contained in the Legendre polynomials $P_L(\cos\theta)$. The expansion coefficients are defined as

$$\bar{u}_L = (1/\rho)\int \sum_n u_{LL:n}(r) n^{(2)}(r)\,\mathrm{d}r, \tag{16}$$

where ρ is the number density, $n^{(2)}(r)$ is the pair distribution function and the $u_{LL:n}(r)$ contain the distance dependence of the intermolecular potential.⁽²¹⁾ The ensemble averages $\bar{P}_L$ completely define the long range order in the mesophase and of these $\bar{P}_2$ is the more familiar order parameter S. The first term in the series corresponds to the Maier–Saupe theory although the coefficient $\bar{u}_2$ need not be associated with just dispersion forces. To predict the orientational order in 4,4′-dimethoxyazoxybenzene only the first two terms need be retained in the pseudo-potential. However to account for the temperature dependence of S shown in Fig. 2 it is essential to allow for the volume dependence of $n^{(2)}(r)$ and hence of the coefficients $\bar{u}_L$.⁽¹⁴⁾ The line in Fig. 2 was calculated by assuming that these expansion coefficients are given by

$$\bar{u}_L = u_L{}^0 V^{-4}. \tag{17}$$

Although the agreement between theory and experiment, indicated in Fig. 2, is very good it is not possible to use measurements of S at constant pressure to test the assumptions involved in Eqs. (15) and (17) separately. Such a distinction ought to be possible if the orientational order is measured at constant volume for then the coefficients $\bar{u}_L$ should be independent of temperature. By taking special precautions a nuclear magnetic resonance experiment can be performed at a variety of pressures and the order parameter for 4,4′-dimethoxyazoxybenzene has been determined as a function of P, V and T using such techniques.(22,23) These results have been analysed to yield the temperature dependence of S at constant volume(24) and this dependence is found to be in complete accord with the pseudo-potential in Eq. (15) restricted to the first two terms.(25) In addition the measurements at different pressures reveal that $(\partial \log_e T/\partial \log_e V)_S$ is equal to -4.0 ± 0.1 in excellent agreement with Eq. (17) obtained by fitting the results of the more usual constant pressure experiments.

4. The Anisotropic Distribution Function

Another test of the pseudo-potential is provided by a determination of the angular distribution function $f(\omega)$ of the molecule with respect to the director since

$$f(\omega)\,\mathrm{d}\omega = \frac{\exp\{-U(\cos\theta)/kT\}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}{2\pi\int\exp\{-U(\cos\theta)/kT\}\sin\theta\,\mathrm{d}\theta} \tag{18}$$

Thus knowledge of the angular dependence of $f(\omega)$ immediately gives that of the pseudo-potential and consequently the relative importance of the various terms in Eq. (15) can be gauged. Such studies are possible because the molecular motion in certain mesophases can be quenched without the sample crystallizing which would destroy any macroscopic alignment. At present there does not appear to have been any nuclear magnetic resonance studies along these lines although the technique has been used to study solute alignment in oriented glasses by electron resonance spectroscopy.(8,26) The spin probe frequently employed in such studies is vanadyl acetylacetonate because of its relatively simple spectrum; for example when the molecular motion is fast the spectrum contains eight lines because of the interaction of the unpaired electron with the spin ($I = 7/2$) of vanadium. In a frozen glass the spectrum is found to contain twice as many lines because the magnetic interactions are cylindrically symmetric. In fact, apart from the increase in the number of spectral lines, the situation is entirely comparable to the nuclear magnetic resonance example described in Sec. 2. Thus there are eight hyperfine lines separated by $A_{\parallel}$ originating from molecules with the V—O bond parallel to the magnetic field and another eight with spacing $A_{\perp}$ from molecules with their planes parallel to the field. Such a spectrum is shown in Fig. 3*a* for the director parallel to the magnetic field. Since the molecular planes of the spin probe tend to be aligned parallel to the director the probability of finding the field along the V—O bond is small as are the intensities of the $A_{\parallel}$ lines; indeed these lines which are marked by closed circles in Fig. 3b cannot be observed in Fig. 3a. However because the motion in the frozen nematic mesophase of 4′-methoxybenzylidene-4-*n*-butylaniline is quenched rotation of the sample also rotates the

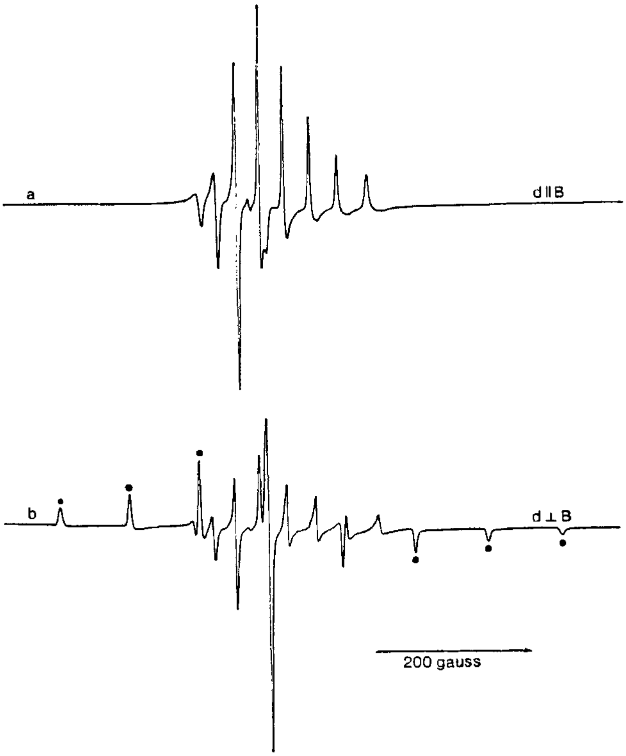

Figure 3. The spectrum of vanadyl acetylacetonate dissolved in a frozen glass of 4′-methoxybenzylidene-4-*n*-butylaniline with the director (a) parallel and (b) perpendicular to the magnetic field.

director and as a consequence the $A_\parallel$ lines increase in intensity as can be seen from Fig. 3b. From a detailed analysis(27) of the angular dependence of this intensity it is possible to obtain the angular distribution function.(8) For the same spin probe in a frozen binary mixture of 60% 4-methoxybenzal-4-amino-α-methylcinnamic acid-*n*-propyl ester and 40% 4-methoxyazobenzene-4-oxy caproate it would seem that the terms involving $P_4(\cos\theta)$ are important especially when the orientational order is high.(27) In contrast the pseudo-potential for vanadyl acetylacetonate dissolved in 4-methoxybenzal-4-amino-α-methylcinnamic acid-*n*-propyl ester at room temperature appears to be dominated by the quadratic term in $P_2(\cos\theta)$.(26) In these experiments even though the molecular motion with respect to the director is slow the reorientation of the director is relatively fast and so the angle made by the director with the magnetic field was changed by aligning the mesophase with an electric field. The analysis of both sets of experiments assumes that the ordering matrix for the spin probe is cylindrically symmetric about the V—O bond. In fact the molecular symmetry is lower than cylindrical and so the angular dependence of the pseudo-potential is

$$U(\theta,\phi) = \sum_{\substack{L(\text{even})\\ m}} (4\pi/2L+1)^{1/2} c_{L,m}\, Y_{L,m}(\theta,\phi), \tag{19}$$

where θ and ϕ define the orientation of the magnetic field in the molecular coordinate system. If the summation is restricted to just the quadratic terms then it is possible to fit the angular dependence of the intensity of the spectral lines for this spin probe dissolved in a frozen glass of 4′-methoxybenzylidene-4-*n*-butylaniline.(28) The results of this analysis give the following elements for the ordering matrix

$$S_{zz} = 0.50,$$

and

$$S_{xx} - S_{yy} = 0.14, \tag{20}$$

where the axis system is shown in Fig. 4. Such a large deviation from cylindrical symmetry may not be unrealistic in view of the results for toluene dissolved in 4-ethoxybenzylidene-4′-*n*-butylaniline where the elements of the ordering matrix(29) are

$$S_{zz} = 0.0847,$$

and

$$S_{xx} - S_{yy} = -0.0743; \tag{21}$$

the coordinate system is also shown in Fig. 4. If, on the other hand, the spin probe is taken to be cylindrically symmetric then the quartic terms have to be included in the pseudo-potential.

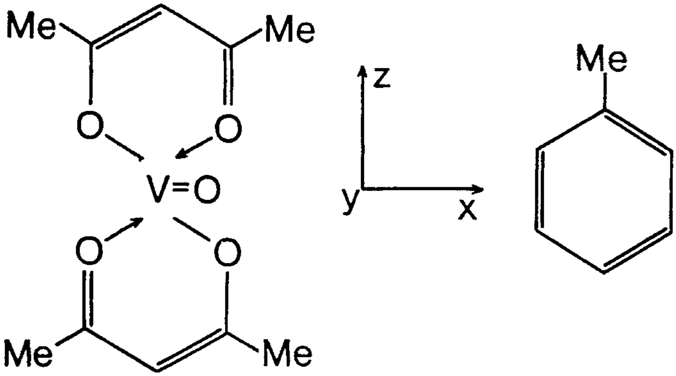

Figure 4. The coordinate system for vanadyl acetylacetonate and toluene.

Clearly to distinguish between these two possibilities it is necessary to find a spin probe for which the cylindrical symmetry of the ordering matrix is dictated by the molecular symmetry. This has not proved to be possible although there are numerous examples of diamagnetic species with the requisite symmetry. Often these species possess a photo-excited triplet state which can be used as a spin probe for the investigation of a frozen mesophase. Krebs and Sackmann⁽³⁰⁾ have taken advantage of this technique to study the frozen nematic mesophase formed by a 1.85 : 1 mixture of cholesteryl chloride and cholesteryl laurate. The species employed as a spin probe was the triplet state of triphenylene-d_{12} whose electron resonance spectrum was measured as a function of the angle between the director and the applied field. Unfortunately it has not proved possible to analyse these spectra with sufficient accuracy to determine the relative importance of the quartic terms in the pseudo-potential.⁽³⁰⁾ In addition the technique cannot be extended to normal nematogens because the aromatic character of their constituent molecules severely reduces the triplet lifetime.

Quite similar concepts to those that we have just discussed are employed in studies of the nematic and smectic mesophases which use Moessbauer spectroscopy.(31) However at present the accuracy of the technique is unable to distinguish between the various forms of the pseudo-potential. Indeed quite accurate measurements will almost certainly be required to detect the quartic terms in the pseudo-potential given by Eq. (15). Thus the ratio of the coefficient for the term involving $P_4(\cos\theta)$ to that for the $P_2(\cos\theta)$ term is $\bar{u}_4\bar{P}_4/\bar{u}_2\bar{P}$ and for a typical nematogen such as 4,4′-dimethoxyazoxybenzene this ratio is only -0.07 even when the order parameter $\bar{P}_2$ is as high as 0.6.

5. The Ordering Matrix for Spin Probes

As we saw there are certain difficulties in using nuclear magnetic resonance spectroscopy to determine the orientational order of a nematic mesophase. There are however no such problems in employing both forms of magnetic resonance spectroscopy to determine the ordering matrix for a spin probe dissolved in a nematic mesophase. Investigations of the solute ordering matrix are of considerable importance not only because they can provide valuable information concerning the form of the anisotropic solute–solvent interaction but they also reflect the solvent order.(32) Although the solute ordering matrix is readily determined experimentally its theoretical interpretation is less straightforward. The ordering matrix is related to the pseudo-potential for the solute and, for rod-like solutes, this potential is calculated from a molecular field model(33) to be

$$U^{(1)}(\cos\theta) = \sum_{L} \{(1-x)\bar{u}_L^{(12)}\overline{P_L^{(2)}} + x\bar{u}_L^{(11)}\overline{P_L^{(1)}}\}P_L^{(1)}(\cos\theta), \tag{22}$$

for a single component dissolved in the nematic mesophase. In this equation x is the mole fraction of solute, $\bar{u}_L^{(12)}$ is the solute–solvent interaction analogous to that introduced in Eq. (16), $\bar{u}_L^{(11)}$ is the corresponding solute-solute parameter and $\overline{P_L^{(1)}}$ is the solute orientational order. The orientational order of the solvent $\overline{P_L^{(2)}}$ may be calculated from the pseudo-potential

$$U^{(2)}(\cos\theta) = \sum_{L(\text{even})} \{(1-x)\bar{u}_L^{(22)}\overline{P_L^{(2)}} + x\bar{u}_L^{(12)}\overline{P_L^{(1)}}\}P_L^{(2)}(\cos\theta), \tag{23}$$

for the nematic solvent. The difficulty in using these equations rests in their coupling via the solute-solvent term in $\bar{u}_L^{(12)}$. Of course this cross term is important only when the solute concentration is high, as in nuclear magnetic resonance experiments. Consequently the simpler approaches[34] often adopted to interpret the ordering matrices determined by nuclear magnetic resonance are, at best, only qualitatively correct.

However when the solute concentration is vanishingly small the equations are decoupled, the pseudo-potential for the solute reduces to

$$U^{(1)}(\cos\theta) = \sum_L \bar{u}_L^{(12)} \overline{P_L^{(2)}} P_L^{(1)}(\cos\theta), \tag{24}$$

and $U^{(2)}(\cos\theta)$ is then identical to that for the pure nematic mesophase. Of course it is still difficult to extract the solute–solvent interaction parameters unless the solvent order $\bar{P}_L$ is known. If this is the case then the mixed interaction parameters can be determined by fitting the temperature dependence of the solute order $\overline{P_2^{(1)}}$. The solute concentration *is* vanishingly small in electron resonance experiments and the order of a spin probe is readily obtained from the change in the hyperfine spacing on partial alignment in the mesophase.[35] Since the hyperfine interaction has a scalar component the hyperfine spacing $\tilde{A}_\parallel$ when the director is parallel to the magnetic field is

$$\tilde{A}_\parallel = a + (2/3)\sum_{ij} S_{ij} A'_{ij}, \tag{25}$$

where $\mathbf{A}'$ is the anisotropic hyperfine tensor.[5,36] The ordering matrix for the spin probe (3-spiro-[2′N-oxyl-3′,3′-dimethyloxazolidine])5α-cholestane is found to be cylindrically symmetric and so the hyperfine shift gives the order $\overline{P_2^{(1)}}$ for the long molecular axis.[37] The temperature dependence of $\overline{P_2^{(1)}}$ for the spin probe dissolved in 4,4′-dimethoxyazoxybenzene is given in Fig. 5. The solid line in the figure was calculated using the pseudo-potential given in Eq. (24) restricted to just the first two terms. However to achieve this excellent agreement it is necessary to assume that in these constant pressure experiments the volume dependence is the same as that found for the pure solvent.[37] It is difficult to relate the interaction parameters determined in this way to the molecular structure of the paramagnetic spin probes when they are so complex. However with

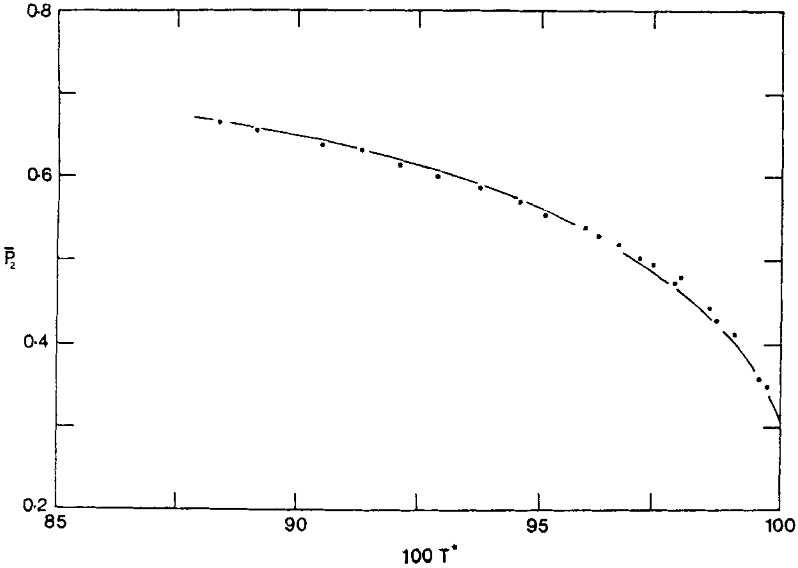

Figure 5. The temperature dependence of the orientational order $\bar{P}_2$ for a nitroxide spin probe dissolved in the nematic mesophase of 4,4′-dimethoxy-azoxybenzene.

the increase in sensitivity of nuclear magnetic resonance provided by the fourier transform technique it should be possible to study the ordering of structurally simpler diamagnetic spin probes.

Although the procedure for studying the orientational order of a spin probe cannot yield the order of the solvent it can often provide qualitative information concerning the molecular organization in a mesophase. Indeed this approach has been employed with some success to study certain of the many smectic morphologies which have been discovered.⁽³⁸⁾ For example 4-*n*-butyloxybenzylidene-4′-acetoaniline exists as a nematic phase between 110 °C and 98 °C when there is a transition to a smectic *A* mesophase which is readily supercooled. The orientational order found⁽³⁹⁾ for the spin probe (3-spiro-[2′N-oxyl-3′,3′-dimethylaxazolidine])5α-cholestane in both phases is shown in Fig. 6. In the nematic phase the order parameter shows its customary marked temperature dependence whereas in the smectic phase the order is rather insensitive to temperature. There is also a discontinuity in the order parameter at the nematic–smectic transition which demonstrates the first-order character of

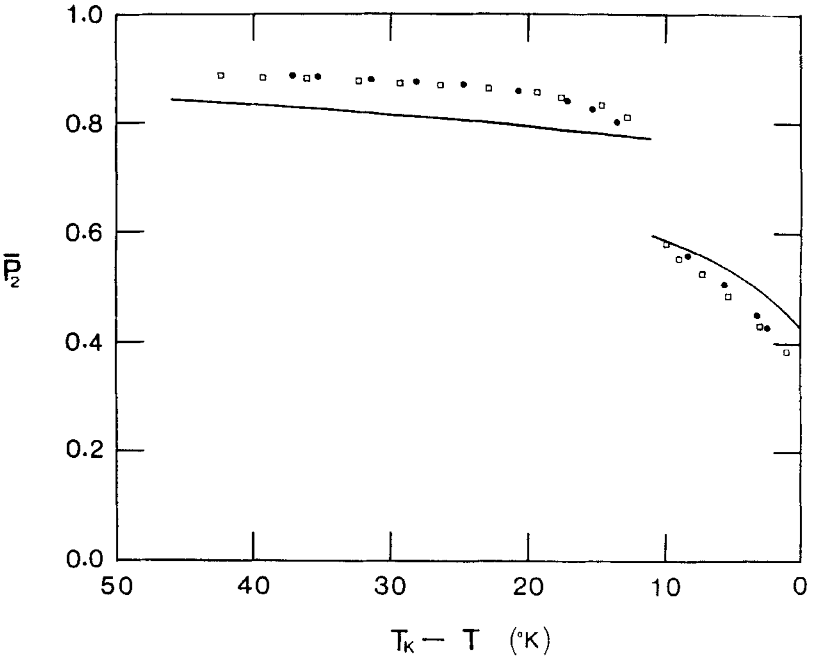

Figure 6. The orientational order of a nitroxide spin probe dissolved in the nematic and smectic *A* phases of 4-*n*-butyloxybenzylidene-4′-acetoaniline.

the transition. The same mesogen has also been investigated using vanadyl acetylacetonate as a spin probe but here the orientational order was found to have the same temperature dependence in both phases and no discontinuity at the nematic-smectic transition.(40) This difference is probably a result of the large linewidths found for vanadyl acetylacetonate and which complicate the spectral analysis. The temperature dependence found for the nitroxide can be understood in a simple phenomenological fashion.(39) The pseudopotential in the nematic mesophase is given by the Maier–Saupe theory:

$$U(\cos\theta) = \bar{u}_2 \bar{P}_2 P_2(\cos\theta), \tag{26}$$

and at the transition to the smectic phase $|\bar{u}_2|$ might be expected to increase because of the change in the molecular organization. If $\bar{u}_2^{(\text{nematic})}$ is calculated from the nematic–isotropic transition and $\bar{u}_2^{(\text{smectic})}$ obtained by fitting the change in $\bar{P}_2$ at the transition to the smectic phase then the predicted temperature dependence of $\bar{P}_2$ is given by the solid lines in Fig. 6. Since no attempt was made to allow for solute–solvent interactions the agreement is reasonable. More rigorous attempts(41) to calculate the orientational order in a smectic A phase by including the spatial order in a molecular field analysis also predict a temperature dependence for $\bar{P}_2$ in close agreement with the observations for the spin probe.

6. Thermal Fluctuations of the Director

It is invariably assumed that a magnetic field, greater than a few kilogauss, is sufficient to align the director, in a nematic mesophase, exactly parallel to the field. However such fields are quite unable to quench the thermal fluctuations in the director which are responsible for the strong light scattering by the mesophase.(42) Consequently the director adopts a range of orientations with respect to the field although the most probable orientation is parallel to the field. The correlation time for these fluctuations is estimated to be about $10^{-7}s$. The fluctuations are therefore fast for a nuclear magnetic resonance experiment but slow for electron resonance studies. The observed electron resonance spectrum is then a sum of spectra from all orientations of the director. Since the distribution function is expected to be steep the spread of orientations will simply broaden the spectral lines and more importantly cause them to deviate from their symmetric shape. The resulting asymmetry can be seen in Fig. 7 which shows the first two low field lines in the electron resonance spectrum of vanadyl acetylacetonate dissolved in the nematic mesophase of 4,4′-dimethoxyazoxybenzene. The dotted line is a theoretical spectrum based on the normal lorentzian lineshape and clearly emphasizes the experimental asymmetry. The observed lineshape can be calculated from the electron resonance analogue of Eq. (3) provided the distribution function $f(\omega)$ for the director is known. The form of this function has not been investigated theoretically although a reasonable form might be the gaussian distribution

$$f(\omega)\,\mathrm{d}\omega = \theta \exp(-\theta^2/\theta_0^2)\,\mathrm{d}\theta\,\mathrm{d}\phi, \tag{27}$$

where θ_0 is the root mean square fluctuation.(44) The temperature

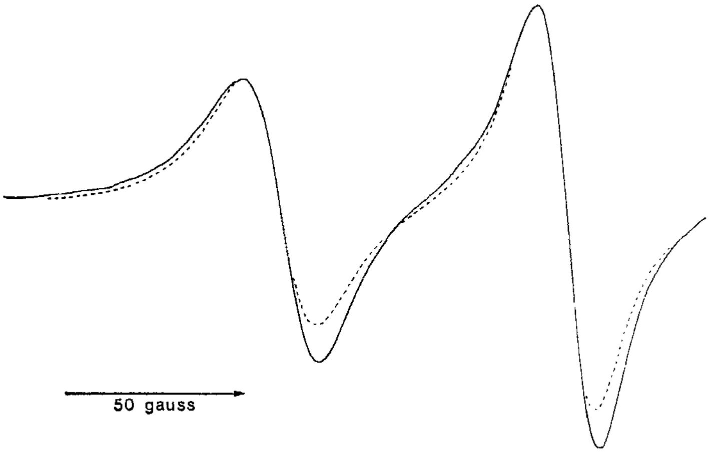

Figure 7. The first two hyperfine lines in the spectrum of vanadyl acetylacetonate dissolved in the nematic mesophase of 4,4′-dimethoxyazoxybenzene. The dotted lines show a reconstruction based on a symmetric lorentzian line shape.

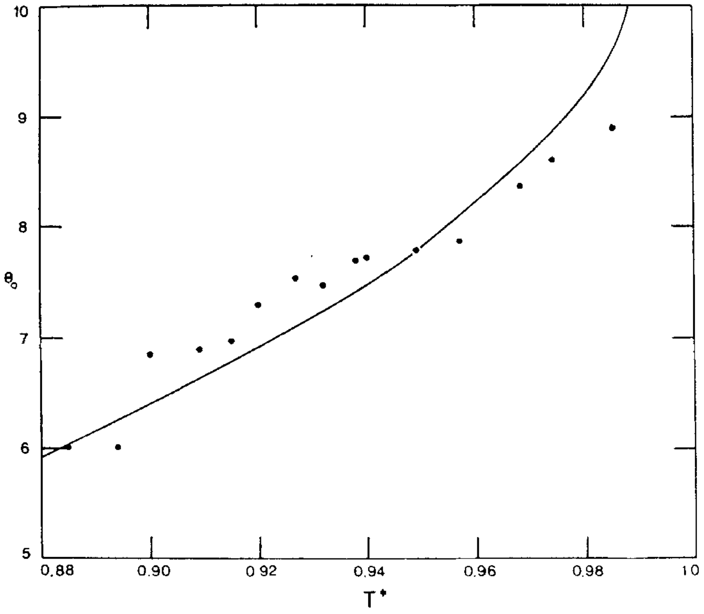

Figure 8. The temperature dependence of the root mean square fluctuation θ_0 in the director for the nematic mesophase of 4,4′-dimethoxyazoxybenzene.

dependence of θ_0 for 4,4′-dimethoxyazoxybenzene, found by fitting the spectral lineshape, is given in Fig. 8 and as expected the magnitude of the thermal fluctuations increase as the transition to the isotropic phase is approached.(45)

The mean square fluctuation $\overline{\theta_0{}^2}$ is equivalent to the auto correlation function $\overline{\mathrm{d}_x(\mathbf{r})^2}$ of the director $\mathbf{d}$ at some point $\mathbf{r}$ where x is an axis orthogonal to the preferred orientation of the director which in this case coincides with the direction of the magnetic field.(42) The magnitude of these fluctuations is given by the transform

$$\overline{d_x(\mathbf{r})^2} = (1/8\pi^3 V)\int_0^\infty \overline{\mathrm{d}_x(\mathbf{q})^2}\,\mathrm{d}\mathbf{q}, \tag{28}$$

and according to continuum theory the amplitude of the thermal fluctuation characterized by the wavevector $\mathbf{q}$ is(42)

$$\overline{\mathrm{d}_x(\mathbf{q})^2} = VkT/Kq^2. \tag{29}$$

This result is derived by assuming that the three elastic constants are equal to K and by ignoring any quenching of the fluctuations by the applied magnetic field. The theory is however only valid for wavevectors q satisfying the relation $q\lambda < 1$ where λ is some length characteristic of the system. The integral in Eq. (28) is then best evaluated by dividing the range into two parts. The first extends from 0 to $1/\lambda$ and is readily evaluated as

$$\theta_0{}^2 = kT/4\pi K\lambda. \tag{30}$$

The second contribution cannot be evaluated but since it comes from fluctuations with small wavelengths it might well be negligible. Experimentally the elastic constants are found to be directly proportional to the square of the orientational order S in the nematic mesophase(46) and so the temperature dependence of θ_0 is given by

$$\theta_0 \sim T^{1/2}/S. \tag{31}$$

The solid line shown in Fig. 8 was calculated from this result using the orientational order determined from a nuclear magnetic resonance study of 4,4′-dimethoxyazoxybenzene.(45) The agreement between the theoretical predictions and experiment is clearly excellent. We shall ignore thermal fluctuations in the remainder of this review since in electron resonance spectroscopy their effect is to broaden but not shift the line. Of course for most nuclear magnetic resonance studies the thermal fluctuations are fast and so cannot distort the shape of the spectral line. However the ordering matrix determined from the positions of these lines is now an average over the motions of the molecule with respect to the director, and of the director itself. In general it is difficult to separate these two averages unless they are uncorrelated and then the deserved ordering matrix S is related to the true ordering matrix S^0 by

$$S = \{1 - (3/2)\theta_0{}^2\}S^0. \tag{32}$$

Thus the numbers in Fig. 8 suggest that the observed ordering matrix could be as much as 15% smaller than its true value.

Finally it is important to realize that although these experiments measure the spectrum of a trace impurity dissolved in the mesophase the analysis of this spectrum does yield information relating to the pure mesophase. This situation, which will be encountered again, obtains because the probe molecule follows the ordering potential generated by the liquid crystal and so indicates the orientation of the director with respect to the magnetic field. Of course when the solute concentration is high, as in nuclear magnetic resonance, then the information from similar experiments designed to determine the orientation of the director should be associated with the liquid crystalline mixture and not the pure nematogen.

7. Electric Field Alignment of the Director

In the majority of magnetic resonance experiments involving liquid crystals the mesophase is aligned by the magnetic field present in the spectrometer. Consequently if a second constraint is now applied to the mesophase there will be a competition for the alignment of the director. This situation is analogous to that employed to determine the elastic constants with the aid of optical techniques(47) and we might suppose that an analysis of the corresponding magnetic resonance spectrum will also yield values for these constants. Two such investigations have been reported and we shall discuss them in detail shortly. For the moment we shall consider the alignment of the director by an electric field.

Providing the frequency of the applied electric field is above a certain critical value, which may be as high as 20 kHz, the alignment of the director depends solely on the anisotropy $(\epsilon_{\parallel} - \epsilon_{\perp})$ in the dielectric tensor. The electric contribution to the orientational free energy density takes the same form as the magnetic contribution $-(\frac{1}{2})\Delta\chi B^2 \cos^2 \gamma$.(42,48) For the vast majority of nematic mesophases $\Delta\chi$ is positive and so the director is aligned parallel to a magnetic field, if $\Delta\epsilon$ is also positive then the director is aligned parallel to the electric field. When the fields are orthogonal the director will be aligned parallel to the field which gives the greatest contribution to the orientational energy.(49) If however the fields make an angle α then the angle γ between the director and the magnetic field is

$$\tan 2\gamma = \frac{\sin 2\alpha}{\cos 2\alpha + \Delta\chi B^2/\Delta\epsilon E^2}\,. \tag{33}$$

The alignment of the director by high frequency electric fields has been investigated by measuring the proton magnetic resonance spectrum of the nematic mesophase of anisal-4-aminoazobenzene.(49) The spectrum contains a doublet caused by the dipolar coupling between the *ortho* protons and, as we saw in Sec. 2, the line separation depends on both the orientational order and the angle between the director and the magnetic field. The separation was measured as a function of both the angle α and the strength of the electric field with the results shown in Fig. 9. The values of γ required to plot these results were calculated from Eq. (33) with the ratio $\Delta\chi/\Delta\epsilon$ set equal to 0.375 volts cm^{-1} gauss^{-1}; this quantity was obtained from an earlier dielectric loss study of this mesophase.(50) The validity of this result and Eq. (33) may then be tested by calculating the dependence of $\overline{\Delta B}(\gamma)$ on the angle γ from Eq. (9). The result of this calculation, which is shown as the solid line in Fig. 9, is in excellent agreement with experiment.

In contrast, the interpretation of comparable electron resonance experiments employing a static electric field is not so straightforward. Basically in these experiments(51,52) the vanadium hyperfine coupling of the spin probe, vanadyl acetylacetonate, dissolved in a nematic mesophase was determined as a function of the angle between the magnetic and electric fields. The strength of the electric field was always sufficiently high to control the alignment of the mesophase. Such investigations have been reported for the two nematogens

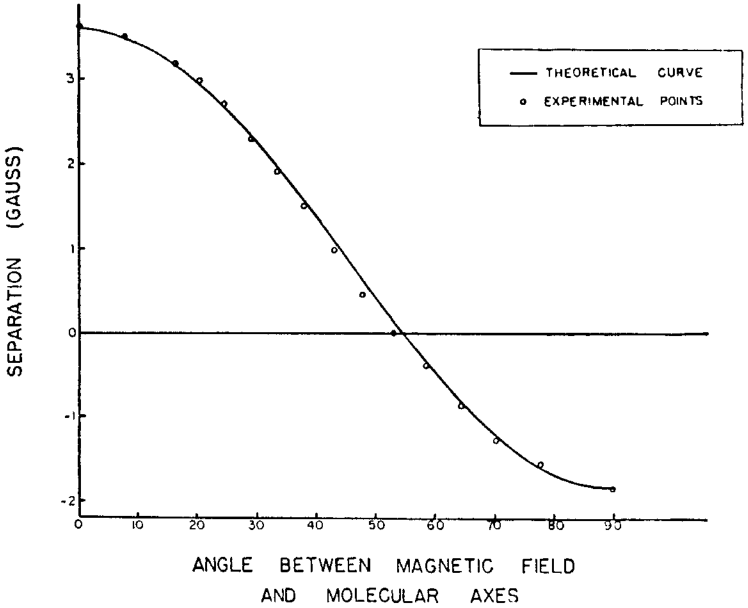

Figure 9. The angular dependence of the dipolar splitting in the nuclear magnetic resonance spectrum from the nematic mesophase of anisal-4-amino-azobenzene. [Reproduced, by permission, from *Mol. Cryst. and Liq. Cryst.*, **18**, 369 (1972)].

4,4′-dimethoxy- and 4,4′-di-*n*-heptyloxyazoxybenzene;(51,52) the results for the former nematogen are shown in Fig. 10. The electron resonance analogue of Eq. (9) for the angular dependence of the hyperfine spacing is

$$\bar{a}(\gamma) = \frac{\{\tilde{A}_\perp^2 \tilde{g}_\perp^4 + (\tilde{A}_\parallel^2 \tilde{g}_\parallel^4 - \tilde{A}_\perp^2 \tilde{g}_\perp^4)\cos^2\gamma\}^{1/2}}{\{\tilde{g}_\perp^2 + (\tilde{g}_\parallel^2 - \tilde{g}_\perp^2)\cos^2\gamma\}}, \tag{34}$$

where γ is the angle made by the director with the magnetic field and all the hyperfine interactions are expressed in field units.(9) The partially averaged g and hyperfine tensors depend on the total anisotropic tensors and the solute ordering matrix as in Eq. (25). The perpendicular components of these tensors are related to the scalar interactions and the parallel components; for the hyperfine interaction

$$\tilde{A}_\perp = (3a - \tilde{A}_\parallel)/2. \tag{35}$$

If the director is taken to be parallel to the electric field then the

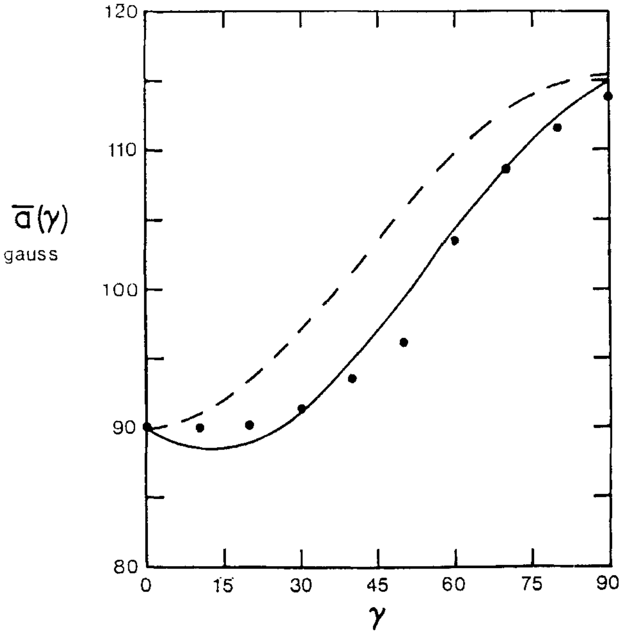

Figure 10. The angular dependence of the vanadium hyperfine splitting for the spin probe vanadyl acetylacetonate dissolved in the nematic mesophase of 4,4′-dimethoxyazoxybenzene aligned by an electric field.

angular dependence of $\bar{a}$ calculated from Eq. (34) is found to be in poor agreement with experiment as may be seen from the dashed line in Fig. 10. Presumably the director is not aligned parallel to the electric field; indeed there is an increase in the vanadium coupling constant when the electric field is applied even if it is parallel to the magnetic field. By using Eq. (34) in conjunction with the magnitude of this change then, for the mesophase of 4,4′-dimethoxyazoxybenzene at 125 °C, the director is found to make an angle of 13° with the electric field.$^{(9)}$ Of course when the two fields are inclined at an angle α although the angle θ between the director and the electric field is fixed, that between the director and the magnetic field can take values ranging from $\alpha - \theta$ to $\alpha + \theta$. However the magnetic interaction with the director, which we have so far ignored, will tend to favour the smallest angle $\alpha - \theta$ since this minimizes the magnetic contribution to the orientational free energy. If this effect dominates then the director will make a single angle, $\alpha - \theta$ with the magnetic field and the angular dependence of the coupling constant is obtained by replacing γ by $\alpha - \theta$ in Eq. (34) provided $\alpha < \pi/2$. The angular dependence of $\tilde{a}$ calculated with θ equal to 13° is shown as the solid line in Fig. 10 and is clearly in good agreement with experiment.(9)

This apparently unusual alignment of the director by a static electric field has been tentatively interpreted(9) in terms of cybotactic clusters(53) within the mesophase which are oriented by shear forces with their planes parallel to the electric field. The structure of a cluster is assumed to be similar to that of a smectic *C* mesophase in which the tilt angle is $90° - \theta$. This novel suggestion also gains some support from the corresponding study of the nematic phase of 4,4′-di-*n*-heptyloxyazoxybenzene(52) which yields a value for θ of about 35° and hence a tilt angle of 55°. This value compares reasonably well with that found for the pure smectic *C* phase of this mesogen from a wide variety of techniques including electron resonance spectroscopy.(54) In addition the notion that shear forces are important is consistent with the observation that the director in the mesophase of 4,4′-dimethoxyazoxybenzene is aligned at 10° to the direction of flow.(55)

8. Magnetohydrodynamic Behaviour of the Nematic Mesophase

If a nematic mesophase, aligned by a magnetic field, is spun about an axis orthogonal to the field then the director will experience a torque caused by the relative motion of the continuum. This is, of course, in addition to the magnetic torque which aligns the director parallel to the field. Below a certain critical spinning speed Ω_c the two torques balance one another and the director is aligned at an angle γ to the field where

$$\sin 2\gamma = \Omega/\Omega_c. \tag{36}$$

This result was originally obtained using the swarm theory of liquid crystals(56) and has since been derived rigorously from continuum theory.(57) In the latter approach the critical speed is predicted to be

$$\Omega_c = -\Delta\chi B^2/2\lambda_1, \tag{37}$$

where λ_1 is the twist viscosity coefficient which vanishes in the isotropic phase.(58) As we have seen, magnetic resonance spectroscopy is quite capable of determining the angle between the director and the applied field; consequently it can be employed to test the validity of Eq. (36) and to measure the material constant $\Delta\chi/\lambda_1$. Thus the proton magnetic resonance spectrum of the mesophase of the nematogen 4,4′-dimethoxyazoxybenzene has been measured as a function of the spinning speed.(59) The magnitude of the dipolar splitting was then used to determine the angle between the magnetic field and the director; these values were apparently in agreement with those calculated from Eq. (36) In addition the critical speed was found to increase markedly with temperature because of the decrease in the viscosity coefficient λ_1. However it was not possible to test the predictions of Eq. (36) with any great precision because the broad spectral lines found for the mesophase preclude the accurate measurement of the dipolar splitting. The spectra of spin probes dissolved in a nematic mesophase do not suffer from this disadvantage and so both diamagnetic(60) and paramagnetic(57) spin probes have been employed in experiments to test the validity of Eq. (36). As an example the dependence of the nitrogen coupling constant, for a nitroxide spin probe dissolved in Merck Phase IV, on the spinning speed is shown in Fig. 11. The theoretical dependence calculated

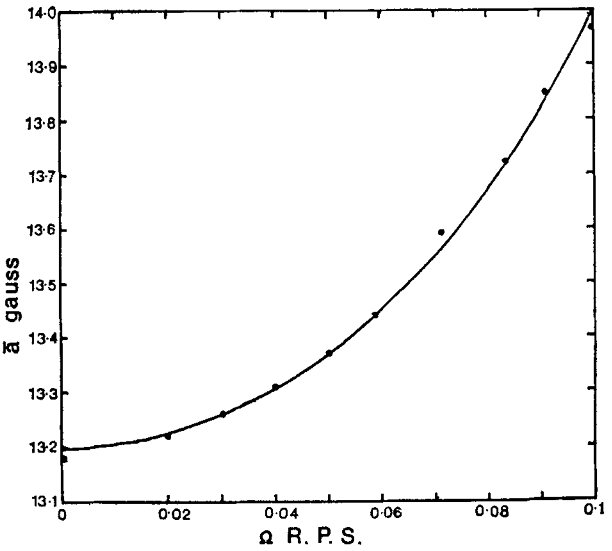

Figure 11. The dependence of the nitrogen coupling constant of a nitroxide spin probe dissolved in a nematic mesophase on the rotational speed of the sample tube.

from Eq. (34) using the angle γ predicted by Eq. (36) is in excellent agreement with experiment as we can see from the solid line in Fig. 11. This technique therefore provides a relatively straightforward yet accurate method for determining the material constant $\Delta\chi/\lambda_1$.

If the inertial term is omitted from the equation of motion for the director then above the critical speed the director is predicted to rotate with a mean angular velocity ω given by⁽⁵⁷⁾

$$\omega = (\Omega^2 - \Omega_c^2)^{1/2}. \tag{38}$$

As a consequence of the time dependence of the angle γ made by the director with the magnetic field the spacing between the spectral lines should now oscillate in time with a frequency equal to approximately twice the rotation speed of the sample tube. These fluctuations are best observed by monitoring the intensity of a spectral line as a function of time for, as the director is rotated, the spectral intensity will decrease to zero and then increase again after the director has rotated through 180°. The results of such an electron resonance experiment, using a nitroxide spin probe dissolved in Merck Phase IV, are shown in Fig. 12. Initially the director is found to rotate with the angular velocity predicted by Eq. (38). However the time spectrum in Fig. 12 shows that director rotation does not correspond to a stable state of the system and eventually the

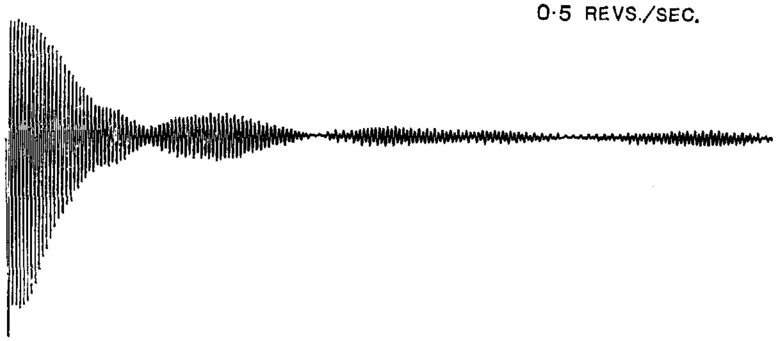

Figure 12. The time dependence of the spectral intensity for a spin probe dissolved in a nematic mesophase.

director adopts a static configuration. The distribution function for the director can be extracted from the observed polycrystalline spectrum of the spin probe and the analysis of preliminary measurements suggests that, at high speeds, the director is distributed as circles orthogonal to the axis of rotation.(61)

The decay from the dynamic to the static situation is clearly not a simple process as may be seen from the beat patterns evident in Fig. 12. This complex behaviour is best investigated by fourier analysing the time spectrum, and the fourier transform of the spectrum in Fig. 12 is shown in Fig. 13.(61) This transform does contain several peaks each corresponding to different angular velocities of the director. For example, close to the rotation speed of the tube there are at least three peaks and it is these which are responsible for the beat pattern. These three rotation speeds found for the director are thought to be associated with the rapid manner in which the sample tube is accelerated from rest to its high angular velocity. In addition the fourier transform contains small peaks at higher harmonics which might be associated with the rotation of the director at speeds greater than that of the sample tube. These peaks are however more correctly related to the effects of director inertia which causes the rotation of the director to become out of step with the rotation of the sample.(62)

Figure 13. The fourier transform of the time spectrum shown in Fig. 12.

9. The Perturbation of a Cholesteric Phase by a Magnetic Field

There have been few magnetic resonance studies of the cholesteric phase even though evidence for the cholesteric–nematic transition induced by a magnetic field was first provided by a proton magnetic resonance study of benzene dissolved in a weakly cholesteric mesophase.(63) The origin of this change to a nematic phase is now well understood theoretically(64) and experimentally.(65) Provided the anisotropy $\Delta\chi$ in the diamagnetic susceptibility is positive the helix axis will be aligned perpendicular to an applied field and for relatively small fields the probability of finding the director either parallel or perpendicular to the field will be equal. Then as the magnetic field is increased in strength there is a greater probability of finding the director parallel rather than perpendicular to the field since this configuration minimizes the magnetic free energy. However the periodic structure of the cholesteric mesophase is maintained and the pitch of the helix is increased until a critical field is reached at which point it becomes infinite and a nematic mesophase is formed.

Within both the perturbed and unperturbed cholesteric phases the director is not uniformly oriented with respect to the magnetic field and in addition the director motion is found to be slow on a magnetic resonance time scale. Consequently if the motion of a spin probe is also slow then it will be exceedingly difficult to extract any information concerning the structure of the mesophase from the magnetic resonance spectrum. If however the molecular motion is rapid then, as we saw at the end of Sec. 2, it is possible to determine the ordering matrix for the probe as well as the angular distribution function for the director. For the weakly cholesteric systems formed by adding an optically active solute to a nematic mesophase the molecular motion is fast and so the observed spectrum of a probe would appear to be a sum of just two spectra. One of these comes from the probe associated with the director parallel to the magnetic field and the other from the director perpendicular to the field. For example if the spin probe is a nitroxide radical then each spectrum will contain three equally spaced lines; the hyperfine separation of one spectrum is $\tilde{A}_\parallel$ and that of the other is $\tilde{A}_\perp$. The central peaks of these two spectra will coincide when the components $\tilde{g}_\parallel$ and $\tilde{g}_\perp$ of the partially averaged g tensor are comparable and consequently the observed spectrum will contain just five lines. Such a spectrum is shown in Fig. 14 for the spin probe (3-spiro-[2′N-oxyl-3′,3′-dimethyloxazolidine])5α-cholestane dissolved in the cholesteric mesophase formed by adding 1% cholesteryl chloride to 4,4′-dimethoxyazoxybenzene.(66) The appearance of the spectrum depends, as we saw earlier, on the distribution function $f(\phi)$ of the director with respect to the magnetic field. This function is readily calculated, from continuum theory, to be

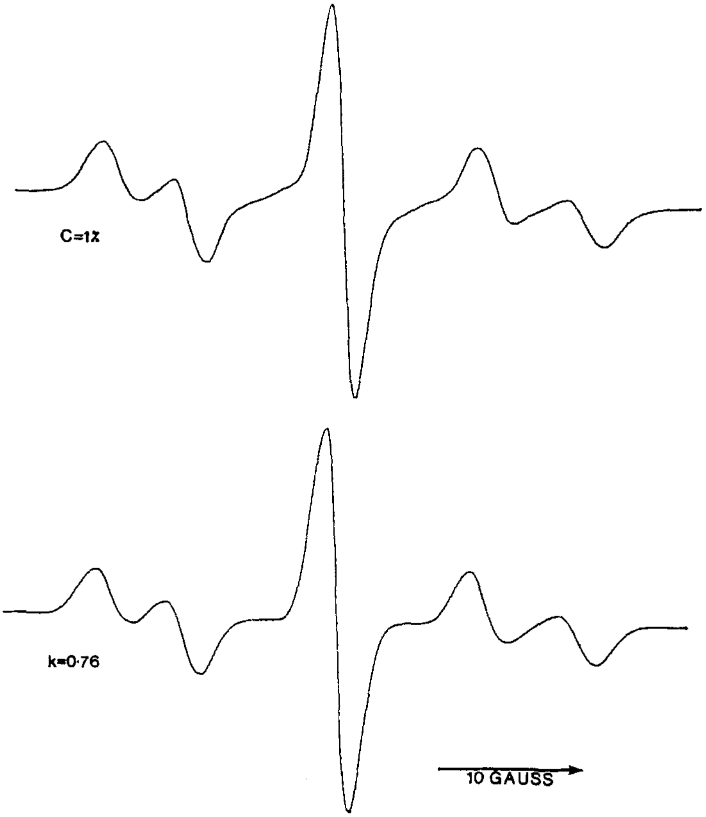

Figure 14. The experimental spectrum for a nitroxide spin probe dissolved in a cholesteric mesophase ($C = 1\%$) and the theoretical simulation ($k = 0.76$).

$$f(\phi)\,\mathrm{d}\phi = \frac{(1 - k^2\cos^2\phi)^{-1/2}\,\mathrm{d}\phi}{\int_0^{2\pi}(1 - k^2\cos^2\phi)^{-1/2}\,\mathrm{d}\phi}, \tag{39}$$

provided the helix axis is aligned perpendicular to the magnetic field.(66,67) Here the parameter k is defined by

$$k = \frac{Z_0 B}{\pi^2}\left(\frac{\Delta\chi}{K_{22}}\right)^{1/2}, \tag{40}$$

where Z_0 is the pitch of the unperturbed helix and K_{22} is the twist elastic constant. It is therefore possible to determine the material constant $(K_{22}/\Delta\chi)^{1/2}$ for the mixture simply by simulating spectra for different values of k until a match with the observed spectrum is obtained. Thus the theoretical spectrum calculated with $k = 0.76$ is found to be in excellent agreement with experiment, as Fig. 14 demonstrates. However to obtain such agreement it is essential to allow for the angular dependence of the linewidths(68) which result from spin relaxation caused by the anisotropic molecular motion with respect to the director.(44) By observing the temperature dependence of the spectrum it is then possible to determine the material constant $(K_{22}/\Delta\chi)^{1/2}$ as a function of temperature. Of course these values relate strictly to the mixture but, because the concentration of the optically active solute is small, they may be equated with those for the pure nematic mesophase. Indeed the results obtained for 4,4′-dimethoxyazoxybenzene are in good although not complete agreement with those determined using an entirely different technique.(66,69)

Ideally one would like to measure the electron resonance spectra using different magnetic fields so as to test the field dependence of k predicted by Eq. (40). Unfortunately such experiments are not readily achieved in electron resonance spectroscopy although they are quite feasible using wide-line nuclear magnetic resonance. It is however possible to test the dependence of k on the pitch of the unperturbed helix because this quantity is inversely proportional to the concentration of the optically active solute.(70) For relatively low concentrations ($<2\%$) of cholesteryl chloride the predictions of Eq. (40) would seem to be in accord with experiment.(66) However for much larger concentrations of solute ($>5\%$) when Z_0 is small the experimental spectra cannot be matched with simulations based on the lowest possible value of k which is zero.(66) This discrepancy, between theory and experiment, is almost certainly caused by the failure of the magnetic field to align the helix axis orthogonal to the field when the solute concentration is high. This failure would appear to result from a reduction in the anisotropy in the diamagnetic susceptibility caused by a decrease in the distances over which there is a high angular correlation. A detailed analysis of the electron resonance spectra for such systems should permit a determination of this correlation length and the factors which govern it.

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