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The Structure of a Cholesteric Mesophase Perturbed by a Magnetic Field†

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Abstract—The application of a magnetic field to a cholesteric mesophase not only aligns the helical structure but also increases the pitch of the helix until at some critical field the cholesteric phase is converted to a nematic mesophase. The theory of this phenomenon has been tested using optical techniques which are however unable to probe the structural changes within the pitch of the helix as it is perturbed by a magnetic field. By employing electron resonance spectroscopy we have been able to verify the predictions of the theory concerning the distribution of the director within the perturbed helix of a weakly cholesteric system formed by adding an optically active solute to a nematic mesophase. Further it has proved possible to determine the temperature dependence of the ratio of the twist elastic constant to the anisotropy in the diamagnetic susceptibility for the nematogen, 4,4′-dimethoxyazoxybenzene, used in this study. Finally although the orientational order of the spin probe is found to be the same in both the cholesteric and parent nematic mesophase the extent of angular correlation decreases on the addition of the optically active solute.

1. Introduction

The liquid crystalline state is characterized by its long range orientational order which often extends over many hundreds of thousands of molecules.[1] At any point in the mesophase of a liquid crystal the long axes of the constituent molecules tend to lie parallel to a given direction. This preferred molecular orientation is usually described by a unit vector field called the director. In the absence of any external constraint the director in the nematic mesophase changes in a continuous but random manner throughout the sample. A uniform sample of the mesophase is obtained on the application of a magnetic

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field which, because of the anisotropy in the diamagnetic susceptibility, aligns the director macroscopically. For the majority of the nematogens the component of the susceptibility tensor parallel to the director is less negative than that perpendicular to it and in these cases the director is aligned parallel to the magnetic field.

In contrast a magnetic field may have an even more dramatic effect on the structure of the cholesteric mesophase. The essential difference between the cholesteric and nematic mesophase is the regular helical arrangement of the director within the cholesteric phase.[1] The behaviour of the cholesteric mesophase in the presence of a magnetic field will depend on the sign of the anisotropy in the diamagnetic susceptibility. Provided the least negative component of the diamagnetic susceptibility tensor is parallel to the director then the helix axis will be aligned perpendicular to the field. In this configuration the alignment of the director at any orientation except parallel to the field is energetically unfavourable and, according to continuum theory,[2,3] the helix will undergo a distortion which increases the probability of finding the director parallel to the magnetic field. The distortion is such that the periodic structure of the cholesteric mesophase is preserved although the pitch of the helix is necessarily increased. The pitch is therefore predicted to increase with increasing field strength until a critical field is attained at which point the pitch becomes infinite and a nematic phase is formed. The change from the cholesteric to the nematic mesophase does not correspond to a phase transition since there is no discontinuity in the free energy at the critical field.[4] Under certain conditions the cholesteric helix may undergo a conical distortion in which the director is no longer constrained to be orthogonal to the helix axis and this axis is aligned parallel to the magnetic field.[3] However, this particular distortion cannot occur in the cholesteric system with which we shall be concerned.

The ability of a magnetic field to convert a cholesteric to a nematic mesophase was discovered prior to the development of the theory for the phenomenon.[5] Subsequently the observed dependence of the pitch on the magnetic field was found to be in good agreement with that predicted theoretically.[6,7] In addition, the critical field strength is predicted to be inversely proportional to the pitch of the unperturbed helix and this aspect of the theory has also been

confirmed.[6] Electric fields have an analogous effect on the cholesteric mesophase and because of the potential application of this behaviour in electro-optic devices the phenomenon has received considerable attention.[8] Although the optical experiments, using both magnetic and electric fields, are in accord with most aspects of the theory they cannot, by their very nature, determine the distribution function for the director within the repeat unit of the distorted helix. However the orientation of the director within the mesophase of a liquid crystal can be determined from the electron resonance spectrum of a spin probe dissolved in the mesophase.[9–11] We have therefore used this technique to explore the structure of a so-called weakly cholesteric mesophase formed by adding an optically active solute to a nematic mesophase.[12] Such a system has two advantages. Firstly the helix axis will be aligned perpendicular to the magnetic field because of the anisotropy in the diamagnetic susceptibility of the nematic mesophase. In addition the pitch of the unperturbed helix may be varied simply by changing the concentration of the optically active solute. It is possible therefore to obtain a cholesteric mesophase for which the critical field is comparable to the magnetic field strength necessarily employed in the electron resonance spectrometer.

2. Experimental

The nematogen, 4,4′-dimethoxyazoxybenzene, used in this investigation was obtained from British Drug Houses Ltd. and was purified by recrystallization from a water–ethanol mixture. The optically active species was cholesteryl chloride which was also purchased from BDH Ltd. but was used without further purification. The spin probe, (3-spiro-[2′N-oxyl-3,3′dimethyloxazolidine])5α-cholestane, was prepared from 5α-cholestan-3-one.[13] The probe itself is optically active but, because of the inherent sensitivity of electron resonance spectroscopy, the amount present in a sample is insufficient to effect the nematic–cholesteric change in the presence of the field of 3 kGauss used in the Varian E-3 spectrometer. Thus the spectrum, shown in Fig. 1, of the spin probe dissolved in the mesophase of pure 4,4′-dimethoxyazoxybenzene contains the three lines expected for a nitroxide radical in a nematic mesophase.[9]

The binary mixtures containing up to 10% by weight of cholesteryl

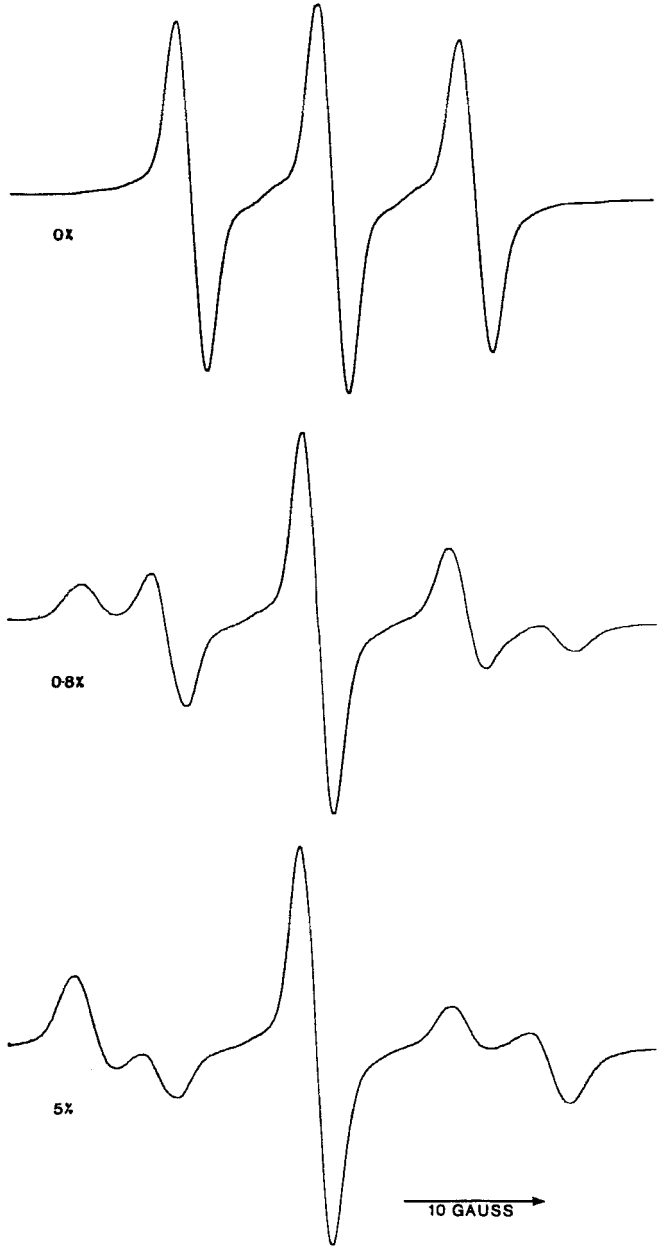

Figure 1. The electron resonance spectrum of the nitroxide spin probe dissolved in the mesophase of 4,4′-dimethoxyazoxybenzene and two of its mixtures with cholesteryl chloride.

chloride were prepared by weighing the components and melting them in the weighing bottle. The melt was thoroughly stirred and then allowed to solidify before a small amount of the mixture together with a trace quantity of the probe were introduced into the sample tube. The addition of cholesteryl chloride to the nematogen depresses the transition to the isotropic phase and so the spectrum of each sample was recorded at a temperature 10 °C below the transition point. In this way spectra were obtained at essentially the same reduced temperature when the properties of the mixtures should be most comparable.[14] Typical spectra from these weakly cholesteric systems are also shown in Fig. 1 and they clearly demonstrate the pronounced change produced by the addition of the optically active solute. The spectra now contain five lines and as the solute concentration increases so does the intensity of the outer spectral lines although at the expense of the inner pair.

Our experiments also indicate a difference in the dynamic behaviour of the nematic and cholesteric mesophases. The spectrum of the probe in the nematic phase appears to be independent of time because the director reaches its equilibrium configuration, parallel to the field, virtually instantaneously. However for the cholesteric phase the relative intensities of the first two spectral lines were observed to change with time and did not obtain their static values until several minutes had passed. Presumably the orientation and unwinding of the helix by the magnetic field have a relatively long relaxation time. Indeed this conclusion is in accord with some earlier observations on the time required to unwind the helix in a mixture of cholesteryl chloride and nonanoate by an electric field.[15] The samples were therefore left in the magnetic field for at least five minutes before attempting to record the spectra.

The spectrum of the probe dissolved in 4,4′-dimethoxyazoxybenzene was measured as a function of temperature which was monitored with a copper–constantan thermocouple. The sample was heated, in this and the other experiments, with a Varian E-4557 variable temperature unit. The spectrum from the sample containing 1% of cholesteryl chloride was also measured throughout the entire range of the mesophase. This particular concentration was selected for a detailed investigation because the helix is significantly distorted by a magnetic field of 3 kGauss.

3. Analysis

When analysing the magnetic resonance spectrum of a spin probe dissolved in a mesophase it is often possible to treat the probe as if it was a fictitious species for which all of the magnetic interactions are cylindrically symmetric with their symmetry axes parallel to the director.[9,11] This equivalence is established only if the orientation of the probe, with respect to the director, changes rapidly with a correlation time less than the inverse of the total anisotropy in the magnetic interactions. The magnitude of the partially averaged interaction is related to the strength of the total magnetic interaction and the extent of the solute alignment. For example, in the case of the electron–nuclear hyperfine interaction the component parallel to the director is

$$\tilde{A}_{\parallel} = a + (2/3) \sum_{\alpha,\beta} \mathcal{O}_{\alpha\beta} A'_{\alpha\beta}, \tag{1}$$

and the perpendicular component is

$$\tilde{A}_{\perp} = a - (1/3) \sum_{\alpha,\beta} \mathcal{O}_{\alpha\beta} A'_{\alpha\beta}. \tag{2}$$

Here $\mathbf{A}'$ is the anisotropic hyperfine tensor, a is the scalar interaction and $\mathcal{O}$ is the ordering matrix which describes the solute alignment. The director is parallel to the magnetic field in the majority of electron resonance experiments and so only the component $\tilde{A}_{\parallel}$ can be observed. None the less if the anisotropic hyperfine tensor and the scalar interaction are known it is possible to investigate the factors which determine the anisotropy in the solute–solvent interaction.[16] The nitrogen hyperfine tensor for the spin probe used in this investigation is essentially cylindrically symmetric about an axis, 3, perpendicular to the oxazolidine ring.[17] The element of the ordering matrix for this axis may therefore be calculated from

$$\tilde{A}_{\parallel} = a + \mathcal{O}_{33} A_{\parallel}'. \tag{3}$$

where $A_{\parallel}'$ is found to be 51.33 MHz from the spectra of the radical dissolved in both fluid and solid *o*-terphenyl. The scalar coupling is measured to be 41.60 MHz in the isotropic phase of the nematogen. The ordering matrix element $\mathcal{O}_{33}$ determined in this way from the temperature dependence of the spectrum of the probe dissolved in 4,4′-dimethoxyazoxybenzene is plotted against the reduced temperature in Fig. 2.

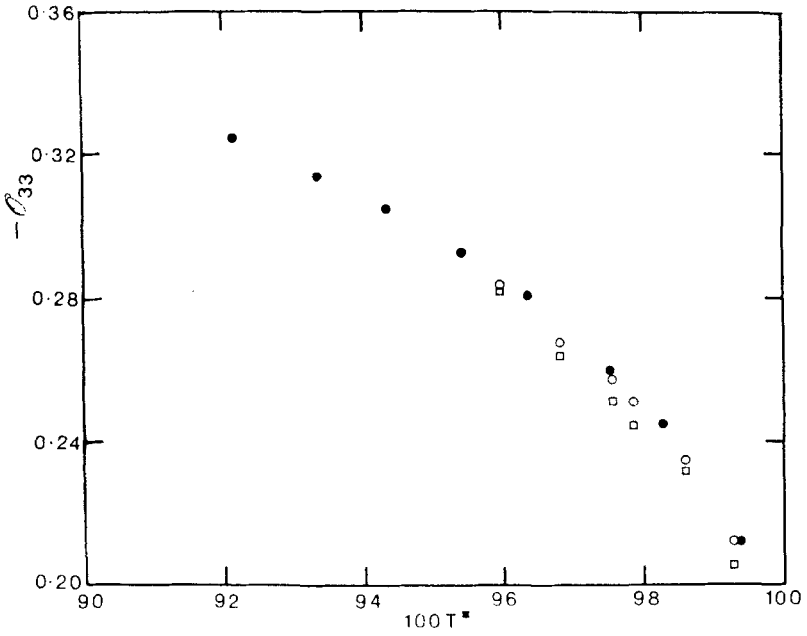

Figure 2. The temperature dependence of the orientational order $\mathcal{O}_{33}$ for the spin probe dissolved in the nematic phase of 4,4′-dimethoxyazoxybenzene (●) and the cholesteric mesophase formed by adding 1% of cholesteryl chloride (○ from $\tilde{A}_{\parallel}$ and □ from $\tilde{A}_{\perp}$).

The form of the spectrum is not expected to change even if the director makes an angle γ with the magnetic field. However the resonance fields now depend on both components of the partially averaged tensors and for a spin probe containing a single magnetic nucleus of spin I are given by[18]

$$B_r(\gamma) = B_0 - \frac{hKm}{g\beta} - \frac{h^2\tilde{A}_\perp{}^2}{4g^2\beta^2B_0}\left\{\frac{\tilde{A}_\parallel{}^2+K^2}{K^2}\right\}\{I(I+1)-m^2\}$$
$$-\frac{h^2m^2}{2g^2\beta^2B_0}\left\{\frac{\tilde{A}_\parallel{}^2-\tilde{A}_\perp{}^2}{K}\right\}^2\left\{\frac{\tilde{g}_\parallel{}^2\tilde{g}_\perp{}^2}{g^4}\right\}\cos^2\gamma\sin^2\gamma. \quad (4)$$

In this expression

$$B_0 = h\nu/g\beta, \quad (5)$$

$$g^2 = \tilde{g}_\perp{}^2 + (\tilde{g}_\parallel{}^2 - \tilde{g}_\perp{}^2)\cos^2\gamma, \quad (6)$$

$$\text{and } K^2g^2 = \tilde{A}_\perp{}^2\tilde{g}_\perp{}^2 + (\tilde{A}_\parallel{}^2\tilde{g}_\parallel{}^2 - \tilde{A}_\perp{}^2\tilde{g}_\perp{}^2)\cos^2\gamma, \quad (7)$$

where ν is the kylstron frequency and m is the nuclear quantum number associated with the transition. The dependence of the resonance fields on the quadrupole coupling is not included in Eq. (4) because it has been shown to be negligibly small for the nitroxide spin probe.[19] Since the spectra from the cholesteric samples contain more than three lines the director cannot be uniformly oriented with respect to the magnetic field. In this situation the observed spectrum is an appropriately weighted sum of spectra from all orientations of the director and the spectral intensity at an arbitrary magnetic field B is proportional to

$$h(B) = \sum_r \int P_r(\omega) L(B, B_r, T_2^{-1}) f(\omega) \mathrm{d}\omega . \tag{8}$$

Here ω represents the spherical polar angles made by the symmetry axis or director in the coordinate system defined by the orthogonal static and oscillating magnetic fields in the spectrometer. The first term in the integrand denotes the anisotropic transition probability caused by the anisotropy in the g tensor. The second $L(B, B_r, T_2^{-1})$ is the shape of the line centred at B_r and has a width T_2^{-1}. For the nitroxide radical the unresolved proton hyperfine structure produces an essentially Gaussian line shape:

$$L(B, B_r, T_2^{-1}) = \frac{T_2^3}{(2\pi)^{1/2}} (B_r - B) \exp \{ - T_2^2 (B_r - B)^2/2 \} . \tag{9}$$

Finally $f(\omega)\mathrm{d}\omega$ is the probability of finding the director having an orientation between ω and $\omega + \mathrm{d}\omega$.

Although the expression for the spectrum is formidable when the director is not uniformly oriented it is possible to give a qualitative account of the appearance of the spectrum. As we have seen, spectra from all orientations of the director contribute to the observed spectrum but, because of the first derivative display employed in electron resonance, only spectra corresponding to extreme values of the resonance fields make any significant contribution.[20] Consequently the electron resonance spectrum for a nitroxide spin probe will consist of three lines with a separation $\tilde{A}_\parallel$ corresponding to the director parallel to the field and another three with a spacing $\tilde{A}_\perp$ when the field is perpendicular to the director. The experimental spectra shown in Fig. 1 contain five and not six lines because $\tilde{g}_\parallel$ is comparable to $\tilde{g}_\perp$ and so the central lines of both spectra overlap to

give a single line. Further the intensities of these two component spectra are determined by the probability of finding the magnetic symmetry axis, and hence the director, either parallel or perpendicular to the magnetic field. Thus in the spectrum from the nematic mesophase there are just three lines with a spacing $\tilde{A}_{\parallel}$ which shows that there is zero probability of finding the director perpendicular to the field. However on addition of cholesteryl chloride two extra lines appear separated by $2\tilde{A}_{\perp}$ and these show that the director is now to be found perpendicular to the field. As more cholesteryl chloride is added the intensity of the $\tilde{A}_{\perp}$ peaks increases which demonstrates an increase in the probability of finding the director perpendicular to the field. This increase is presumably caused by a decrease in the pitch of the helix which is therefore less distorted by the magnetic field. In the limit of course the probabilities of finding the director either parallel or perpendicular to the field are equal.

Since both sets of lines are observed in the spectra from the cholesteric mesophase it is possible to determine $\tilde{A}_{\perp}$ and $\tilde{A}_{\parallel}$. These parameters have been measured as a function of temperature for the mixture containing 1% of cholesteryl chloride. According to Eq. (2) the perpendicular component of the fictitious hyperfine tensor $\tilde{\mathbf{A}}$ is also related to the solute order:

$$\tilde{A}_{\perp} = a - (1/2)\mathcal{O}_{33} A_{\parallel}' \tag{10}$$

and so it is possible to obtain two estimates for $\mathcal{O}_{33}$. These two sets of values for $\mathcal{O}_{33}$ are plotted as a function of the reduced temperature in Fig. 2 and, for a given reduced temperature, are within experimental error as indeed they should be. In addition the orientational order of the spin probe in the nematic mesophase is identical to that in the cholesteric phase. The formation of the cholesteric phase would therefore seem to have no effect on the pseudo-potential for the solute.[14,21] In principle, of course, the pseudo-potential for the spin probe should be modified by the presence of the cholesteryl chloride but the concentration of this component is so small that the modifications must be negligible.

At present it does not appear to be possible to obtain the distribution function $f(\omega)$ from the polycrystalline spectrum by a simple transformation. We are therefore forced to test specific forms for $f(\omega)$ by simulating spectra from Eq. (8) and comparing these with

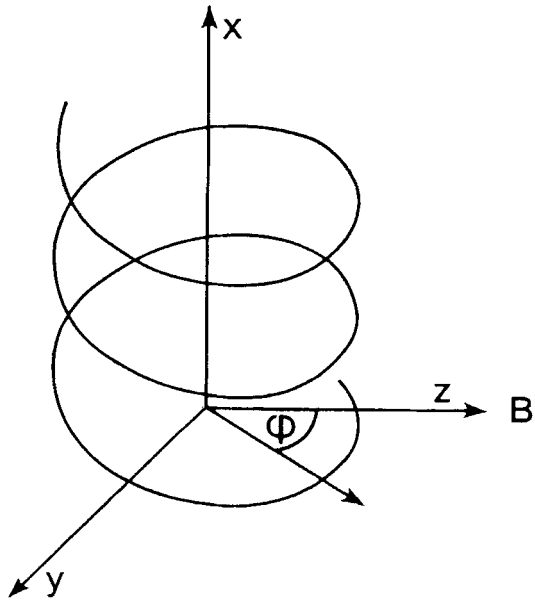

Figure 3. The helical configuration adopted by the director in the cholesteric mesophase.

the experimental spectra. In this way we are able only to test the form of the distribution function and to obtain numerical values for the parameters appearing in it. The starting point for the spectral analysis is then the derivation of an expression for $f(\omega)$. Provided the anisotropy in the diamagnetic susceptibility for the helix is sufficiently large the helix axis will be aligned orthogonal to the applied magnetic field. This situation is depicted in Fig. 3 where the field direction defines the z-axis. The yz plane is orthogonal to the helix axis and so the orientation of the director with respect to the magnetic field is defined by the single angle ϕ. We therefore require $f(\phi)$ where $f(\phi)\mathrm{d}\phi$ is the probability of finding the director between ϕ and $\phi + \mathrm{d}\phi$. However $f(\phi)\mathrm{d}\phi$ is equal to the probability $f(x)\mathrm{d}x$ of finding the director at a position between x and $x + \mathrm{d}x$. The probability of finding the director at any position x is independent of x and so

$$f(\phi) \propto \mathrm{d}x/\mathrm{d}\phi . \tag{11}$$

This derivative is readily obtained[22] from de Gennes' treatment[2]

of the perturbation of a cholesteric mesophase by a magnetic field. His analysis starts with the free energy per unit area in the yz plane:

$$F = \tfrac{1}{2}\int\left\{K_{22}\left[\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)+\frac{2\pi}{Z_0}\right]^2 - \Delta\chi B^2\cos^2\phi\right\}\mathrm{d}x + \text{constant}. \qquad (12)$$

Here K_{22} is the twist elastic constant, Z_0 is the pitch of the unperturbed helix and $\Delta\chi$ is the anisotropy in the diamagnetic susceptibility per unit volume. The form of the director which minimizes the free energy is found, by application of the Euler equation, to satisfy:

$$K_{22}\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} - \Delta\chi B^2\sin\phi\cos\phi = 0. \qquad (13)$$

The derivative $\mathrm{d}x/\mathrm{d}\phi$ is now obtained by a single integration of this result which gives

$$\frac{\mathrm{d}x}{\mathrm{d}\phi} = \frac{\xi k}{(1-k^2\cos^2\phi)^{1/2}}, \qquad (14)$$

where the magnetic coherence length ξ is defined as

$$\xi^2 = K_{22}/\Delta\chi B^2, \qquad (15)$$

and k is a constant of integration. The normalized angular distribution function is then

$$f(\phi) = \frac{(1-k^2\cos^2\phi)^{-1/2}}{\int_0^{2\pi}(1-k^2\cos^2\phi)^{-1/2}\mathrm{d}\phi}. \qquad (16)$$

The appearance of this distribution function is controlled therefore by the single parameter k which may take values from zero, corresponding to an unperturbed helix, to unity for the aligned nematic mesophase. The shape of the function $f(\phi)$, which is shown in Fig. 4 for a range of k values, is most dependent on k when this is close to one.

The spectral intensity $h(B)$ in Eq. (8) may now be written as

$$h(B) = \int_0^{\pi/2}\tilde{g}_\perp{}^2\{1+(\tilde{g}_\parallel/g)^2\}L(B, B_r, T_2{}^{-1})(1-k^2\cos^2\phi)^{-1/2}\mathrm{d}\phi, \qquad (17)$$

where the upper limit of the integration is $\pi/2$ because both $B_r(\phi)$ and $f(\phi)$ are even functions of ϕ. The normalization factor has been omitted from the distribution function because it is essentially

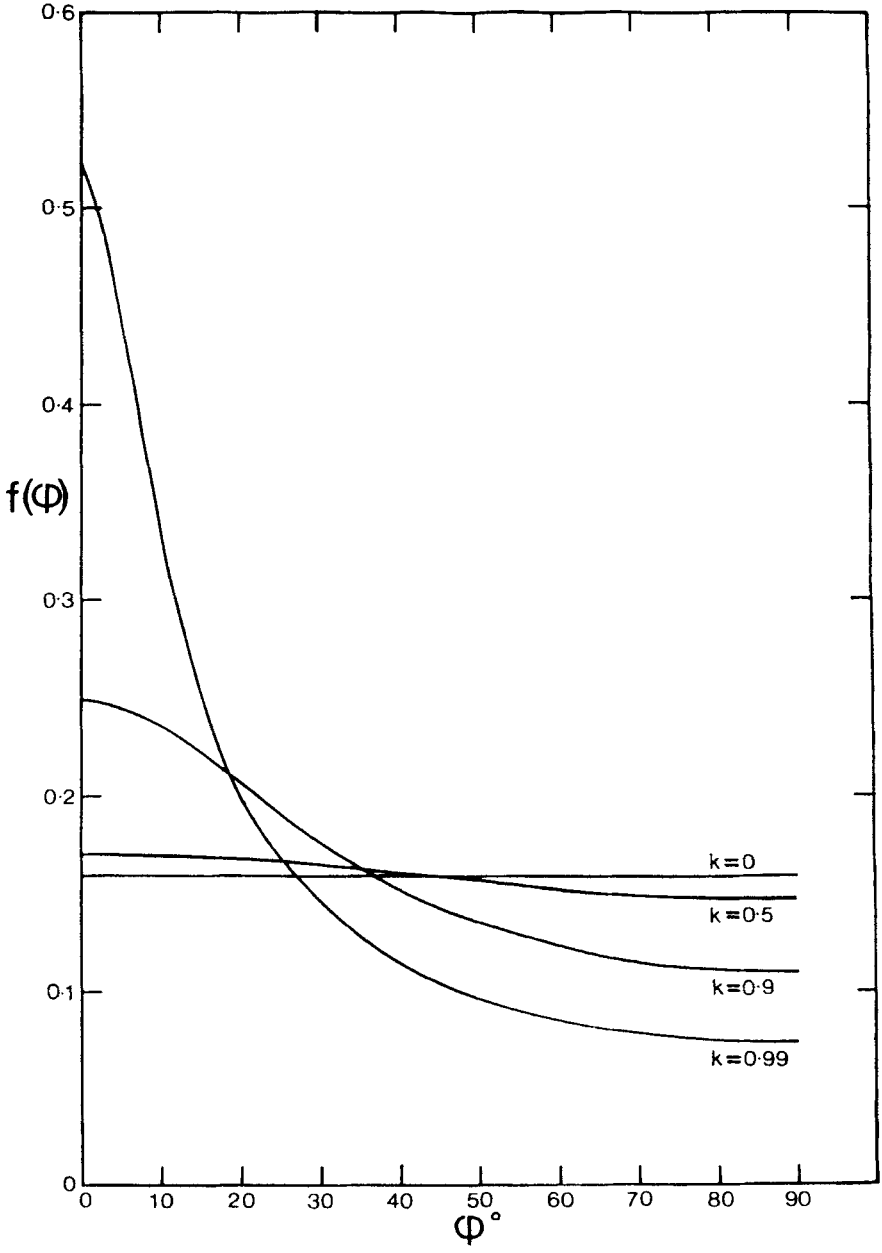

Figure 4. The angular distribution function for the director in a cholesteric helix perturbed by a magnetic field.

independent of B and so affects all of the spectral intensities equally. Finally the anisotropic transition probability is

$$P_r(\omega) = \tilde{g}_\perp^2\{1 + (\tilde{g}_\parallel/g)^2\}, \tag{18}$$

but this has little effect on the spectrum since for this spin probe the fictitious g tensor is virtually isotropic. In principle the simulation of the spectrum given by Eq. (17) demands a knowledge of a large number of parameters. However it is possible to obtain values for $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ directly from the observed polycrystalline spectrum. This then leaves us with the problem of determining the linewidth T_2^{-1} and the parameter k. We have therefore simulated spectra for reasonable values of T_2^{-1} and for values of k between 0 and 1. These simulations demonstrate that the spectrum, like the distribution function, is most sensitive to changes in k when this is close to unity. We decided therefore to study a mixture for which k is approximately one in order to obtain the most accurate values for this parameter. It is necessary then to be able to estimate k from the composition of the mixture.

This parameter is related to the other variables by

$$\frac{k}{E(k)} = \frac{Z_0 B}{\pi^2}\left(\frac{\Delta\chi}{K_{22}}\right)^{1/2} = B/B_c, \tag{19}$$

where $E(k)$ is an elliptic integral of the second kind and B_c is the critical field.[2] This result might complicate our analysis of the spectra for it shows that k does depend on the magnetic field and so should change when the electron resonance spectrum is measured. Fortunately the variation in the field required to record the spectrum of the nitroxide spin probe is only 40 G and, in comparison with the absolute field of 3300 G, this small fractional change has a negligible effect on k. Of course neglect of the field dependence of k would be quite inappropriate for a spin probe such as vanadyl acetylacetonate where the field changes from 2860 to 3740 G during measurement of the spectrum.[14] Indeed we have recorded spectra for this spin probe dissolved in mixtures of cholesteryl chloride and 4,4′-dimethoxyazoxybenzene for which the low field part of the spectrum clearly corresponds to a value of k less than one. However as the magnetic field increases k also increases until in the high field region

it has reached its limiting value of unity and the spectrum is characteristic of a nematic mesophase. The critical fields B_c have been determined for mixtures of cholesteryl chloride and 4,4'-dimethoxyazoxybenzene[6] and using these results together with B equal to 3.3 kG we calculate that a 1% by weight mixture corresponds to a value of k close to unity. It was this observation which prompted us to study a 1% mixture as a function of temperature.

The agreement between the theoretical and experimental spectra for this mixture is good but not perfect. The lack of complete agreement might be attributed to a discrepancy in the distribution function but we prefer to associate it with our implicit assumption of equal widths for all the spectral lines. Thus examination of the spectrum, shown in Fig. 1, from the nematic mesophase reveals that the widths of the hyperfine lines are not exactly the same. In fact the widths of the three hyperfine lines of a nitroxide radical tumbling in solution often exhibit a marked dependence on the nuclear quantum number m of the form[23]

$$T_2^{-1}(m) = A + Bm + Cm^2 . \tag{20}$$

For the spin probe employed in this investigation the linewidth coefficient B is small and may be neglected. There is however a further complication for when the linewidth is a consequence of spin relaxation caused by molecular reorientation the linewidth coefficients for a radical dissolved in a liquid crystal are predicted and observed to depend on the orientation of the director with respect to the magnetic field.[24] The theoretical angular dependence of the linewidth coefficients is found to be of the form

$$A = A_0 + A_2 P_2(\cos\phi) + A_4 P_4(\cos\phi), \tag{21}$$

where $P_L(\cos\phi)$ is the Lth. Legendre polynomial. The use of such expressions in the lineshape calculation is clearly difficult because they introduce six arbitrary parameters. We have therefore adopted the simpler angular dependence for the linewidths:

$$T_2^{-1}(m = \pm 1) = T_\perp^{-1} + (T_\parallel^{-1} - T_\perp^{-1}) \cos^2\phi . \tag{22}$$

The width of the central line is taken to be independent of the orientation since it is caused essentially by unresolved proton hyperfine structure.

These expressions for the linewidths were substituted into Eq. (17)

and a variety of simulated spectra were obtained for a range of values for the linewidth parameters. The widths which gave the best overall fit to the shape of a particular line are

$$T_{\perp}^{-1} = 1.3 \text{ G},$$

$$T_{\parallel}^{-1} = 1.2 \text{ G},$$

$$\text{and } T_2^{-1} (m = 0) = 1.1 \text{ G}.$$

These values were found to be independent of temperature and were then employed to simulate spectra for different values of k. Comparison of the simulated spectra with those obtained from the 1% mixture enabled us to determine k as a function of temperature. In

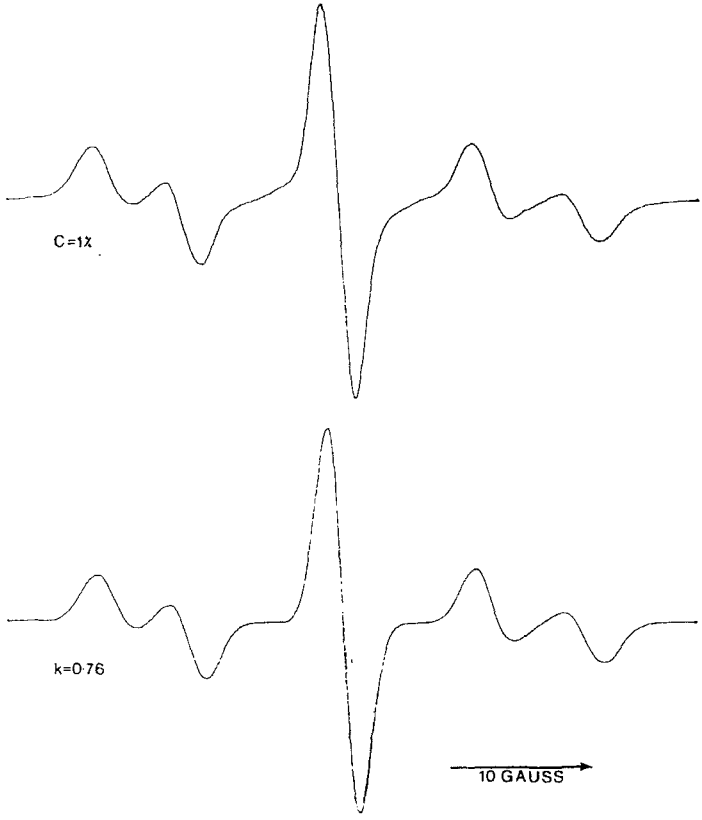

Figure 5. A comparison between the experimental ($C = 1\%$) and simulated ($k = 0.76$) spectrum for the spin probe dissolved in the cholesteric mesophase at 118.9 °C.

general the agreement between the experimental and theoretical spectra was found to be excellent. The level of agreement is illustrated in Fig. 5 which shows the experimental spectrum at 118.9 °C together with the spectrum simulated for k equal to 0.76. The slight discrepancy between these spectra in the wings of the central line is probably caused by a deviation of the line shape from a true Gaussian curve. The value of k found by fitting the spectra from the 1% mixture at different temperatures are given in Table 1.

TABLE 1 The temperature dependence of k and the associated material constant $(K_{22}/\Delta\chi)^{1/2}$

Temperature (°C)	k	Pitch $Z_0(\mu m)$	$(K_{22}/\Delta\chi)^{1/2}$ (dyn$^{1/2}$) This work	Freedericksz and Zwetkoff[27]	$(K_{22}/\Delta\chi S)^{1/2}$ (dyn$^{1/2}$)
129.0	0.86	34.7	1.63	1.50	2.45
126.4	0.82	34.3	1.74	1.55	2.48
123.4	0.80	33.7	1.79	1.60	2.49
122.2	0.78	33.5	1.86	1.62	2.56
119.2	0.76	33.0	1.89	1.65	2.56
115.7	0.72	32.4	2.02	1.68	2.67

The parameter k is related, via Eq. (19), to the ratio $(K_{22}/\Delta\chi)^{1/2}$ of the material constants for the mesophase. However to obtain this quantity it is necessary to know the pitch Z_0 of the unperturbed helix. For weakly cholesteric systems Z_0 has been found to be inversely proportional to the mass concentration C of the optically active species provided C is less than about 0.1.[25] The magnitude of the proportionality constant depends on the molecular structure of the constituents and is also slightly temperature dependent. For cholesteryl chloride dissolved in 4,4'-dimethoxyazoxybenzene the constant is found to be 0.34 μm at 129 °C.[6] Further for a 2% mixture the pitch is found to decrease from 18 μm at 133 °C to 15 μm at 102 °C.[26] The proportionality constant therefore takes the value 0.36 μm at 133 °C, 0.34 μm at 129 °C and 0.30 μm at 102 °C; these values were then used to estimate the temperature dependence of the pitch for the 1% mixture with the results given in the table. These values were subsequently employed to obtain the ratio

$(K_{22}/\Delta\chi)^{1/2}$ which is also listed in the table. Our value for this ratio of 1.63 $dyn^{1/2}$ at 129 °C is surprisingly close to the value of 1.69 $dyn^{1/2}$ obtained by Durand *et al.*[6] who measured the critical magnetic field as a function of Z_0. The material constants will depend, of course, on the nature and concentration of the various components in the mesophase. However in our experiments the concentration of cholesteryl chloride is so low that the parameter $(K_{22}/\Delta\chi)^{1/2}$ which we determine can safely be identified with that found for the pure nematic mesophase. Freedericksz and Zwetkoff[27] have measured $(K_{22}/\Delta\chi)^{1/2}$ for 4,4′-dimethoxyazoxybenzene by studying the distortions induced by a magnetic field in a slab of the oriented nematic mesophase. Their results, which are included in the table, are, on average, 12% smaller than the values we have determined; in addition our values have a slightly stronger dependence on temperature. We gauge the error in the parameter k to be about $\pm 2\%$ but this is negligible compared with the error in Z_0 which is estimated[6] to be $\pm 9\%$. Although this error might explain the difference between the magnitudes of the two sets of results it could not account for the stronger temperature dependence since Z_0 changes by less than 7% in the temperature range of interest to us. However since these two methods for determining $(K_{22}/\Delta\chi)^{1/2}$ are so completely different we regard the agreement between the two sets of results as most gratifying.

According to the molecular theory of the elastic constants developed by Saupe,[28] K_{22} should be proportional to the square of the orientational order in the mesophase. Here the orientational order S is defined, in a similar manner to the solute ordering matrix, as the ensemble average of $(3\cos^2\theta - 1)/2$ where θ is the angle between the long molecular axis and the director. The diamagnetic susceptibility per unit volume also depends on the orientational order, S. In fact the components of this partially averaged tensor are given by equations analogous to those (Eqs. (1) and (2)) for the hyperfine tensor $\tilde{\mathbf{A}}$. Thus the anisotropy $\Delta\chi$, which could be written as $\tilde{\chi}_{\parallel} - \chi_{\perp}$, is directly proportional to the orientational order S and consequently the ratio $(K_{22}/\Delta\chi S)^{1/2}$ should be independent of temperature. Reliable values of S for 4,4′-dimethoxyazoxybenzene have been determined using nuclear magnetic resonance[29] and we have employed these results to calculate the values of $(K_{22}/\Delta\chi S)^{1/2}$ given in the table. Although the temperature dependence of this ratio

is clearly less marked than that of the original parameter $(K_{22}/\Delta\chi)^{1/2}$ it does not show the required independence of temperature. This discrepancy might be attributed to experimental error. However, a recent extension of Saupe's theory predicts that K_{22} should depend on S as well as S^2.[30] Such a dependence would be in accord with our results.

4. High Cholesteryl Chloride Concentrations

As the concentration of cholesteryl chloride increases so the pitch Z_0 decreases and consequently the parameter k should also decrease. In the limit k vanishes and the distribution function becomes

$$f(\phi) = \tfrac{1}{2}\pi, \tag{23}$$

which corresponds to an isotropic two-dimensional distribution of the director with respect to the magnetic field. A theoretical spectrum for this limiting distribution is shown in Fig. 6. In fact the form of the spectrum is quite insensitive to changes in k from 0 up to about 0.5 as we might have anticipated from the distribution functions plotted in Fig. 4. According to the measurements[6] of the critical magnetic field for this weakly cholesteric system k is less than 0.5 when the concentration of cholesteryl chloride exceeds 2%. We therefore expected the electron resonance spectrum to change as the cholesteryl chloride concentration is increased until the concentration is about 2% when the spectrum should have taken the limiting form shown in Fig. 6. However we were surprised to discover that the spectrum continued to change even after the cholesteryl chloride concentration had reached 5%. The increase in the concentration caused the outer $\tilde{A}_\perp$ lines to increase in intensity while that of the inner $\tilde{A}_\parallel$ lines diminished. This effect is illustrated in Fig. 6 by the electron resonance spectrum recorded for the mixture containing 10% of cholesteryl chloride at 111.3 °C.

The increase in the intensity of the $\tilde{A}_\perp$ lines above and beyond that expected for a two dimensional isotropic distribution indicates that even for an unperturbed helix there is a greater probability of finding the director perpendicular rather than parallel to the magnetic field. Such an increase can occur only if the helix axis is no longer constrained to be perpendicular to the magnetic field. If this restriction

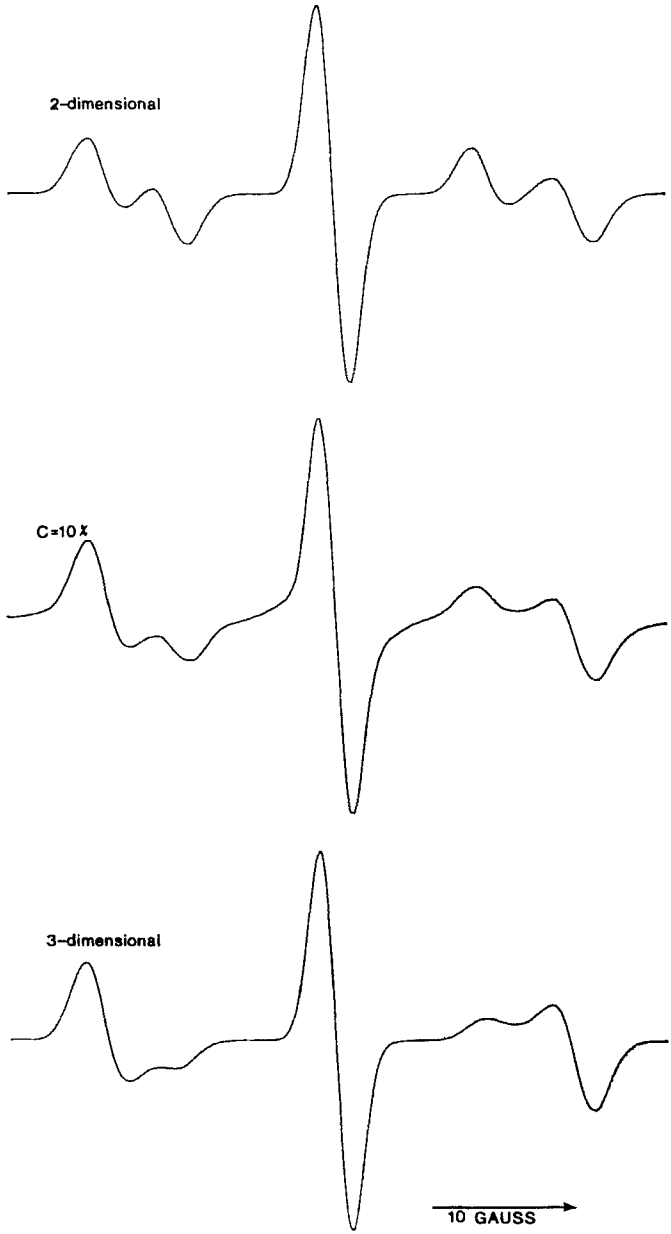

Figure 6. The experimental spectrum from the mixture containing 10% cholesteryl chloride together with the theoretical spectra corresponding to an isotropic distribution in two and three dimensions.

is removed completely then all orientations of the director are equally probable and the distribution function becomes

$$f(\phi) = \sin \phi / 4\pi . \tag{24}$$

This three dimensional isotropic distribution function was used, together with the same magnetic parameters as in the two-dimensional simulation to calculate the third spectrum shown in Fig. 6. The form of the experimental spectrum is clearly intermediate between those for the two- and three-dimensional distributions. Presumably although the helix axis is no longer held orthogonal to the magnetic field the most probable orientation of the helix axis is in this direction. However the constraint appears to have been removed completely when the mixture contains 20% cholesteryl chloride since the electron resonance spectrum is virtually identical to that for an isotropic distribution in three dimensions.

The helix axis will only be completely aligned if the magnetic free energy, which is responsible for the alignment, is greater than the disordering thermal energy. For a given field strength the magnetic energy is determined by $\Delta\chi$, the anisotropy in the diamagnetism per unit volume. Now as we have seen the magnitude of $\Delta\chi$ is proportional to the orientational order but in addition $\Delta\chi$ will be dependent on the diamagnetic susceptibilities χ and the amounts of the individual components. There is however a third effect. The macroscopic alignment of a mesophase is determined by the total magnetic energy which is obtained from the volume integral of the magnetic free energy density. The relevant magnetic free energy will depend therefore on the volume over which there is extensive angular correlation between the molecules as well as the nature of the individual components and the orientational order.

Since $\Delta\chi$ is proportional to the order S this anisotropy should increase with decreasing temperature; similarly the extent of angular correlation might also be expected to increase with decreasing temperature. Consequently both effects should serve to increase the magnetic free energy and hence increase the probability of finding the helix axis orthogonal to the field as the temperature is lowered. Experimentally then the electron resonance spectra for mixtures containing high concentrations of cholesteryl chloride should tend to that simulated for an isotropic two dimensional distribution with

decreasing temperature. Such changes have indeed been observed in the spectra from the mixture containing 10% of cholesteryl chloride and these observations seem to confirm our ideas concerning the alignment of the helix by the magnetic field.

The anisotropy in the diamagnetic susceptibility for cholesteric compounds is opposite in sign and considerably smaller than that for 4,4′-dimethoxyazoxybenzene.[31] As a consequence addition of cholesteryl chloride will decrease the magnetic free energy density and might be responsible for the random orientation of the helix axis. However we have estimated that the minimum field required for the complete alignment of the helix is only equal to the magnetic field in the spectrometer when the cholesteryl chloride concentration is about 40%. Since this is considerably higher than the concentration at which disorientation effects are observed it seems unlikely that the reduction in $\Delta\chi$ by cholesteryl chloride is an important contribution to the decrease in the magnetic free energy. In order to confirm this possibility we have repeated these experiments using active amyl *p*-(4-cyanobenzylideneamino) cinnamate as the optically active solute. Because the diamagnetic susceptibility for this solute should be comparable to that of 4,4′-dimethoxyazoxybenzene the addition of the optically active solute should have a negligible effect on the anisotropy in the diamagnetic susceptibility. However the electron resonance spectra from mixtures containing a relatively high solute concentration also demonstrate the essentially random alignment of the helix axis. This observation confirms the unimportance of the reduction in $\Delta\chi$ caused by the addition of cholesteryl chloride. Finally since, as we have seen, the orientational order in the cholesteric and nematic mesophases are identical we conclude that the addition of optically active solutes to the nematic mesophase reduces the extent of angular correlation between the molecules.

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