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Orientational order in the lamellar *G* phase of the sodium decanoate-*n*-decanol-water system. An electron resonance investigation

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We have measured the angular variation of the electron resonance spectra of three nitroxide spin probes dissolved in the lamellar *G* phase of the sodium decanoate-*n*-decanol-water system. The angular dependence of the line positions is analysed to yield the second rank orientational order parameter for the spin probe. The analysis of the linewidths is not so straightforward and it is shown that it is insufficient to employ a theory which assumes the nuclear spin to be quantized parallel to the magnetic field. Correct analysis of the linewidths yields the fourth rank order parameter as well as rotational correlation times relating to the motion of the probe. The order parameters for the rigid spin probe, derived from cholestane, are in agreement with a simple theory for the single particle orientational energy. In contrast the results for the two flexible probes, derivatives of stearic acid, are not accounted for by this simple theory, in conflict with previous contentions.

1. INTRODUCTION

One of the most powerful techniques for studying the orientational order in liquid crystals, both thermotropic and lyotropic, is deuterium nuclear magnetic resonance [1]. The observation of quadrupolar splittings from each methylene group in an appropriately deuteriated component provides the element of the second rank ordering matrix along the C–D bond. Electron resonance spectroscopy is apparently less useful because the unpaired electron is usually contained in an oxazolidine ring which, it is argued, may provide a major perturbation to the system, unlike the replacement of hydrogen by deuterium [2]. However, whereas nuclear magnetic resonance only provides the second rank orientational ordering parameters electron resonance can provide both the second and fourth rank order parameters [3]. This information is of some importance because it permits a more detailed investigation of the form of the distribution function governing the orientations of the segment in the alkyl

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chain with respect to the layer normal. The value of such studies has already been demonstrated for rigid probes in thermotropic liquid crystals [4]. Of course the quantitative behaviour of the spin probe will not match that of the amphiphilic component of the lyotropic phase. However there is no reason to believe that the qualitative behaviour of the two will not be similar provided the structure of the probe is suitably matched to the component of interest.

Here we describe an electron resonance investigation of the lamellar *G* phase formed by sodium decanoate, *n*-decanol and water. This phase has a bilayer structure and has been used as a simple model system for the lipid bilayer in biological membranes. Two of the spin probes used in this study are stearic acids with the nitroxide group attached at either the 12 or the 5 positions. These probes were chosen because they are expected to bind with their polar heads in the ionic region of the lamellar structure and so should mimic the amphiphilic components of the *G* phase. We have also used a steroidal spin probe for comparison purposes ; it is essentially a rigid structure and in addition has been used for studies of thermotropic lamellar or smectic phases [5]. The structures for these three probes are shown in figure 1. The same lyotropic phase and similar spin probes have been studied previously by Seelig and his colleagues [6]. However they did not observe the complete angular variation of the spectra and, as we shall see, the quantitative information may therefore be much less accurate.

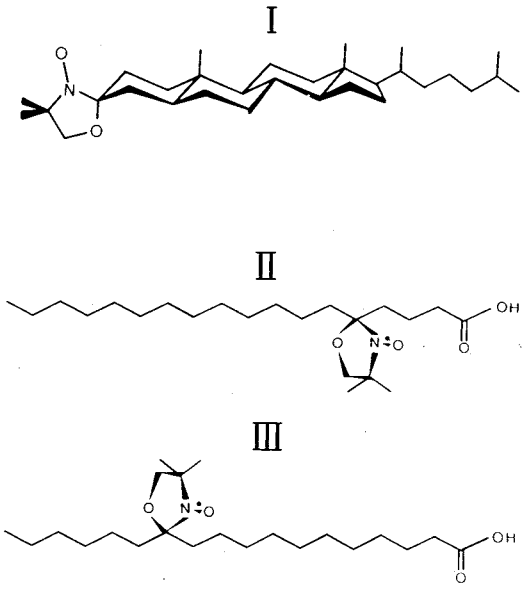

Figure 1. The structures of the stearic acid and cholestane nitroxide spin probes.

The basic theory required to extract the order parameters from the electron resonance spectra is outlined in § 2. The experiments used to obtain these spectra are described in § 3. The analysis of the spectra and the significance of the results are discussed in § 4.

2. Theory

In the fast motion regime the static spin hamiltonian for a spin probe in a uniaxial environment is identical to that for a species with cylindrically symmetric magnetic interaction tensors [2, chapter 2]. By analogy with thermotropic liquid crystals we call this symmetry axis the director which is the preferred molecular orientation. These cylindrically symmetric parameters are denoted by a tilde ; they are related to the long range orientational order of the probe by, for example,

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

$$\tilde{A}_{\perp} = a - (\tfrac{1}{3}) \sum_{\alpha,\beta} A'_{\alpha\beta} S_{\alpha\beta}, \tag{2}$$

where a is the scalar interaction and $\mathbf{A}'$ is the traceless anisotropic interaction [7]. The order of the spin probe is described by the Saupe ordering matrix $\mathbf{S}$ which is defined by

$$S_{\alpha\beta} = \overline{(3l_\alpha l_\beta - \delta_{\alpha\beta})}/2, \tag{3}$$

where l_α is the direction cosine between axis α set in the molecule and the director ; the upper bar denotes an ensemble average [8].

For a nitroxide spin probe in a monodomain sample, the spectrum contains three lines and the spacing between adjacent peaks is

$$\tilde{K}(\gamma) = (\tilde{A}_{\parallel}^2 \cos^2\gamma + \tilde{A}_{\perp}^2 \sin^2\gamma)^{1/2}, \tag{4}$$

where γ is the angle between the director and the applied magnetic field [3]. Thus measurement of the angular variation of the nitrogen hyperfine interaction gives both $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ although this is clearly insufficient to determine the five independent elements of the ordering matrix. However the nitrogen hyperfine tensor is essentially cylindrically symmetric about an axis orthogonal to the oxazolidine ring [9] ; consequently equations (1) and (2) reduce to

$$\tilde{A}_{\parallel} - \tilde{A}_{\perp} = (\tfrac{3}{2}) A'_{\parallel} \bar{P}_2, \tag{5}$$

where $\bar{P}_2$ is used to denote the component of the ordering matrix along this axis. The observation of the line positions therefore provides information about the second rank orientational order parameters. We shall now see how the linewidths may be employed to yield the fourth rank order parameter.

Provided the rate of molecular reorientation is not too fast the anisotropy in the g and nitrogen hyperfine tensors results in a variation in the widths of the three spectral lines. As for isotropic fluids the lines are predicted to be lorentzians with widths given by

$$T_2^{-1}(m) = A + Bm + Cm^2, \tag{6}$$

where m is the nitrogen spin quantum number associated with a line [2, chapter 2]. The linewidth coefficients are related, quite generally, to certain spectral densities [9]

$$A = \frac{(\frac{2}{3})\omega_0^2}{\bar{g}^2} j_0^{(gg)} + \frac{I(I+1)}{4} j_1^{(AA)}, \tag{7}$$

$$B = \tfrac{4}{3} \frac{\omega_0}{\bar{g}} j_0^{(gA)}, \tag{8}$$

$$C = \tfrac{2}{3} j_0^{(AA)} - \tfrac{1}{4} j_1^{(AA)}. \tag{9}$$

Here ω_0 is the klystron frequency and $\bar{g}$ denotes the average g tensor which we take to be a scalar. The spectral densities are unusual in that, like the hyperfine spacing, they depend on the angle between the director and the magnetic field. The form of this angular dependence is predicted to be [10]

$$j_0^{(gg)} = \sum_{p,q} |g^{(2,p)}|^2 j_{q-p}\, d_{0,q}^{(2)}(\gamma)\, d_{0,q}^{(2)*}(\gamma), \tag{10}$$

$$j_0^{(gA)} = (\tfrac{3}{2})^{1/2} \sum_{p,q,r} g^{(2,p)}\, A^{(2,p)*}\, j_{q-p}\, d_{0,q}^{(2)}(\gamma)\, d_{r,q}^{(2)*}(\gamma) \times d_{0,r}^{(1)}(\chi) C(112\,;\ 0, r), \tag{11}$$

$$j_m^{(AA)} = \frac{1}{C(112\,;\ m, 0)^2} \sum_{p,q,r,r'} |A^{(2,p)}|^2\, j_{q-p}\, d_{r,q}^{(2)}(\gamma)\, d_{r',q}^{(2)*}(\gamma) \times C(112\,;\ 0, r) C(112\,;\ 0, r')\, d_{m,r}^{(1)}(\chi)\, d_{m,r'}^{(1)*}(\chi), \tag{12}$$

where $d_{p,q}^{(L)}(\beta)$ is a reduced Wigner rotation matrix and $C(LL'L''\,;\ p, q)$ is a Clebsch–Gordan coefficient. The angle χ is that between the magnetic field and the axis along which the nuclear spin is quantized ; this angle is zero when the hyperfine interaction is purely scalar. The nitrogen hyperfine tensor $\tilde{\mathbf{A}}$ is not a scalar because of the partial alignment of the probe in the liquid crystal and so χ is given by

$$\cos\chi = (\tilde{A}_\perp \sin^2\gamma + \tilde{A}_\parallel \cos^2\gamma)/\tilde{K}(\gamma), \tag{13}$$

$$\sin\chi = (\tilde{A}_\perp - \tilde{A}_\parallel) \sin\gamma \cos\gamma/\tilde{K}(\gamma). \tag{14}$$

Earlier theories [3, 5, 6, 11, 12] had assumed that χ was zero but as we shall see it is essential to treat the nuclear quantization correctly in the linewidth theory.

The dynamics of the problem are contained in the spectral densities j_{q-p} [10] which are defined by

$$j_{p-q} = \tfrac{1}{2} \int_{-\infty}^{\infty} \{\overline{D_{q,-p}^{(2)}(0) D_{q,-p}^{(2)*}(t)} - \overline{D_{0,-p}^{(2)}}\ \overline{D_{0,-p}^{(2)*}}\ \delta_{0q}\}\, dt, \tag{15}$$

where $D_{q,p}^{(L)}$ is a Wigner rotation matrix connecting the molecular and director coordinate systems. The averages $\overline{D_{0,-p}^{(2)}}$ provide another description of the orientational order of the probe and together they constitute the ordering tensor ; this is related to the Saupe ordering matrix in a manner described in the Appendix. The choice of the molecular frame with which to evaluate the rotation matrices presents no serious difficulties for rigid spin probes such as the cholestane probe where the principal axes of the inertial tensor seem an intuitively obvious candidate [9]. This is not the case for flexible molecules such as the stearic acid spin probes. Here the internal motion of the molecule as well as its reorientation are responsible for the time dependence of the correlation function of the rotation matrices. In the absence of any evidence to the contrary we shall set the z axis orthogonal to the oxazolidine ring. As we shall see this choice results in some simplification and reflects the molecular shape, at least in the all trans configuration. The theory does not contain correlation functions of the form $\overline{D_{q,-p}^{(2)}(0) D_{q',-p'}^{(2)*}(t)}$; their neglect can be justified for uniaxial mesophases composed of rigid cylindrically symmetric molecules [5]. It is more difficult

to justify their absence for flexible molecules although we shall ignore them because their inclusion would complicate the theory. In addition, as we shall see, the analysis of the experimental results with this simple theory is self-consistent. Finally we shall ignore those spectral densities involving Fourier transforms of the correlation function at frequency ω_0; this is valid providing $\omega_0^2 \tau^2 \gg 1$ where τ is a correlation time describing the motion [9].

It is necessary to adopt some model for the molecular dynamics so that the order parameters can be extracted from the spectral densities j_{qp}. In fact we shall assume that

$$j_{qp} = (-1)^{q-p} \sum_{L(\text{even})} \{C(22L\,;\; q-q)C(22L\,;\; p-p)\bar{P}_L - \bar{P}_2^2\, \delta_{0q}\delta_{0p}\}\tau_p. \quad (16)$$

This result is predicted by a variety of models for rigid molecules with $D_{\infty h}$ symmetry. Thus it is given [3] by the strong collision model where the molecular orientation can change by any amount as a result of sudden variations in the torque on the molecule. At the other extreme the Debye diffusion model suitably modified to include the effect of the long range ordering potential gives a similar result for moderately ordered systems ($\bar{P}_2 \lesssim 0{\cdot}6$) [13]. Finally a treatment based on the expansion of the conditional probability for molecular reorientation [14] gives the spectral density in equation (16); however the expressions for specific spectral densities are wrong presumably because the Clebsch–Gordan coefficients were not evaluated correctly.

We cannot justify the use of the spectral density given in equation (16) for non-rigid molecules in the same way. However, we shall use this form for the spectral density because it results in the minimum number of arbitrary parameters. The expression (16) for the spectral density also assumes that both second and fourth rank ordering matrices are cylindrically symmetric. In other words the ordering of the unit containing the oxazolidine ring is taken to depend on the single angle β between the director and the axis orthogonal to the ring. As we shall see the results obtained with these assumptions are both consistent and reasonable.

Measurement of the angular variation of the linewidth coefficients therefore enables us to determine the fourth rank order parameter $\bar{P}_4$ together with the correlation times τ_p.

3. Experiment

The composition of the lyotropic system was 42 per cent by weight of 1-*n*-decanol, 28 per cent sodium 1-*n*-decanoate and 30 per cent water, which is identical to that employed by Schindler and Seelig [6]. The spin probes were synthesized from the appropriate ketone using the procedure described by Keana *et al.* for the cholestane probe [15] and by Waggoner *et al.* [16] for the two stearic acid probes. The spin probe was first placed in a small test tube by evaporating a chloroform solution. Then the components of the liquid crystal were added and were mixed thoroughly. The doped mesophase was placed on the surface of a quartz plate (60 mm × 8 mm) and a second added. The plates were then squeezed together subject to two copper spacers 0·05 mm thick, to produce a monodomain sample of the mesophase with the director orthogonal to the plates. The uniformity of the lamellar phase was assessed by measuring its electron

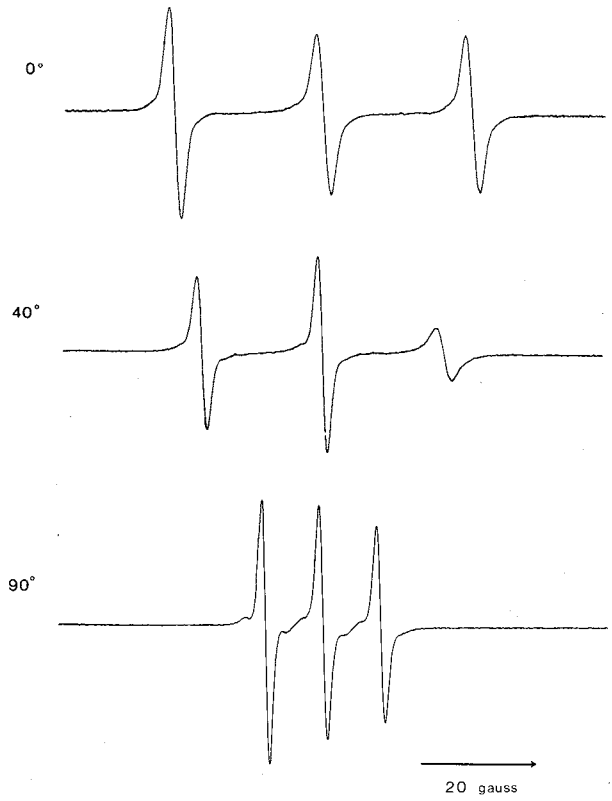

Figure 2. The electron resonance spectra for the 5-doxyl stearic acid probe in the lamellar *G* phase for three orientations of the director with respect to the magnetic field.

resonance spectrum ; only those samples which gave antisymmetric lineshapes, indicating a good monodomain, were studied. The plates were attached to a quartz rod which was mounted in a goniometer fixed to the cavity of a Varian E–9 spectrometer. The three probes were studied at room temperature ($\sim$22°C). The electron resonance spectra were measured for different orientations of the director with respect to the magnetic field, at essentially 10° intervals between 0° and 180°. Typical spectra for 5-doxyl stearic acid are shown in figure 2.

4. Analysis

The angular dependence of the line separation $\tilde{K}$ is given accurately by equation (4) and the components of $\tilde{\mathbf{A}}$ obtained by fitting equation (4) to the observed variation are given in table 1.

The determination of the linewidth coefficients is not so straightforward. The lineshape is not lorentzian, as predicted by theory, because the proton hyperfine structure broadens each nitrogen line inhomogeneously. The correct way to allow for this broadening is to simulate each of the three lines using proton coupling constants which contain both scalar and anisotropic contributions [17]. Alternatively we might ignore the anisotropic proton coupling which would

Table 1. The components of the partially averaged nitrogen hyperfine tensor and the order parameter $\bar{P}_2$, for an axis orthogonal to the oxazolidine ring, derived from them.

Probe	$\tilde{A}_{\parallel}$/Mrad s^{-1}	$\tilde{A}_{\perp}$/Mrad s^{-1}	$\bar{P}_2$
I	175	287	−0·38
II	456	175	0·61
III	322	214	0·23

simplify the analysis considerably ; the resultant error would probably be confined to the A coefficient whereas we shall only be concerned with the B and C linewidth coefficients. The need for detailed matching of the experimental spectra may be avoided altogether by using the following relationship

$$(T_2^{-1})^2 = \Delta H_p^2 - \Delta H_G^2, \tag{17}$$

between the true linewidth T_2^{-1}, the peak-to-peak separation ΔH_p and a correction factor ΔH_G which allows for the deviation from a lorentzian lineshape caused by the unresolved proton structure [18]. The magnitude of this correction is determined from simulated spectra using proton coupling constants for the particular radical. For the cholestane spin probe the proton coupling constants are

$$a(1),\ 19{\cdot}6\ \text{Mrad s}^{-1}\ ;\ a(4),\ 11{\cdot}5\ \text{Mrad s}^{-1}\ ;\ a(8),\ 1{\cdot}8\ \text{Mrad s}^{-1},$$

where the number of protons with this coupling is shown in parenthesis. Use of these values shows that equation (17) is well obeyed and ΔH_G^2 is found to be 57 Mrad^2 s^{-2}. Similar spectral simulations for the stearic acid spin probes give ΔH_G^2 as 13 Mrad^2 s^{-2}.

For each system studied the peak-to-peak separation was measured for the three nitrogen hyperfine components at a given orientation. The true width of the constituent proton lines was then estimated from equation (17) and from these widths the linewidth coefficients were determined. The angular variation of the B and C coefficients for the three spin probes is shown in figure 3.

The angular dependence of B and C found for 5-doxyl stearic acid is of particular relevance for studies of powder samples. Occasionally, it is impossible to study the angular variation of the electron resonance spectrum of the spin probe because a monodomain sample of the liquid crystal cannot be prepared. However it is possible to record the powder spectrum corresponding to a random distribution of the director in either two or three dimensions. Such spectra are dominated by contributions from the director both parallel and perpendicular to the magnetic field. In other words the spectrum yields, in essence, the linewidths for γ equal to 0° and 90°. We see that, for 5-doxyl stearic acid in the lamellar G phase, the linewidth coefficients are a minimum for these two orientations but a maximum when γ is about 60°. Consequently the parameters derived from powder spectra could well be subject to considerable uncertainty. This is unlikely to be the case when the complete angular variation of the linewidth coefficients is available.

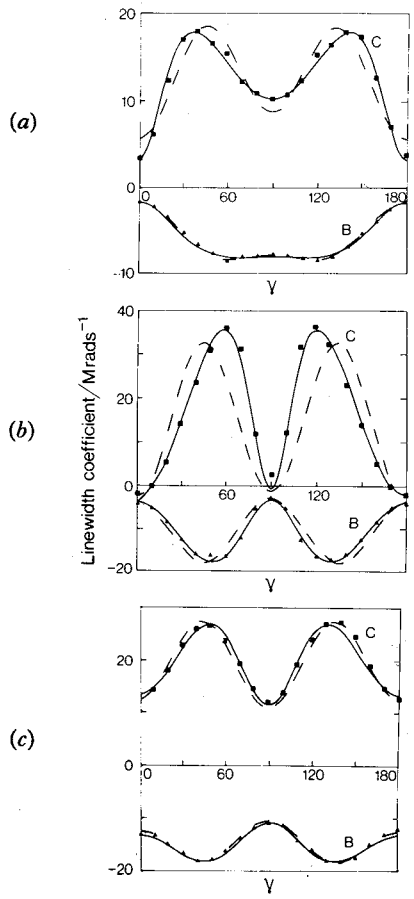

Figure 3. The angular variation of the B and C linewidth coefficients for (*a*) 3-doxyl-5α-cholestane, (*b*) 5-doxyl stearic acid and (*c*) 12-doxyl stearic acid dissolved in the lamellar G phase of the sodium decanoate-*n*-decanol-water system.

5. Interpretation

As we have seen the second rank order parameter for the axis orthogonal to the oxazolidine ring is obtained from the partially averaged nitrogen hyperfine tensor via equation (5). The value of $A'_{\parallel}$ required in the calculation varies slightly from one spin probe to another and it is also dependent on the environment of the probe. However it has been discovered that for the doxyl group the ratio of the components of the nitrogen hyperfine tensor $A_{\perp}/A_{\parallel}$ is essentially independent of the structure of the probe and its environment [19]; this ratio is found to be 0·188. To determine $A_{\parallel}$ and hence $A'_{\parallel}$ we require another relationship between $A_{\parallel}$ and $A_{\perp}$. This is provided by the trace of the tensor which is invariant under rotation and so

$$(A_{\parallel}+2A_{\perp})=(\tilde{A}_{\parallel}+2\tilde{A}_{\perp}). \tag{18}$$

Since we have determined $\tilde{\mathbf{A}}$ we are able to calculate $A'_{\parallel}$ for each spin probe dissolved in the lamellar G phase. Using these values and our results for $\tilde{\mathbf{A}}$

we find the order parameters listed in table 1 ; these parameters are in good accord with those found previously [19]. As we might have anticipated $\bar{P}_2$ for 5-doxyl stearic acid (0·61) is greater than that (0·23) for 12-doxyl stearic acid where the probe is further from the carboxyl group which is bound in the polar region of the bilayer. Unlike the stearic acid probes the axis orthogonal to the oxazolidine ring is not the major symmetry axis for the ordering matrix of the steroidal spin probe. Here S is essentially cylindrically symmetric about an axis constrained in the ring and making an angle of about 70° with the N–O bond [20]. We can obtain the order parameter for this major axis simply by multiplying $\bar{P}_2(S_{zz})$ by -2 and so find a value of 0·76. This result is quite high when compared with thermotropic nematics [21] and is comparable to that found for thermotropic smectic phases [5, 22]. It demonstrates the strong ordering ability of the lamellar phase even though it is composed of flexible molecules whose individual rigid segments have order parameters less than that of the steroidal spin probe.

We now turn to the B and C linewidth coefficients to determine the fourth rank order parameters. In the coordinate system assumed for the stearic acid spin probes the irreducible components of the g and nitrogen hyperfine tensors are [23]

$$g^{(2,0)} = -0{\cdot}0043 \qquad A^{(2,0)} = 359 \text{ Mrad s}^{-1}$$
$$g^{(2,\pm1)} = 0 \qquad A^{(2,\pm1)} = 0$$
$$g^{(2,\pm2)} = 0{\cdot}0016 \qquad A^{(2,\pm2)} = 0.$$

As a consequence the summation in equations (11) and (12) is restricted to those terms with $p = 0$. The theory therefore contains just two unknowns $\bar{P}_4$ and τ_0, since the other quantity, χ, in equations (11) and (12) can be calculated from $\tilde{\mathbf{A}}$ together with equations (13) and (14). We have obtained the best values for τ_0 and $\bar{P}_4$ by optimizing the agreement between theory and experiment. This optimization was performed separately for the B and C coefficients ; the best values for the parameters are given in table 2 for both stearic acid spin probes. The theoretical angular variation of the linewidth coefficients is shown as the solid line in figures 3 (*b*) and 3 (*c*) ; the agreement with experiment is seen to

Table 2. The order parameter $\bar{P}_4$ and the correlation times τ_0 and τ_2 obtained from a strong collision analysis of the B and C linewidth coefficients. Values in parenthesis were obtained by taking the nuclear spin to be quantized parallel to the magnetic field.

Probe	From B			From C		
	$\bar{P}_4$	$\tau_0/10^{-10}$ s rad^{-1}	$\tau_2/10^{-10}$ s rad^{-1}	$\bar{P}_4$	$\tau_0/10^{-10}$ s rad^{-1}	$\tau_2/10^{-10}$ s rad^{-1}
I	0·39	68	4·3	0·46	88	6·7
	(0·39)	(73)	(4·1)	(0·48)	(94)	(5·1)
II	0·07	15·5	—	0·14	27	—
	(0·07)	(14·5)	—	(0·13)	(24·5)	—
III	−0·09	13·5	—	−0·07	20·0	—
	(−0·10)	(13·0)	—	(−0·08)	(19·5)	—

be rather good especially as the theory contains just two variables. The values of $\bar{P}_4$ and τ_0 extracted from B and C should be the same and, as the results in table 2 show, they are similar but not identical. The differences observed might result from the assumptions made in the theoretical analysis. However these differences are no greater than those found for rigid spin probes and so they cannot necessarily be attributed to the failure of the assumptions taken from the treatment of rigid spin probes and applied to their flexible counterparts.

Before we attempt to interpret our results for $\bar{P}_4$ and τ_0 we shall analyse the linewidth variations for the steroidal spin probe. The irreducible spherical tensor components of the g and hyperfine tensors in the principal coordinate system for **S** are [20, 23]

$$g^{(2,0)} = 0{\cdot}0007 \qquad A^{(2,0)} = -172 \text{ Mrad s}^{-1}$$

$$g^{(2,\pm 1)} = 0{\cdot}0010i \qquad A^{(2,\pm 1)} = 0$$

$$g^{(2,\pm 2)} = -0{\cdot}0032 \qquad A^{(2,\pm 2)} = 216 \text{ Mrad s}^{-1}.$$

As a consequence of the non-zero value of the ± 2 components for both **g** and **A** there is a third unknown, τ_2, in equations (11) and (12) for the linewidth coefficients. The best values for the three variables $\bar{P}_4$, τ_0 and τ_2 were obtained by optimizing the agreement between the observed angular variation of the linewidth coefficients ; as before the quantization angle χ was calculated from $\tilde{\mathbf{A}}$. The results found from the B and C coefficients are listed in table 2. The theoretical angular variation, calculated with these values, is shown as solid lines in figure 3 (a) ; the agreement between theory and experiment is clearly very good. The values obtained from the C linewidth coefficients differ slightly from those found from the B coefficient. The differences are similar to those encountered in analogous studies of thermotropic liquid crystals [4, 5]. They are, as we noted earlier, certainly no smaller than those determined for the flexible stearic acid spin probes.

For comparison we have also analysed the angular dependence of the linewidth coefficients using the simpler theory in which the nuclear spin is assumed to be quantized parallel to the magnetic field for all director orientations. This theory predicts the angular dependence of the linewidth coefficients to be of the form

$$C = C_0 + C_2 P_2(\cos\gamma) + C_4 P_4(\cos\gamma), \tag{19}$$

where the angular linewidth coefficients depend on the rotational correlation times and the order parameters [3, 5]. A least squares fit of the linewidth results to such expressions (19) gave the dashed lines shown in figure 3. It is clear that the agreement between experiment and this simpler theory is not as good as that with the theory which allows for nuclear quantization. This failure of the simpler theory is the more dramatic because both theories have the same number of adjustable parameters. The discrepancy between experiment and the simpler theory is greater for the C coefficient than the B ; in addition the deviation is larger for the highly ordered systems. Both observations are in complete accord with predictions of the more complete theory [10]. Analysis of the angular linewidth coefficients using the simple theory gave the correlation times and fourth rank order parameters shown in parenthesis in table 2. It is clear that these values are probably within experimental error of those obtained by

allowing for nuclear quantization. This agreement contrasts with the marked differences between the angular variation of the linewidth coefficients obtained from the two theories.

We now consider the significance of the values determined for the order parameters $\bar{P}_2$ and $\bar{P}_4$. The orientational contribution to the energy of a single cylindrically symmetric molecule in a uniaxial mesophase is a function of the angle β between the microscopic and macroscopic symmetry axes. This contribution can be expanded in a complete set of Legendre polynomials $P_L(\cos\beta)$:

$$\frac{-U(\beta)}{kT} = \sum_{L(\text{even})} \lambda_L P_L(\cos\beta); \tag{20}$$

the symmetry of the mesophase restricts this summation to even values of L. In the Maier–Saupe theory of the nematic mesophase the summation is restricted to the first term with the expansion coefficient given by

$$\lambda_2 = \frac{\epsilon}{kT}\bar{P}_2, \tag{21}$$

where ϵ is a positive constant proportional to the nematic–isotropic transition temperature [24]. The success [25] of the Maier–Saupe theory suggests that even for a rigid molecule in a lyotropic mesophase the expansion might still be truncated at the second rank term. The form of λ_2 is unknown for such a system but we can determine its magnitude from the value of the second rank order parameter. Given λ_2 we can then calculate the fourth rank order parameter $\bar{P}_4$. The order parameters measured for steroidal spin probes in thermotropic liquid crystals have been found to be in good agreement with such calculations [4, 5]. For our lamellar G phase the order parameter $\bar{P}_2$ of the spin probe is 0·76 from which we predict $\bar{P}_4$ to be 0·43. This is in remarkably good agreement with the value of 0·39 found from the B coefficient and 0·46 from C. Analogous studies of steroidal spin probes in lecithin–cholesterol multibilayers have also confirmed the form of the single particle energy given by the truncated expansion [11].

This success suggests that the same truncation might also be appropriate for flexible spin probes. However, this extension is not immediate because the single particle orientational energy has contributions from both inter and intramolecular interactions. Nonetheless, linewidth investigations by Schindler and Seelig [6] of 4-doxyl stearic acid spin probes in the sodium decanoate-decanol-water system do appear to confirm this simple form for the single particle energy, although the order parameter $\bar{P}_4$ was not determined explicitly. Such a comparison is possible from our experiments and the results are given in table 3.

For 5-doxyl stearic acid $\bar{P}_2$ is found to be 0·61 corresponding to a calculated $\bar{P}_4$ value of 0·25 which is in poor agreement with the experimental values of 0·07 from the B linewidth coefficient and 0·14 from C. Similar disagreement is found for 12-doxyl stearic acid. Here $\bar{P}_2$ is 0·23 and so according to the simple potential $\bar{P}_4$ should be 0·04 whereas from the B and C linewidth coefficients we find it to be $-0{\cdot}09$ and $-0{\cdot}07$, respectively.

This failure of the truncated potential is surprising in view of the claims made by Schindler and Seelig [6] based on linewidth studies of a very similar

Table 3. The orientational order parameters and the theoretical estimates of $\bar{P}_4$.

Probe	$\bar{P}_2$	$\bar{P}_4$ Observed†	$\bar{P}_4$ Maier–Saupe theory	$\bar{P}_4$ Seelig model
I	0·76	0·43	0·43	—
II	0·61	0·11	0·25	0·55
III	0·23	−0·08	0·04	0·12

† This is the average of the values obtained from the B and C linewidth coefficients.

system. However in their investigations the complete angular dependence of the linewidths was not determined. Instead powder spectra were used and as we have seen this is liable to produce considerable errors for the systems studied. We believe therefore that the truncated form of the single particle potential is not suitable for a description of orientational order for the methylene segments of these flexible spin probes. Indeed it seems unlikely that it will be successful for any alkyl chains either in the bilayer or attached to a rigid core in a thermotropic liquid crystal.

Seelig has proposed an alternative theory of the order along an alkyl chain which does take into account explicitly the different internal configurations available to the chain [26]. According to this model interactions with neighbouring molecules restrict these configurations to those which preserve the essential alignment parallel to the director. The chain is therefore allowed to exist in an all trans configuration or those with a kink generated by a gauche ($\pm$)-trans-gauche ($\mp$) sequence. If these are the only configurations and if they are in rapid dynamic equilibrium then the order parameter for a particular segment will just be the weighted average of that for a kink and trans configuration. Then for any order parameter

$$\bar{P}_L = x_t P_L(\cos 0^\circ) + x_k P_L(\cos 60^\circ), \tag{22}$$

since in a trans configuration the angle between the normal to the oxazolidine ring and the director is 0° while for a kink this angle is 60°. The fraction of trans bonds at a segment, x_t, is just $(1-x_k)$ and so the order parameters $\bar{P}_2$ and $\bar{P}_4$ are

$$\bar{P}_2 = 1-(9/8)x_k, \tag{23}$$

$$\bar{P}_4 = 1-(165/128)x_k. \tag{24}$$

Our results for the order parameters of the two stearic acid spin probes may be used, therefore, to provide a severe test of this model. Thus we may calculate the fraction of kinks from $\bar{P}_2$ and use this to estimate $\bar{P}_4$; the results of these calculations are shown in table 3. They are in poor agreement with experiment and the model clearly over estimates the fourth rank order parameter. Indeed the predictions of this model are even worse than those of the simple Maier–Saupe like theory. It is clear that both theories are gross over simplifications of a very complex system.

Although our major concern was with the order parameters we conclude by considering briefly the rotational correlation times determined from the linewidths. The two times τ_0 and τ_2 found for the cholestane probe are similar to

the values measured in a thermotropic smectic A phase [27]. The large value of τ_0 reflects the slowness of the reorientation of the long axis while the smaller value of τ_2 indicates rapid rotation about the long axis. The ratio τ_0/τ_2 is large because of the highly anisotropic nature of both the environment and the spin probe; the value of this ratio appears to be intermediate between that found for nematics [4] and that measured for a highly ordered smectic A phase [5]. The correlation times determined for the stearic acid spin probes describe the reorientation of an axis orthogonal to the oxazolidine ring. The two values, shown in table 2, are very close. At first sight this is surprising because the environment of the probe at the polar end of the alkyl chain is thought to be in a less fluid region of the bilayer than at the end near the methyl group. However the oxazolidine ring may change its orientation as a result of internal as well as external reorientation. Our results for the two stearic acid spin probes may indicate that the internal changes are dominant and independent of the environment.

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Appendix

Here we give the explicit relation between the elements of the Saupe ordering matrix **S** and those of the ordering tensor $\overline{D^{(2)}}$. This relation has been incorrectly reported in a number of papers and so we shall sketch our derivation [14]. The average component of a tensor **F** parallel to the director, which is taken to define the laboratory z axis, is

$$F_{zz} = F_{\text{iso}} + \tfrac{2}{3} \sum_{\alpha,\beta} S_{\alpha\beta} F_{\alpha\beta}, \tag{A 1}$$

$$= F_{\text{iso}} + (\tfrac{2}{3})^{1/2} \sum_{p} \overline{D_{0,p}^{(2)*}}\, F^{(2,p)}, \tag{A 2}$$

in the cartesian and irreducible formalism, respectively. The Wigner rotation matrices and irreducible tensors are defined using the convention of Rose [28]. We equate equations (A 1) and (A 2)

$$(\tfrac{2}{3})^{1/2} \sum_{\alpha\beta} S_{\alpha\beta} F_{\alpha\beta} = \sum_{p} \overline{D_{0,p}^{2*}}\, F^{(2,p)}; \tag{A 3}$$

the irreducible components $F^{(2,p)}$ are related to their cartesian counterparts by

$$F^{(2,0)} = (\tfrac{2}{3})^{1/2} \{F_{zz} - (F_{xx} + F_{yy})/2\}, \tag{A 4}$$

$$F^{(2,\pm 1)} = \mp (F_{xz} \pm i F_{yz}), \tag{A 5}$$

$$F^{(2,\pm 2)} = \tfrac{1}{2}(F_{xx} - F_{yy} \pm 2iF_{xy}). \tag{A 6}$$

Substitution of these components into the right-hand side of equation (A 3) gives a relation that has to hold for any tensor **F**; we can therefore equate term

by term the coefficients of $F_{\alpha\beta}$. This gives the desired relations as

$$S_{zz} = \overline{D_{0,0}^{(2)}}, \tag{A 7}$$

$$S_{xx} - S_{yy} = (6)^{1/2} \text{ Re } \overline{D_{0,2}^{(2)}} = (\tfrac{3}{2})^{1/2}(\overline{D_{0,2}^{(2)}} + \overline{D_{0,-2}^{(2)}}), \tag{A 8}$$

$$S_{xy} = (\tfrac{3}{2})^{1/2} \text{ Im } \overline{D_{0,2}^{(2)}} = i(\tfrac{3}{8})^{1/2}(\overline{D_{0,-2}^{(2)}} - \overline{D_{0,2}^{(2)}}), \tag{A 9}$$

$$S_{xz} = -(\tfrac{3}{2})^{1/2} \text{ Re } \overline{D_{0,1}^{(2)}} = (\tfrac{3}{8})^{1/2}(\overline{D_{0,-1}^{(2)}} - \overline{D_{0,1}^{(2)}}), \tag{A 10}$$

$$S_{yz} = -(\tfrac{3}{2})^{1/2} \text{ Im } \overline{D_{0,1}^{(2)}} = i(\tfrac{3}{8})^{1/2}(\overline{D_{0,1}^{(2)}} + \overline{D_{0,-1}^{(2)}}). \tag{A 11}$$

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