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Molecular Organisation in the Smectic Mesophase of Ethyl 4-azoxybenzoate

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The static and dynamic properties of the nematic mesophase have been studied in numerous electron resonance experiments. Similar studies of the smectic mesophase are much rarer.(1,2,3) In these experiments the smectic phase had been oriented by cooling the preceding nematic mesophase, aligned by a magnetic field, to a temperature below the nematic–smectic transition point. Even if the mesogen does not possess a nematic phase it has been claimed(4) that an oriented smectic mesophase can be obtained by cooling the isotropic melt in the presence of a magnetic field. This claim is supported by a recent nuclear magnetic resonance experiment(5) although the high solute concentration may mean that this behaviour is not characteristic of the pure smectogen. We had hoped therefore to use this technique to align the smectic mesophase of ethyl 4-azoxybenzoate which does not possess a nematic mesophase. As we shall see these expectations were not completely realised although the mesophase was aligned by an alternative technique. The results of our investigation of the molecular organisation in the smectic mesophase are presented in this Note.

The sample of the smectogen was obtained from Eastman Organic Chemicals and purified by recrystallisation from ethanol. The melting point of this material was 113.5 °C and the smectic–isotropic transition point was 121.5 °C. The paramagnetic probe (3-spiro-[2′N-oxyl-3′,3′dimethyloxazolidine])5-α androstane-17-β-ol, was prepared from 5-α androstane-17-β-ol using standard techniques.(6) This type of probe is ideal for investigations of a mesophase because

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its rigid elongated structure produces a high degree of alignment. However, the probe is optically active and could, in principle, induce a transition to a cholesteric state. In practice the concentration required for an electron resonance experiment is insufficient to cause this transition. The electron resonance spectra were recorded on a Varian E-3 spectrometer fitted with an optical transmission cavity to permit observation of the sample. The hyperfine splittings and g factors were measured with the aid of the Varian F.8A Fluxmeter and a Hewlett-Packard Electronic Counter fitted with a 5255A Frequency Converter.

For the initial experiments the sample was placed in a cylindrical tube and the temperature was slowly lowered from just above to just below the isotropic–smectic transition point in a field of 3 k-Gauss. The spectrum from the smectic mesophase obtained in this way was found to be invariant under rotation about the cylindrical axis of the tube. A typical electron resonance spectrum is shown in Fig. 1. The spacing between adjacent spectral lines is less than the largest component of the nitrogen hyperfine tensor$^{(7)}$ but greater than the isotropic coupling constant. This observation is important for it shows that the probe executes rapid anisotropic rotational diffusion. Presumably the molecules of the host are also in motion within the smectic layers. Provided the ordering potential has cylindrical symmetry it is possible to regard the dynamic probe as a static radical with cylindrically symmetric magnetic interaction tensors.$^{(8)}$ In irreducible tensor notation the only non-zero component of a second rank interaction is

$$\tilde{F}^{(2,0)} = \sum_{p} (-1)^p F^{(2,p)} \overline{\mathscr{D}^{(2)}_{0,-p}},$$

where $F^{(2,p)}$ is the total tensor and the averaged rotation matrix $\overline{\mathscr{D}^{(2)}_{0,-p}}$ describes the alignment of the probe.$^{(8)}$ The symmetry axis of these interactions is parallel to that of the ordering potential and hence the director. Since the spectrum is invariant under rotation the director may be either randomly oriented or approximately parallel to the axis of the sample tube. The spectrum expected for a random orientation is readily calculated$^{(9)}$ and a theoretical polycrystalline spectrum is included in Fig. 1. The absence of the weak inner pair of lines from the experimental spectrum demonstrates the alignment of the director parallel to the sample tube axis. This

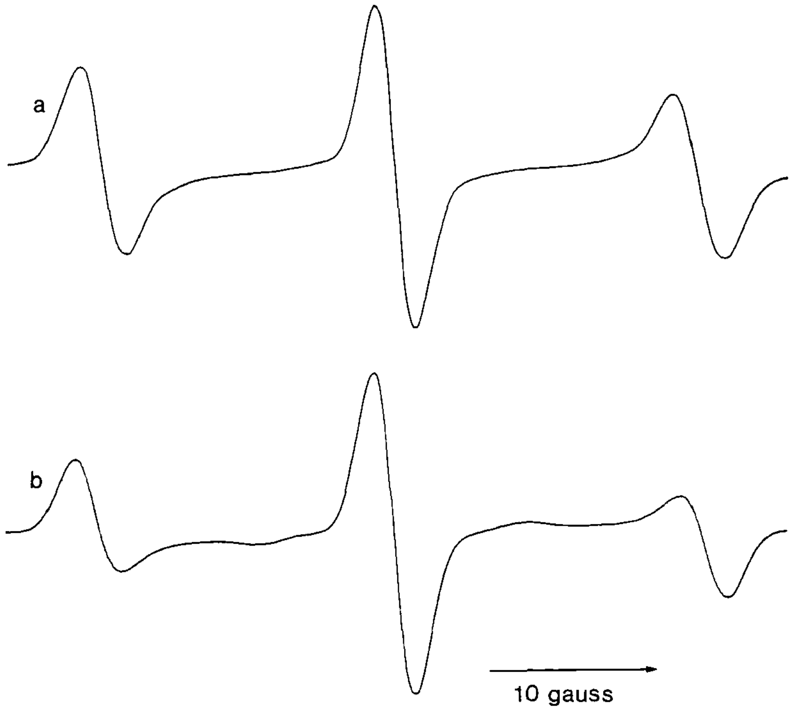

Figure 1. The experimental electron resonance spectrum (a) of the nitroxide probe dissolved in the smectic mesophase of ethyl 4-azoxybenzoate and (b) a theoretical reconstruction based on a random distribution of the director.

conclusion is confirmed by the symmetric appearance of the outer pair of spectral lines. The slight asymmetry which remains is produced by a small departure from perfect alignment of the director. In later experiments we were able to obtain a uniform alignment by cycling the sample temperature through the isotropic-smectic transition point. The smectic phase obtained in this way was quite transparent although a transient polygon texture was observed at the wall of the tube near the transition point. The alignment of the director parallel to the sample tube is presumably caused by a combination of surface forces and the temperature gradient within the sample. In contrast the mesophase obtained on melting the solid is turbid and its electron resonance spectrum indicates random alignment of the director.

In these experiments the expected alignment of the mesophase by the magnetic field, with the director parallel to the field, was not realised. The experiments were therefore repeated with a more intense field of 6500 Gauss which is the maximum attainable with an E-3 spectrometer. Under these conditions the intensity of the inner pair of lines is greatly increased although the outer pair never vanish. These results show that although the director tends to be aligned parallel to the magnetic field the alignment is not uniform. In addition it proved difficult to reproduce a given alignment possibly because of the random manner in which the smectic phase grows from the isotropic melt. In principle the degree of solute alignment could be extracted from the spectrum shown in Fig. 1. However, more accurate results are available from an analysis of the angular dependence of the spectrum from a uniformly oriented sample. Accordingly we attempted to align the smectic mesophase between two glass plates.

The plates were washed first in acetone and then in alcohol before being wiped dry with a paper tissue. They were placed in a metal holder which was attached to a goniometer so that the angle between the plates and the magnetic field could be measured accurately. The sample was melted between the plates and the mesophase, obtained from the solid, exhibited a simple fan-shaped texture.(10) The electron resonance spectrum showed that although the director tended to be orthogonal to the plates it was not uniformly distributed. However, we were able to obtain a perfectly aligned sample with the following procedure. The temperature of the mesogen was reduced until the majority of the mesophase had crystallised. At this point the temperature was raised sufficiently to convert all of the sample back to the smectic mesophase. This cycle was repeated several times and was found to yield a perfectly oriented pseudoisotropic preparation. The electron resonance spectrum of the probe was then measured as a function of the angle, γ, between the field and an axis normal to the plates. The angular dependence of the nitrogen coupling constant was found to be accurately predicted by the expression

$$\bar{a}(\gamma) = \left\{\frac{\tilde{g}_\perp{}^2\tilde{A}_\perp{}^2 + (\tilde{g}_\parallel{}^2\tilde{A}_\parallel{}^2 - \tilde{g}_\perp{}^2\tilde{A}_\perp{}^2)\cos^2\gamma}{\tilde{g}_\perp{}^2 + (\tilde{g}_\parallel{}^2 - \tilde{g}_\perp{}^2)\cos^2\gamma}\right\}^{1/2}.$$

In this equation the || subscript denotes the component of the g or hyperfine tensor of the pseudo-molecule parallel to the director. Similarly the $\perp$ subscript denotes the components perpendicular to the director. Experimentally these parameters were found to be independent of temperature within the smectic range with the values:

$$\tilde{A}_{\parallel} = 21.2\,\text{MHz}, \quad \tilde{A}_{\perp} = 51.8\,\text{MHz},$$

$$\tilde{g}_{\parallel} = 2.0062 \quad \text{and} \quad \tilde{g}_{\perp} = 2.0058.$$

This particular angular dependence of the coupling constant is expected if the director is perpendicular to the plates.(3) Since the smectic planes should be parallel to the surfaces of the plates ethyl 4-azoxybenzoate must have a smectic-A mesophase in which the molecular long axes are perpendicular to the layers. The experiments therefore confirm a previous assignment of the structure of this smectic mesophase based on quite different techniques.(11)

The magnitude of the parameters $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ can now be used to determine the degree of order for the probe. The total nitrogen hyperfine tensor is cylindrically symmetric(7) and so the two components of the hyperfine tensor for the pseudo molecule are given by

$$\tilde{A}_{\parallel} = a + A_{\parallel}'\overline{\mathscr{D}^{(2)}_{0,0}},$$

and

$$\tilde{A}_{\perp} = a - \tfrac{1}{2}A_{\parallel}'\overline{\mathscr{D}^{(2)}_{0,0}}.$$

Here a is the isotropic coupling constant and the prime denotes the anisotropic component of the total tensor.(3,8) At 125 °C the isotropic coupling constant for the probe dissolved in ethyl 4-azoxybenzoate is 41.4 MHz and the anisotropic component $A_{\parallel}'$ is 46.5 MHz.(7) We can therefore obtain two estimates for the solute order, $\overline{\mathscr{D}^{(2)}_{0,0}}$ and these, -0.43 and -0.45, are in good agreement. Since the parameters $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ are temperature independent the solute order must also be independent of temperature which is in marked contrast to the behaviour in the nematic mesophase. The maximum negative value for $\overline{\mathscr{D}^{(2)}_{0,0}}$ is -0.5 and so the probe must be extremely well ordered by the smectic mesophase. This may also indicate a high degree of order for the mesophase itself. To be able to judge the significance of this high solute order we determined the value of $\overline{\mathscr{D}^{(2)}_{0,0}}$ for the probe dissolved in two nematic mesophases. The largest value in 4,4'-dimethoxyazoxybenzene was −0.30 which was obtained in the supercooled mesophase at 90 °C. In the nematic mesophase of 4,4'-di-*n*-heptyloxyazoxybenzene the solute order is slightly larger and at the nematic–smectic transition point is −0.32. Clearly the order in the smectic-*A* mesophase of ethyl 4-azoxybenzoate is considerably larger than in either nematic mesophase. It would, however, be unwise to regard this as a general result. For example, the mesogen terephthal-bis-(4-*n*-butylaniline) has both a nematic and smectic-*A* mesophase.(12) The degree of order for the probe, vanadylacetylacetonate, was found to be −0.172 in the nematic mesophase which is only slightly smaller than −0.188 found in the smectic phase.(3)

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