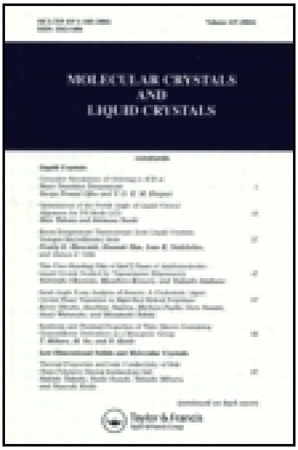

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Orientational Order in Cholesteric Liquid Crystals

S. G. Carr [a b] , S. K. Khoo [a] , G. R. Luckhurst [a] & H. J. Smith [a c]

[a] Department of Chemistry, The University, Southampton, SO9 5NH, England

[b] 52, Ormond Road, Kensington, Melbourne, Victoria, Australia

[c] 25, Morton Road, Fernhill Health, Worcester, England

To cite this article: S. G. Carr , S. K. Khoo , G. R. Luckhurst & H. J. Smith (1978): The Orientational Order in Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 45:3-4, 161-181

To link to this article: http://dx.doi.org/10.1080/00268947808085000

Mol. Cryst. Liq. Cryst., 1978, Vol. 45, pp. 161–181

Printed in Holland

The Orientational Order in Cholesteric Liquid Crystals

S. G. CARR†, S. K. KHOO, G. R. LUCKHURST and H. J. SMITH‡
Department of Chemistry, The University, Southampton, SO9 5NH, England.

(*Received July 25, 1977*)

The investigation of the orientational order in the mesophase of steroidal cholesterogens has been all but neglected by experimentalists, possibly because of the lack of an appropriate technique. However electron resonance spectroscopy can be used to determine the order parameter of a spin probe dissolved in a cholesteric mesophase. In addition the structure of the spin probe may be made to resemble that of the cholesteric solvent. Here this technique is employed to determine the orientational order for cholesteryl and cholestanyl benzoate, as a function of temperature. The results of these experiments yield order parameters which are comparable, or slightly smaller, than those typically observed for nematics. A comparison of these values with mean field theories suggests that the low order parameters of steroidal cholesterogens stems from deviation of the constituent molecules from cylindrical symmetry.

1 INTRODUCTION

The liquid crystal state is characterized by the long-range orientational order, which is destroyed at the transition to the isotropic liquid. In principle this order can be defined in terms of a hierarchy of distribution functions involving both spatial and orientational coordinates. In practice even the singlet orientational distribution function, which gives the probability of finding a molecule at a particular orientation with respect to the director, is difficult to determine.[1] However the order parameter, defined as the ensemble average of the second Legendre function $P_2(\cos\theta)$, where θ is the angle between the molecular long axis and the director, can be obtained from a variety of experiments. Indeed the variation of $\bar{P}_2$ with both temperature and pressure has been measured for numerous nematic liquid crystals. The results of these experiments are important because they provide a valuable

---

Present address:

† 52, Ormond Road, Kensington, Melbourne, Victoria, Australia.
‡ 25, Morton Road, Fernhill Heath, Worcester, England.

test bed for the various theoretical models of the liquid crystal state.[1] In addition it is to be expected that the nature of the anisotropic intermolecular forces responsible for the liquid crystal might also be deduced from such measurements.

In spite of the considerable attention devoted to nematics there has been only one attempt,[2] as far as we are aware, to determine the order parameter for a steroidal cholesterogen. This lack of interest by experimentalists in cholesterics is surprising for two reasons. Thus the first liquid crystal to be discovered, over 80 years ago, was cholesteryl benzoate.[3] More importantly the molecular structure of such cholesterogens is quite different to that of nematic liquid crystals, whose molecules invariably contain highly polarisable phenyl groups. Consequently repulsive forces should be considerably more important for steroidal cholesterics than for nematics; we might then expect this difference to be reflected in the magnitude of the order parameter together with its temperature dependence.[1] We have therefore attempted to determine the orientational order for two cholesterogens, cholesteryl benzoate and cholestanyl benzoate, and report the results of our experiments in this paper.

The technique employed in our studies was electron resonance spectroscopy and so the cholesterogens, which are diamagnetic, must be doped with a spin probe. Strictly therefore we are only able to determine the order parameter of the spin probe dissolved in the mesophase. However, the order

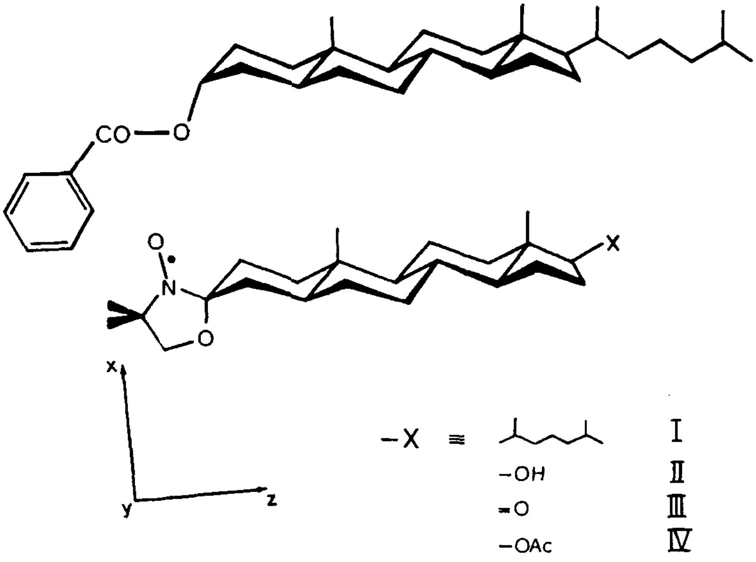

FIGURE 1

parameter for the solute should tend to that of the solvent as the molecular structure of the spin probe approaches that of the liquid crystal. As a consequence we have employed four steroidal spin probes in these studies one of which, 3-(2′-spiro-{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-cholestane (I) has a structure very similar to that of the cholesterogens, as we can see from the formula in Figure 1. Thus we believe that the order parameter for this spin probe will be virtually identical to that of the two cholesteric mesophases. Our account of this investigation begins in Section 2, with a brief description of the electron resonance theory underlying the spectral analysis. The experiments themselves are outlined in Section 3 while the interpretation of the spectra and the results are given in Section 4. Finally a rationalisation of the order parameters determined for the spin probes in the two cholesteric liquid crystals is presented in Section 5.

2 ELECTRON RESONANCE THEORY

There are two important magnetic interactions for the nitroxide spin probes employed in this investigation. The first is the Zeeman coupling of the magnetic field to the electron spin while the second is its hyperfine interaction with the spin of the nitrogen nucleus.[4] There are, of course, smaller hyperfine couplings to certain protons in the spin probe but these only serve to produce an inhomogeneous broadening of the three nitrogen hyperfine components.[5] In a liquid crystal mesophase the probe is subject to an anisotropic ordering potential which results in its partial alignment. Provided the rate of molecular reorientation is fast the probe may be thought of as a static species in which the total magnetic tensors are replaced by partially averaged quantities.[6] The symmetry of these tensors is dictated by that of the ordering potential. For example in a uniaxial phase, such as a nematic or smectic A, the partially averaged tensors are cylindrically symmetric and the same symmetry will also hold for a cholesteric. This situation obtains because although the overall symmetry of the director in the cholesteric phase is S_∞ the pitch is large in comparison with the range of the intermolecular potential and so the local potential has $D_{\infty h}$ symmetry.

In general, the components of a partially averaged second-rank tensor $\tilde{\mathbf{F}}$, are given by

$$\tilde{F}_{\parallel} = f + \frac{2}{3}\sum_{i,j} S_{ij}F'_{ij} \tag{1}$$

and

$$\tilde{F}_{\perp} = f - \frac{1}{3}\sum_{i,j} S_{ij}F'_{ij}, \tag{2}$$

where f is the scalar interaction and $\mathbf{F}'$ denotes the anisotropic part of the total tensor.[6] The extent of the alignment is characterised by the ordering matrix $\mathbf{S}$. These equations can be simplified for the hyperfine tensor $\tilde{\mathbf{A}}$ because the anisotropic nitrogen tensor $\mathbf{A}'$ is cylindrically symmetric about an axis perpendicular to the oxazolidine ring. Therefore it will be possible to determine only the component of the ordering matrix along this axis, from the partially averaged hyperfine tensor. However, the ordering matrix for the steroidal spin probe (I) in nematic mesophases is found to be essentially cylindrically symmetric about an axis which is parallel to the oxazolidine ring.[7] If the same symmetry holds in the cholesteric phase then the partially averaged components of the nitrogen hyperfine tensor may be written as

$$\tilde{A}_{\parallel} = a - \tfrac{1}{2}\bar{P}_2 A' \tag{3}$$

and

$$\tilde{A}_{\perp} = a + \tfrac{1}{4}\bar{P}_2 A', \tag{4}$$

where $A'_{\parallel}$ is the parallel component of the anisotropic hyperfine tensor. We shall call $\bar{P}_2$ the order parameter for the spin probe even though it is only identical to that for the molecular long axis when the ordering matrix is cylindrically symmetric. Strictly however $\bar{P}_2$ must be identified with minus twice the component of $\mathbf{S}$ perpendicular to the oxazolidine ring. The scalar hyperfine coupling can be obtained from the spectrum in the isotropic phase and does not change on passing to the mesophase. It is possible therefore to determine $\bar{P}_2$ from measurements of either $\tilde{A}_{\parallel}$ or $\tilde{A}_{\perp}$; however, observation of both allows a to be eliminated from Eqs. (3) and (4).

When the director is aligned at some angle γ to the magnetic field the spectrum contains three nitrogen hyperfine components and the spacing between them, $\tilde{K}(\gamma)$, is related to $\tilde{\mathbf{A}}$ by the familiar expression[6]

$$\tilde{K}(\gamma) = \{\tilde{A}_{\parallel}^2 \cos^2\gamma + \tilde{A}_{\perp}^2 \sin^2\gamma\}^{1/2}, \tag{5}$$

provided the small anisotropy in $\tilde{\mathbf{g}}$ is ignored. The resonant magnetic field for a line with nuclear spin quantum number m is then

$$B_m(\gamma) = \frac{h\nu}{\tilde{g}(\gamma)\beta} - \frac{\tilde{K}(\gamma)m}{\tilde{g}(\gamma)\beta}, \tag{6}$$

where

$$\tilde{g}(\gamma) = \{\tilde{g}_{\parallel}^2 \cos^2\gamma + \tilde{g}_{\perp}^2 \sin^2\gamma\}^{1/2}. \tag{7}$$

The second order corrections to the line positions have been omitted because, at X-band frequencies, the hyperfine splitting is small in comparison with the Zeeman separation. Measurement of the angular variation of the spectrum then provides both partially averaged tensors, $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$, and so permits a determination of the order parameter, $\bar{P}_2$. This approach is not possible for a cholesteric phase because of the non-uniform alignment of the director in a bulk sample. Of course a magnetic field could be employed to unwind the helix and so produce a uniformly aligned mesophase, however the fields required for steroidal cholesterogens far exceed the 3 kG available in an electron resonance spectrometer.[8] As a consequence the spectrum observed from a cholesteric mesophase in a normal sample tube is simply a sum of spectra associated with all orientations of the director. This sum may be written as the integral[6]

$$h(B) = \sum_r \int_0^\pi L\{B, B_r(\gamma), T_2^{-1}(m, \gamma)\} \sin \gamma \, d\gamma, \tag{8}$$

where $L\{B, B_r(\gamma), T_2^{-1}(m, \gamma)\}$ denotes a lorentzian lineshape. The subscript r represents all resonant fields and, to allow for unresolved proton hyperfine structure, we must extend Eq. (6) to

$$B_r(\gamma) = \frac{h\nu}{\tilde{g}(\gamma)\beta} - \frac{\tilde{K}(\gamma)m}{\tilde{g}(\gamma)\beta} - \frac{\sum_i a_i m_i}{\tilde{g}(\gamma)\beta}, \tag{9}$$

where a_i is the coupling constant of the ith proton. Strictly the proton coupling constants are orientation dependent but for our purposes it is sufficient to retain just the scalar component. The linewidths are virtually independent of the proton quantum numbers but are certainly dependent on that of the nitrogen nucleus.[4] In addition the linewidths are frequently observed to be orientation dependent[9] and it is essential to allow for this dependence when fitting the observed line shapes. To reduce the number of adjustable parameters in the simulation we shall assume

$$T_2^{-1}(m,\gamma) = T_{\parallel}(m)\cos^2 \gamma + T_{\perp}(m)\sin^2 \gamma, \tag{10}$$

where $T_{\parallel}(m)$ and $T_{\perp}(m)$ are the widths of the mth hyperfine line when the magnetic field is either parallel or perpendicular to the director.[10] We expect this approximation, to the correct angular variation, to be particularly good because the observed spectrum is dominated by contributions from director orientations both parallel and perpendicular to the field.

Comparison of the spectra simulated in this way with their experimental counterparts would then give the partially averaged hyperfine tensor, $\tilde{\mathbf{A}}$, and hence the order parameter, $\bar{P}_2$, for the spin probe. Although we have followed this path the optimisation of the agreement between the observed and simulated spectra can be tedious; fortunately an alternative route is available. It is possible to align a cholesteric phase between two glass plates so that the helix axis is normal to the plates. In such a situation the director is always parallel to the surfaces of the plates and so when the magnetic field is applied normal to the plates it will also be orthogonal to the director for all positions in the sample. The spectrum will therefore contain three nitrogen hyperfine lines with a spacing equal to $\tilde{A}_\perp$ from which $\bar{P}_2$ may be determined. In contrast when the magnetic field is parallel to the surface the director is randomly aligned with respect to the field but now in just two dimensions; thus the observed spectrum is given by

$$h(B) = \sum_r \int_0^{2\pi} L\{B, B_r(\gamma), T_2^{-1}(m, \gamma)\} \mathrm{d}\gamma. \qquad (11)$$

We shall see, in Section 4, that it is valuable to observe such two-dimensional powder spectra and to analyse them using computer simulations based on Eq. (11). However before we turn to this analysis we shall describe how the spectra were obtained and tabulate the systems studied.

3 THE EXPERIMENTS

Two cholesterogens were investigated, one of these was cholesteryl benzoate (T_{S-C} 153°C, T_{C-I} 182°C) and the other was the closely related cholestanyl benzoate (T_{S-C} 139°C, T_{C-I} 157°C). The spin probe, 3-(2′-spiro-{3′*N*-oxyl-4′-4′-dimethyloxazolidine})5α-cholestane (I) is most similar in structure to the two cholesterogens. However, we also wished to monitor the influence of the substituent at the 17 position on the order parameter for the spin probe. We therefore used three other steroidal nitroxides, the first of which was 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17β-ol (II) in which the alkyl chain is replaced by a hydroxyl group. In the remaining spin probes the hydroxyl group was either converted to the acetate (IV) or replaced by a ketone (III). These two compounds are of particular value because specific interactions involving the hydroxyl group which might occur for (II) are no longer possible.

The cholesteryl benzoate was purchased from E. Merck, Darmstadt, and used without further purification because the transition temperatures were in good accord with their literature values. Cholestanyl benzoate was prepared by esterifying cholestanol with benzoylchloride and recrystallized from alcohol. The four spin probes (I–IV) were synthesised from the corresponding steroidal ketones.[11] The starting materials for (I–III) were obtained commercially while the steroidal ketone for (IV) was synthesised from 5α-androst-3-one-17β-ol and acetic anhydride (m.p. 163°C). Samples were prepared by doping the two cholesterogens with the four spin probes, they were then placed in 4 mm Pyrex tubes and sometimes between quartz plates. The plates were approximately 7 mm × 100 mm and were cleaned in chromic acid, washed in water and finally in acetone. After drying they were rubbed about 200 times along their length with Green's lens tissue

(C105) in order to induce planar alignment. The sample was melted on one plate and the other placed on top; in addition the two plates were moved relative to one another in the direction of rubbing to ensure good alignment. The nature of the sample container for the various systems is shown in Table I together with their cholesteric-isotropic transition points; as we can see addition of the spin probe results in the expected depression of this transition temperature.

TABLE I

The systems and the containers used in their investigation. The cholesteric–isotropic transition temperature (T_K) of the solution is given together with the scalar nitrogen coupling constant (a) of the spin probe.

		Cholestanyl benzoate		Cholesteryl benzoate	
Spin probe		Plates	Tube	Plates	Tube
I	T_K/°C	155	155	179	—
	a/MHz	41.2	41.3	41.3	
II	T_K/°C	154	155	—	180
	a/MHz	40.9	41.0		41.4
III	T_K/°C	—	155	—	178
	a/MHz		41.0		41.0
IV	T_K/°C	154	155	178	179
	a/MHz	41.0	41.2	41.0	41.1

The electron resonance spectra were recorded on a Varian E-3 spectrometer as a function of temperature over the entire range of the cholesteric mesophase which was invariably extended by supercooling. Typical spectra are shown in Figure 2 for cholestanyl benzoate doped with the cholestane spin probe at about 132°C; Figure 2a is a three line spectrum observed when the magnetic field is orthogonal to the plates, in contrast Figure 2b shows a two dimensional powder spectrum found when the plates are parallel to the field and finally Figure 2c gives a three dimensional powder spectrum for the same sample contained in a tube. The spin probes tend to decompose at the relatively high temperatures of the mesophases and so fresh samples had to be prepared to obtain a complete set of results. The sample temperature was monitored with a copper-constantan thermocouple which was placed either inside the tube or attached to the outer surface of the glass plate. Finally the spectra for each spin probe were recorded in the nematic phase of 4,4′-dimethoxyazoxybenzene to provide a set of order parameters to compare with the results for the cholesterogens.

In concluding this Section we wish to comment on our choice of cholesterogens. As we saw in the previous Section the proposed spectral analysis is only valid when the reorientation of the spin probe is fast. If this condition is not

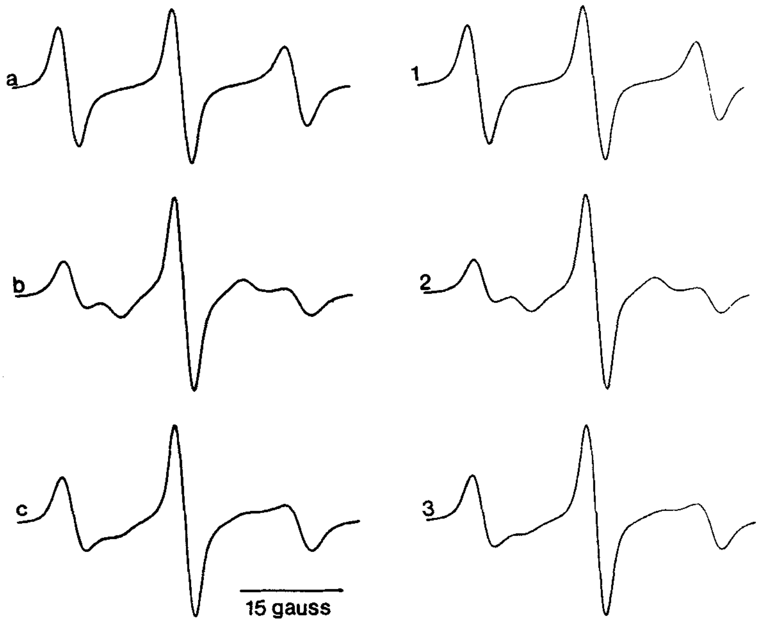

FIGURE 2 The electron resonance spectrum of the cholestane spin probe (I) dissolved in the cholesteric phase of cholestanyl benzoate (a) at 132.4°C with the magnetic field perpendicular to the plates (b) at 132.4°C with the field parallel to the plates and (c) at 132.6°C in a tube. The spectra labelled (1), (2) and (3) are the theoretical counterparts.

satisfied then the orientational order parameter cannot be obtained from the electron resonance spectrum. Now the rate of molecular reorientation is often related to the bulk viscosity of the solvent and for cholesterogens this viscosity appears to decrease with the temperature of the cholesteric phase. Indeed we have found that when the spin probe is dissolved in a low temperature cholesterogen, such as cholesteryl nonanoate ($T_{S\text{–}C}$ 79°C, $T_{C\text{–}I}$ 90°C), the order parameter of the probe cannot be determined.[12] However for steroidal cholesterogens with a mesophase above about 130°C, it is possible to measure the order parameter. The method which we propose here is not of complete generality and the most reliable technique must be based on the deuterium nuclear magnetic resonance of appropriately deuteriated cholesterogens.

4 SPECTRAL ANALYSIS

The perpendicular component of the partially averaged hyperfine tensor can be measured directly from the spectrum when the magnetic field is orthogonal to the plates. The order parameter is then determined using Eq. (4) with $A'_{\parallel}$

set equal to 46.5 MHz, a value measured for (I) in a single crystal of cholesteryl chloride.[13] The scalar coupling constant also required in the calculation was taken from the spectrum recorded in the isotropic phase of the cholesterogens, with the results given in Table I. To check the value of $\tilde{A}_\perp$ we have simulated the spectrum obtained for the field parallel to the plates as well as that recorded from the tube. The component $\tilde{A}_\parallel$ was calculated from $\tilde{A}_\perp$ and a; for the spectra in Figure 2 this gave $\tilde{A}_\parallel = 28.0$ MHz and $\tilde{A}_\perp = 47.8$ MHz while the partially averaged g tensor was assigned the values $\tilde{g}_\parallel = 2.0060$ and $\tilde{g}_\perp = 2.0056$. The linewidths are also required in the spectral simulation and, to avoid the introduction of too many variables the width, $T_2^{-1}(0)$, of the central line was taken to be orientation independent.[10] An attempt was made to obtain $T_\perp(m)$ from the perpendicular spectrum in Figure 2a. The spectrum was simulated with the line positions given by Eq. (9) with γ set equal to 90°. The proton hyperfine structure in these calculations was approximated by a set of five equivalent protons with a coupling constant of 2.0 MHz.[14] The agreement between the experimental and simulated spectra was optimised by varying the three linewidths $T_\parallel(m)$. The optimised values of the linewidths are given in Table II and were employed to simulate the spectrum, shown in Figure 2a, which is in very good agreement with its experimental counterpart. These values of $T_\parallel(m)$ were then used to calculate the two and three dimensional spectra; attempts were made to optimise the agreement with experiment by varying just $T_\perp(m)$. However the agreement, although good, was never perfect and so minor adjustments were made to $T_\parallel(m)$; such small changes are quite justified because the sample temperature was never exactly the same after the plates had been rotated through 90°. The optimised values of the linewidths are also given in Table II and the two-dimensional powder spectrum simulated with them is shown in Figure 2b. The agreement with the experimental spectrum is seen to be excellent and this enables us to use our analysis of the plate spectra to obtain the order parameter with some confidence.

TABLE II

The linewidth parameters (in gauss) employed for the simulation of the three spectra shown in Figure 2.

	$m = 1$			$m = -1$	
Spectrum	$T_\parallel$	$T_\perp$	$T(0)$	$T_\parallel$	$T_\perp$
1	—	1.4	1.1	—	1.90
2	1.8	1.2	1.1	2.2	1.8
3	1.8	1.2	1.0	2.2	1.7

Although we have not employed the two-dimensional powder spectra to determine $\tilde{\mathbf{A}}$ we have analysed the three dimensional powder spectra obtained from conventional sample tubes to measure the partially averaged hyperfine tensor. To confirm our analysis we have simulated the spectrum of such a sample using the same parameters as those employed in the simulation of the two-dimensional powder spectrum. Again the agreement with the experimental spectrum, shown in Figure 2c, was found to be good but not perfect and so the linewidth parameters were modified slightly. The resulting simulation, given in Figure 2c, is in complete agreement with experiment; the linewidths employed in the calculation are listed in Table II. Since the components of $\tilde{\mathbf{A}}$ were given the same value in all three simulations we believe that similar analyses of the three-dimensional powder spectra will produce reliable values for $\tilde{\mathbf{A}}$. In these analyses the two components $\tilde{A}_{\parallel}$ and $\tilde{A}_{\perp}$ were not varied independently because they are related, via the scalar coupling, by

$$\tilde{A}_{\parallel} + 2\tilde{A}_{\perp} = 3a. \tag{12}$$

The procedure employed to determine the partially averaged hyperfine tensor for each of the four spin probes dissolved in the two cholesterogens is indicated in Table I. The order parameter, $\bar{P}_2$, for the spin probe was then determined from $\tilde{\mathbf{A}}$ with the aid of Eqs. (3) and (4); again $A'_{\parallel}$ was given the value of 46.5 MHz. The results of all these measurements are plotted as a function of the reduced temperature (T/T_K) in Figure 3; here the subscript K denotes the cholesteric–isotropic transition. For comparison the order parameter determined for each spin probe in the nematic mesophase of 4,4′-dimethoxyazoxybenzene is also included in the figure. In the following Section we shall discuss the significance of these results.

5 INTERPRETATION OF THE ORDER PARAMETER

We begin with a qualitative discussion of the order parameters for all of the spin probes before turning to a quantitative analysis for the results found for the cholestane nitroxide (I) dissolved in the two cholesteric mesogens.

(a) 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-cholestane (I)

The order parameter for this spin probe is plotted as a function of reduced temperature in Figure 3a for cholesteryl benzoate (◆), cholestanyl benzoate (●) and 4,4′dimethoxyazoxybenzene (▲); the corresponding open symbols denote the values obtained from cholesteric samples contained in a tube. The results for the two cholesterogens fall on a common curve. This suggests that the anisotropic molecular interactions within the two solutions are very similar in form and is in accord with the comparable structures for the

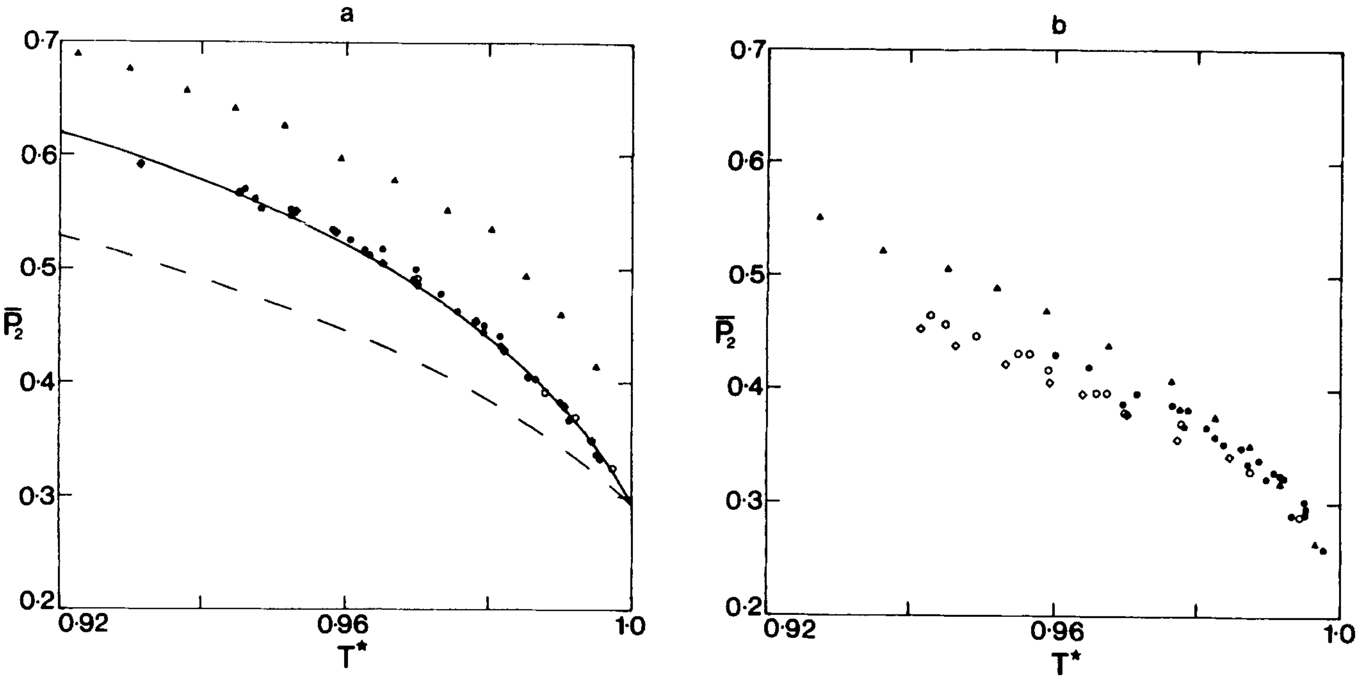

FIGURE 3 The dependence of the order parameter $\bar{P}_2$ on the reduced temperature T^* for the spin probes (a) 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-cholestane (I), (b) 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17β-ol (II), dissolved in the mesophases of cholesteryl benzoate (◆), cholestanyl benzoate (●) and 4,4′-dimethoxyazoxybenzene (▲).

cholesterogens. The spin probe is seen to be more highly ordered in the nematic phase although the temperature variation in $\bar{P}_2$ is essentially the same for all three liquid crystal mesophases. In general an increase in $\bar{P}_2$ may stem from an increase in the solute-solvent anisotropic interaction or in the solvent order parameter or both.[15] As we shall see the order parameter for 4,4′-dimethoxyazoxybenzene is almost certainly greater than that for either cholesterogen at the same reduced temperature. However the results for the other spin probes indicate that the variation in the solute-solvent interactions may not be totally ignored.

(b)

3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17β-ol (II)

We began our investigation of the dependence of the solute order parameter on the structure of the spin probe by replacing the long alkyl chain at the 17 position with the small hydroxyl group. The results for 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine}5α-androstane-17β-ol (II) dissolved in the three mesophases are shown in Figure 3b; the same symbols are employed to denote the values for the solvents as in Figure 3a. The order parameter for this spin probe is about 0.05 smaller than the cholestane probe (I) in the two cholesteric phases at the phase transition and this difference increases to 0.12 at a reduced temperature of 0.92. In addition the temperature dependence of $\bar{P}_2$ is less marked for the spin probe (II). The order parameter for (II) in the nematogen is also reduced, in comparison with (I), but by a larger amount. These results suggest that, as expected, the reduction in the anisotropy of the molecular structure also reduces the solute-solvent anisotropic interaction, although the greater reduction observed in the nematic was not anticipated. We must now see if these changes stem from some specific interaction involving the hydroxyl group.

(c)

3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17-one (III)

This spin probe has a similar size to (II) but there is no possibility of hydrogen bonding. The order parameter for (III) in the three mesophases is shown as a function of reduced temperature in Figure 3c. The order parameter at the transition in the two cholesterics is certainly greater than that for (II) but not as great as (I). The temperature dependence of $\bar{P}_2$ is also intermediate between that for the spin probes (II) and (I). Since a ketone is no larger than a hydroxyl group it would appear that the reduction in the anisotropic solute-solvent interaction found for (II) may be attributed partly to hydrogen bonding. The slightly higher values of $\bar{P}_2$ observed for (III) in the nematic are in accord with this conclusion.

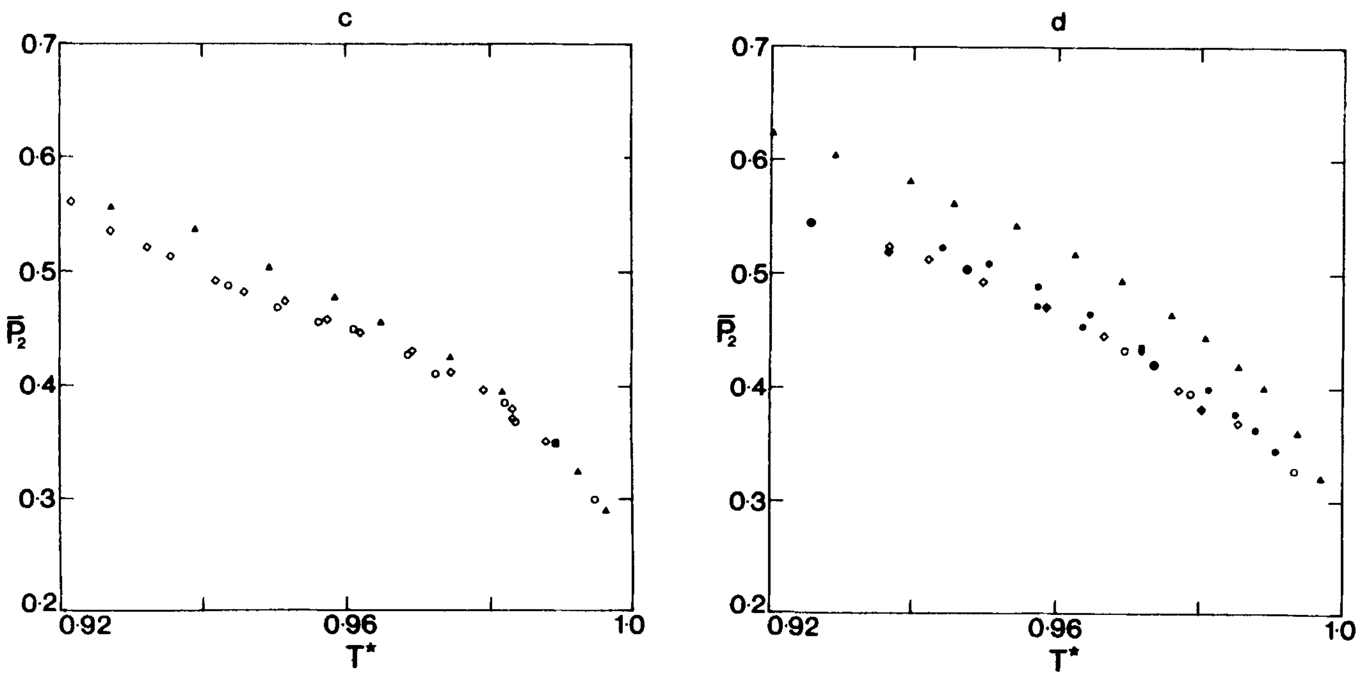

FIGURE 3 The dependence of the order parameter $\bar{P}_2$ on the reduced temperature T^* for the spin probes (c) 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17-one (III), (d) 3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17β-acetate (IV), dissolved in the mesophases of cholesteryl benzoate (◆), cholestanyl benzoate (●) and 4,4′-dimethoxyazoxybenzene (▲).

(d)

3-(2′-spiro{3′*N*-oxyl-4′,4′-dimethyloxazolidine})5α-androstane-17β-acetate (IV)

Finally the results for the spin probe (IV) dissolved in the three mesophases allow us to comment on the influence of the size of the substituent at the 17 position on the order parameter. The temperature dependence of $\bar{P}_2$ for the three systems is shown in Figure 3d. The order parameter is seen to be greater than either (II) or (III) in the corresponding mesogen but not quite as large as for (I). Clearly the relatively small increase in the size of the group at the 17 position, from ketone to acetate, produces a large increase in the order parameter. Indeed the small difference between the values observed for the order parameter for spin probes (I) and (IV) would indicate that the long alkyl chain in (I) plays a significant but not dominant role in determining $\bar{P}_2$.

These results for the four steroidal spin probes clearly demonstrate the dependence of the orientational order parameter on the structure of the probe. However, it should be emphasised that the variation in $\bar{P}_2$ is observed to be relatively small and this leads us to believe that the order parameter for the cholestane spin probe (I) will be close, if not identical, to the value for the cholesteric phase itself. We shall therefore proceed to a quantitative analysis of the order parameter for (I) which we take to be identical to that for the pure cholesterogens. The order parameter at the cholesteric–isotropic transition is estimated, from Figure 3a, to be 0.29. This result is apparently in good agreement with the value of 0.32 determined for both cholesteryl 2,6- and 3,5-difluorobenzoate from their fluorine nuclear magnetic resonance spectra.[2] However, it should be remembered that the benzoate group studied in those experiments is not rigidly bound to the steroidal residue. None-the-less the order parameter determined in both investigations is somewhat smaller than that found for most nematics and so is in poor agreement with the predictions of theories based on purely repulsive intermolecular potentials which yield values as high as 0.8.[16] Consequently we find that even for the steroidal cholesterogens, where the anisotropic dispersion forces should be less important than in the aromatic nematogens, the harsh repulsive term makes a minor contribution to the effective potential determining the orientational order. Indeed the Maier–Saupe theory based purely on weak dispersion forces is more successful for it predicts the order parameter $\bar{P}_2$, at the nematic–isotropic transition to be 0.42.[1] The relatively small difference between the theoretical and experimental values of $\bar{P}_2$ suggests that it should be possible to remove the discrepancy by extending the Maier–Saupe theory; indeed two such extensions have been described.[18,19]

In the first of these the restriction of the anisotropic intermolecular potential, by Maier and Saupe, to dispersion forces is removed and a perfectly general expression for the pair potential between cylindrically symmetric molecules, is employed.[18] The single particle orientational potential is then found to be

$$U(\cos\theta) = \sum_{\substack{L\neq 0\\ (\text{even})}} \bar{u}_L \bar{P}_L P_L(\cos\theta), \tag{13}$$

where θ is the angle between the molecular symmetry axis and the director. The expansion coefficients in this pseudo-potential depend on the strength of the starting pair potential; $P_L(\cos\theta)$, is the Lth Legendre function and its average is the appropriate order parameter.[18] Restriction of the expansion to just the first term gives a pseudo-potential identical in form to that of the Maier–Saupe theory. However because the theory is based on a general expression for the pair potential it is not necessary to assume that the coefficient $\bar{u}_2$ depends solely on dispersion forces. As we have seen when the expansion is restricted to a single term the order parameter $\bar{P}_2^{(K)}$ at the transition is fixed at 0.42. However retention of the term in $\bar{u}_4$ allows $\bar{P}_2^{(K)}$ to vary with the ratio $\bar{u}_4/\bar{u}_2$, which we denote by λ.[18] The variation of $\bar{P}_2^{(K)}$ with λ is shown in Figure 4 and it is possible to interpret the order parameter for many nematics with relatively small values of λ.[18,20] Indeed since the theory is based on a truncated expansion of the pair potential its use in the analysis of experimental data is only meaningful if λ is found to be considerably less than unity. However we see that to explain the value for $\bar{P}_2^{(K)}$ of 0.29

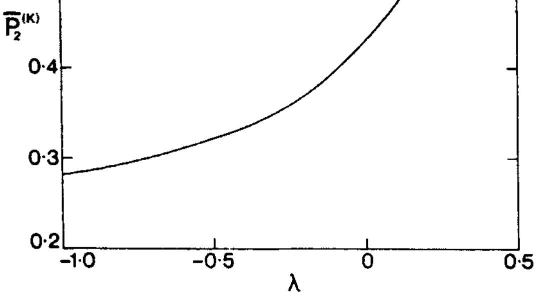

FIGURE 4 The variation of the order parameter $\bar{P}_2^{(K)}$ at the nematic–isotropic transition with λ, the ratio $\bar{u}_4/\bar{u}_2$ of the coefficients in the expansion of the orientational pseudo-potential for cylindrically symmetric molecules.

found for the cholesteric phase λ would have to be -0.9. This is an apparently unreasonably high value for λ and so we conclude that this extension of the Maier–Saupe theory cannot account for the smallness of the order parameter at the transition. We must therefore turn to the second modification of the Maier–Saupe theory.

The theories, which we have just encountered, assume that the constituent particles are cylindrically symmetric even though the molecules of real nematogens are invariably of lower symmetry. The orientational pseudo-potential will now depend on the two spherical polar angles, β and γ, which the director makes with the molecular coordinate system. Provided the general expansion of the pair potential is restricted to second-rank terms the pseudo-potential is found to take the form[19]

$$U(\beta\gamma) = a\, d^{(2)}_{0,0}(\beta) + b\, d^{(2)}_{0,2}(\beta) \cos 2\gamma, \tag{14}$$

where $d^{(2)}(\beta)$ is a reduced Wigner rotation matrix.[21] When dispersion forces make the sole contribution to the anisotropic intermolecular potential the coefficients a and b are given by

$$a = \bar{u}_{200}(\overline{d^{(2)}_{0,0}} + 2\lambda\, \overline{d^{(2)}_{0,2} \cos 2\gamma}) \tag{15}$$

and

$$b = 2\lambda a, \tag{16}$$

where by convention λ is now used to denote the ratio c_{220}/c_{200}.[19] Here the parameters c_{200} and c_{220} are related to averages of the coefficients in the expansion of the pair potential, in addition the deviation from cylindrical symmetry is determined by c_{220} and hence by λ. The dependence of the order parameter, for the long molecular axis, at the transition on λ is shown in Figure 5, the magnitude of $\bar{P}^{(K)}_2$ is seen to fall rapidly as λ increases. Indeed quite reasonable values of λ are able to account for a relatively low order parameter at the transition.

However before we compare these theoretical predictions with experiment it is important to realise that measurement of the nitrogen hyperfine coupling can only give the component of the ordering matrix orthogonal to the oxazolidine ring, when the molecule is not cylindrically symmetric. Consequently the values of the order parameter, $\bar{P}_2$, reported in Figure 3 cannot be compared directly with theory for they are minus twice the ordering matrix element, S_{yy}, for the y axis shown in Figure 1. We could obtain the largest of the principal components for the long molecular axis by measurement of the partially averaged g tensor. These experiments and their subsequent analysis are difficult, especially for the polycrystalline electron resonance spectra invariably observed for the cholesteric phase. Consequently we prefer to use the theory to predict S_{yy}, the component of the ordering

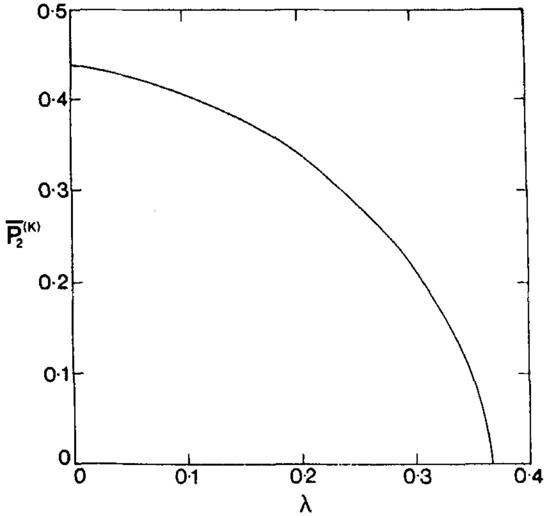

FIGURE 5 The dependence of $\bar{P}_2^{(K)}$ on the deviation, λ, of the particles from cylindrical symmetry.

matrix perpendicular to the long molecular axis. Of course the theory gives two components, and we do not know for certain which of these should be associated with the observed value, S_{yy}. None-the-less there are good reasons to believe that S_{yy} is the least negative of the two elements. Thus measurements of the principal components of S for the cholestane spin probe (I) dissolved in the nematic phase of 4,4′-dimethoxyazoxybenzene show this to be the case[22] and change of liquid crystal solvent is unlikely to reverse this order. The assignment is also supported by theory. The parameters c_{200} and c_{220} are strictly determined by the polarizability tensor but this is unknown for the cholesterogens with which we are concerned. However the molecular polarizability is related to the dimensions of the molecule; indeed it has been suggested[19] that if the molecule is taken to be a block with length L, width W and breadth B, corresponding to the z, x and y axes respectively, then

$$c_{200} = -\frac{2B(W^2 + L^2) + 2W(L^2 + B^2) - L(W^2 + B^2) - 8WBL}{3} \tag{17}$$

and

$$c_{220} = \frac{(L^2 - BW)(B - W)}{\sqrt{6}}. \tag{18}$$

This particular parameterisation of the coefficients in the intermolecular potential does not yield the pseudo-potential given by Eqs. (14–16). However provided the orientational order is not high and the molecular length is greater than both the breadth and width the coefficients given by Eqs. (17) and (18) may be used in Eq. (14) for the orientational pseudo-potential. Examination of molecular models suggests that the cholestane spin probe (I) can be accommodated in a rectangular box with L equal to 23.0 Å, W equal to 6.5 Å and B equal to 8.0 Å. With these dimensions λ is negative and $\overline{d_{02}^{(2)} \cos 2\gamma}$, which is the difference $(S_{xx} - S_{yy})/\sqrt{6}$, is also found to be negative; in other words S_{yy} is again expected to be the least negative of the two elements. This result is entirely reasonable, for configurations in which the director tends to be parallel to the shortest axis are going to be less probable than those in which the director is parallel to the next shortest axis. Consequently the ordering matrix element for the shortest axis will be more negative than that for the next shortest axis.

We have calculated the larger of the two elements of the ordering matrix at the nematic–isotropic transition as a function of the parameter $\lambda\,(c_{220}/c_{200})$ and find complete agreement with the experimental value of -0.145 when λ is -0.17. In addition the value of λ calculated from the molecular dimension is -0.18 which is remarkably close to the experimental result. Although this close agreement provides strong support for the theoretical analysis, based on departure from molecular cylindrical symmetry, it must be realised that λ is essentially linear in the difference $(B - W)$ whose estimation is open to some error.

To make further comparisons between experiment and theory we must predict the temperature dependence of S_{yy}. This calculation is straightforward at constant volume but is more difficult when experiments are performed at constant pressure, as ours are, for then the parameters c_{200} and c_{220} vary with temperature because of their volume dependence. We require, therefore, the variation of the density of cholesteryl benzoate with temperature. Unfortunately this temperature dependence does not appear to have been reported and, in addition, such experiments are difficult because of the high temperature range of cholesteryl benzoate. These measurements may not be essential for it has been shown that the reduced volume, V/V_K, is a universal function of the reduced temperature T/T_K for several nematogens.[23] We expect this universality to apply to cholesterogens but with a different function. The density of cholesteryl nonanoate was determined as a function of temperature;[24] this cholesterogen was chosen because of its significantly lower transition temperatures. The reduced volume, in the cholesteric phase, was found to be linear in the reduced temperature, with

$$\frac{V}{V_K} = 0.7559 + 0.2441\,\frac{T}{T_K}. \tag{19}$$

We shall assume that the same relationship is also valid for cholesteryl benzoate.

The next problem is to decide on the volume dependence of the parameters c_{200} and c_{220}. It is reasonable to suppose that both parameters will have the same dependence on volume and so their ratio λ will be temperature independent. The coefficient c_{200} is strictly defined as an average over an ensemble in which the anisotropic part of the intermolecular potential has been removed; it is therefore given by

$$c_{200} = \sum_m \frac{(-1)^m}{5} \frac{\int u_{2m00}(r)\exp\{-U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT\}d\mathbf{r}_1, \ldots, d\mathbf{r}_N}{\int \exp\{-U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT\}d\mathbf{r}_1, \ldots, d\mathbf{r}_N}, \quad (20)$$

where $u_{2m00}(r)$ is a coefficient in the expansion of the total intermolecular potential. The scalar potential, $U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of the N molecules in the ensemble is clearly dependent on the volume although the form of this dependence is extremely difficult to determine. As a consequence an empirical approach is often adopted and the parameters are written as

$$c_{200} = c_{200}^0 V^{-\gamma}, \quad (21)$$

where the exponent γ is determined by comparison with experiment.[18] More recently it has been argued that in order for the Maier–Saupe theory to exhibit statistical-thermodynamic consistency the coefficients $\bar{u}_L$ in Eq. (13) must be linear in the density.[25] The same arguments may be applied to the parameter defined by Eq. (20) and so the exponent γ in Eq. (21) should be 1.

We have therefore calculated the temperature dependence of the order parameter S_{yy} with γ set equal to 1 and the results are plotted as the broken line in Figure 3a. The slope of the line is not in good agreement with experiment and similar discrepancies have also been found for nematics.[18,26] As it is difficult to reconcile the definition of c_{200} with a linear dependence on density we have also adjusted γ in Eq. (21) to obtain complete agreement with experiment. This was obtained with γ equal to 6 as the solid line in Figure 3a clearly demonstrates. The value of the exponent compares favourably with the results found for nematics; thus γ is 4 for 4,4′-dimethoxyazoxybenzene[18,27] and as high as 10 for 4-methoxybenzylidene-4′-*n*-butylaniline.[26] It would be unwise, at this stage, to interpret these exponents in terms of molecular structure and interactions.

6 CONCLUSIONS

Our experiments reveal that it is possible to determine the order parameter of a spin probe dissolved in a steroidal cholesterogen even though a monodomain sample cannot be obtained. The results for a number of steroidal spin probes suggests that the order parameter for 3-(2′-spiro-{3′*N*-oxyl-4′,4′-dimethoxazolidine})5α-cholestane (I) is likely to be extremely similar to those for cholesteryl and cholestanyl benzoate. If this is so then the orientational order in both nematics and cholesterics must be comparable. This similarity does not necessarily imply the importance of the same anisotropic intermolecular forces in both phases but simply that the expansion of the orientational pseudo-potential is rapidly convergent for the two kinds of liquid crystal. The orientational order in the two cholesterogens which we have studied is considerably lower than the Maier–Saupe theory predicts and this difference is difficult to explain by the inclusion of higher order terms in the intermolecular potential. However allowance for deviations from molecular cylindrical symmetry does allow us to understand the observed order parameter and also emphasises the inadequacies of a description of the orientational order based on a single parameter. The observed deviation from the Maier–Saupe theory is also in accord with the dimensions of the spin probe. Finally, the temperature variation of the order parameter is not accounted for by the linear dependence of the pseudo-potential coefficients on density apparently imposed by statistical-thermodynamic consistency. Indeed the coefficients are found to depend on the sixth power of the density.

Acknowledgements

We are most grateful to Dr. A. M. Giroud of Centre d'Etudes Nucleaires de Grenoble, for the synthesis of three spin probes and to Dr. D. A. Dunmur of Sheffield University, for measuring the density of cholesteryl nonanoate. We wish to thank the Science Research Council for awards of a grant towards the cost of the electron resonance spectrometer, a Fellowship to Dr. S. G. Carr and a CASE Studentship to Dr. H. J. Smith; Mr. S. K. Khoo acknowledges a Tutorship Grant from the University of Malaya.

References

1. see, for example, T. E. Faber and G. R. Luckhurst, *Ann. Rep. A*, 31 (1975).
2. P. J. Collings, T. J. McKee, and J. R. McColl, *J. Chem. Phys.*, **65**, 3520 (1976).
3. F. Reinitzer, *Monatsh.*, **9**, 421 (1888).
4. see, for example, P. L. Nordio, Spin Labelling Theory and Applications, ed. L. J. Berliner (Academic Press, 1976).
5. G. Poggi and C. S. Johnson Jr., *J. Magn. Resonance*, **3**, 436 (1970); G. R. Luckhurst and M. Setaka, *J.C.S. Faraday Trans. II*, **72**, 1340 (1976).
6. G. R. Luckhurst, Liquid Crystals and Plastic Crystals, Vol. 2, ed. G. W. Gray and P. A. Winsor, Chap. 7 (Ellis Horwood, 1974).
7. G. R. Luckhurst and M. Setaka, *Mol. Cryst. and Liq. Cryst.* **19**, 279 (1973).
8. P. G. de Gennes, *Solid State Commun.* **6**, 163 (1968); R. B. Meyer, *App. Phys. Letters* **12**, 281 (1968).
9. G. R. Luckhurst and A. Sanson, *Mol. Phys.* **24**, 1297 (1972); G. R. Luckhurst and R. N. Yeates, *J.C.S. Faraday Trans. II*, **72**, 996 (1976).
10. G. R. Luckhurst and H. J. Smith, *Mol. Cryst. and Liq. Cryst.*, **20**, 319 (1973).

11. J. F. W. Keana, S. B. Keana, and D. Beetham, *J. Amer. Chem. Soc.*, **89**, 3055 (1967).
12. H. J. Smith, Thesis, University of Southampton, 1974.
13. W. L. Hubbel and H. M. McConnell, *J. Amer. Chem. Soc.*, **93**, 314 (1971).
14. G. R. Luckhurst and R. Poupko, *Chem. Phys. Letters*, **29**, 191 (1974).
15. R. L. Humphries, P. G. James, and G. R. Luckhurst, *Symp. Faraday Soc.*, **5**, 107 (1971).
16. L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949): R. Alben, *Mol. Cryst. Liq. Cryst.*, **13**, 193 (1971); M. A. Cotter, *Phys. Rev.* **A10**, 625 (1974).
17. W. Maier and A. Saupe, *Z. Naturforsch.*, **13a**, 564 (1958); **14a**, 882 (1959); **15a** 287 (1960).
18. R. L. Humphries, P. G. James, and G. R. Luckhurst, *J.C.S. Faraday Trans. II* **68**, 1031 (1972).
19. G. R. Luckhurst, C. Zannoni, P. L. Nordio, and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).
20. R. L. Humphries and G. R. Luckhurst, *Mol. Cryst. and Liq. Cryst.*, **26**, 269 (1974).
21. M. E. Rose, Elementary Theory of Angular Momentum (John Wiley, 1957).
22. S. G. Carr, S. K. Khoo, G. R. Luckhurst, and C. Zannoni, *Mol. Cryst. Liq. Cryst.*, **35**, 7 (1976). The values given for $(S_{x'x'} - S_{y'y'})$ in Figure 3 of this reference should be negative and not positive, as reported.
23. D. H. Chen, P. G. James, and G. R. Luckhurst, *Mol. Cryst. Liq. Cryst.*, **8**, 71 (1969).
24. These measurements were made by D. A. Dunmur using an Anton Paar DMAO2 density meter.
25. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **39**, 173 (1977).
26. S. Jen, L. A. Clark, P. S. Pershan, and E. B. Priestley, *Phys. Rev. Letters*, **31**, 1552 (1973).
27. R. L. Humphries and G. R. Luckhurst, *Chem. Phys. Letters*, **17**, 514 (1972).