

Electron Resonance Investigation of a Cholesteric Mesophase Induced by a Chiral Probe

By MARCO GIORDANO,* DINO LEPORINI, MASSIMO MARTINELLI AND L. PARDI
Istituto di Fisica dell'Università and Gruppo Nazionale Struttura della Materia del
C.N.R., P.za Torricelli 2, 56100 Pisa, Italy

AND CARLO A. VERACINI*

Istituto di Chimica-Fisica dell'Università, Via Risorgimento 35, 56100 Pisa, Italy
AND CLAUDIO ZANNONI*

Istituto di Chimica Organica, Facoltà di Chimica Industriale, Viale Risorgimento
4, 40136 Bologna, Italy

Received 22nd April, 1981

An induced cholesteric phase has been produced by dissolving the chiral nitroxide probe 5 α -cholestane-3-spiro-2'-N'-oxyl-3',3'-dimethyloxazolidine in the nematic phase of 4,4'-bis-n-heptyloxybenzene (HEPTAB). The chiral solute has been studied by e.s.r., and order parameters and correlation times obtained by spectral simulation using angular-dependent linewidth theory. Inhomogeneous broadening has been taken into account by using a Voigt convolution lineshape function. The unwinding of the induced cholesteric helix when cooling to the smectic phase has been followed, and the distortion parameter for the helix has been determined at various temperatures.

1. INTRODUCTION

The cholesteric phase is a twisted version of the nematic.^{1,2} Its molecules tend to be aligned with respect to a local director as in a nematic, but the preferred direction is spontaneously distorted into an helix. Such a phase can be produced from optically active mesogens or by dissolving a chiral solute in a nematic host. These induced cholesteric phases are also called weak cholesterics³ since here the helical director distribution normally has a fairly long pitch compared with ordinary cholesterics. Induced phases have been studied using a variety of methods³⁻⁸ and in particular with macroscopic optical techniques.⁴⁻⁶ The emphasis in a number of these studies has been on the so-called cholesteric-nematic transition, *i.e.* on the observation of the helix unwinding by application of suitably oriented electric or magnetic fields.⁶⁻⁸ If we induce a cholesteric by dissolving a small amount of chiral solute in a nematic host with, say, positive diamagnetic susceptibility $\Delta\chi$, the helix will have its axis perpendicular to the direction of an applied magnetic field.¹ As the field strength B increases the helix will be distorted until complete unwinding takes place at a critical field B_c , and a nematic is obtained.

A pioneering microscopic study of induced cholesterics formed by cholesteryl chloride dissolved in 4,4'-dimethoxyoxybenzene has been performed by Luckhurst and Smith³ using a spin-probe electron resonance (e.s.r.) technique. Note that the probe [5 α -cholestane-3-spiro-2'-N'-oxyl-3',3'-dimethyloxazolidine (**I**)] used in that investigation, as in many others on the nematic phase, is chiral, and thus the probe itself should in principle be capable of inducing a cholesteric phase.

What normally happens, however, is that for probe concentrations typically used in e.s.r. (10^{-3} – 10^{-4} mol dm $^{-3}$) the pitch of the helix induced by the cholestane probe is so long that the helix can be unwound by the magnetic field of the spectrometer at X band levels (330 mT). This allows the use of probes of the cholestane type even in studies of nematics, but it means that the spectrum contains no information on chiral solute–solvent interactions of the probe with the mesophase. On the other hand, whether or not the cholesteric phase induced by the chiral spin-probe is observed depends, for a given probe concentration, on the strength of the chiral solute–solvent interaction and the elastic constants of the mixture; thus, for a given probe, it depends on the liquid-crystal solvent.

We report here a case where the spin-probe (**I**) itself, when dissolved in the nematic phase of 4,4'-bis-*n*-heptylazoxybenzene (HEPTAB) in concentrations > 2 mmol dm $^{-3}$, produces a cholesteric phase which is not unwound at 330 mT. This offers the possibility of looking at the chiral solute that is inducing the chiral perturbation and thus learning something about chiral solute–solvent interactions at a microscopic level. In particular we are able, by employing the methods described in section 4, to obtain the order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$ and $\langle D_{02}^2 \rangle$ for our solute.⁹ We believe this to be the first measurement of these parameters for a chiral solute inducing a cholesteric phase. This microscopic information might be of importance in the light of proposed theories of the cholesteric phase which relate the helix pitch and its temperature dependence to orientational order parameters.^{9–11} We also show that the e.s.r. method offers a convenient method of following the unwinding of the helix near the smectic phase.¹²

2. EXPERIMENTAL

The cholestane nitroxide spin-label (**I**) was synthesized *via* the procedure developed by Keana *et al.*¹³ from chiral cholestan-3-one ($[\alpha]_D^{20} = +42^\circ$) and carefully purified by recrystallization. The mesogen *p, p'*-*n*-heptylazoxybenzene employed in this study was prepared according to the method of Van der Veer *et al.*¹⁴ and purified by recrystallization and zone melting. The temperatures of the transitions crystal–smectic A (307.5 K), smectic A–nematic (326.5 K) and nematic–isotropic (344.5 K) were checked by differential scanning calorimetry.

Electron spin resonance measurements were performed with a home-made spectrometer working in the X band (9.05 GHz). The sample was placed in a standard TE₁₀₂ microwave cavity, inside a quartz tube of 4 mm internal diameter previously rinsed with diethyl ether. Several efforts were made to keep the sample temperature as constant as possible during experiments and to avoid temperature gradients in the sample, since these can seriously affect the determination of physical constants of mesophases. In the set-up chosen temperature regulation was achieved by means of a nitrogen flow with rate controlled by both a high-performance pressure regulator and a differential flow regulator (Brooks model 8800). The nitrogen heater was fed with a d.c.-regulated power supply equipped with a multi-turn dial to obtain high-resolution voltage setting. The nitrogen temperature was then changed according to the driving voltage. To ensure maximum temperature homogeneity, the whole sample tube was embedded in a high-thermal-conductivity paste of sufficient mass to act as a heat reservoir. The temperature was measured with a NiCr–constantan thermocouple inserted in the conductive paste and read using a digital microvoltmeter. In this configuration the short-term-reproducibility and accuracy in the temperature measurements approaches $\pm 0.1^\circ\text{C}$.

Samples with the following concentrations of spin-probe were prepared: 0.6, 1.25, 2.5, 5.0 and 10.0 mmol dm $^{-3}$. All the samples were carefully degassed using the freeze–thaw technique before measurements.

Optical observations have been performed by suspending a small amount of the sample with a 2.5 mmol dm $^{-3}$ concentration of (**I**) in an experimental apparatus that allows measurements on mesophases with two free surfaces.¹⁵ In this apparatus a beam of white light is

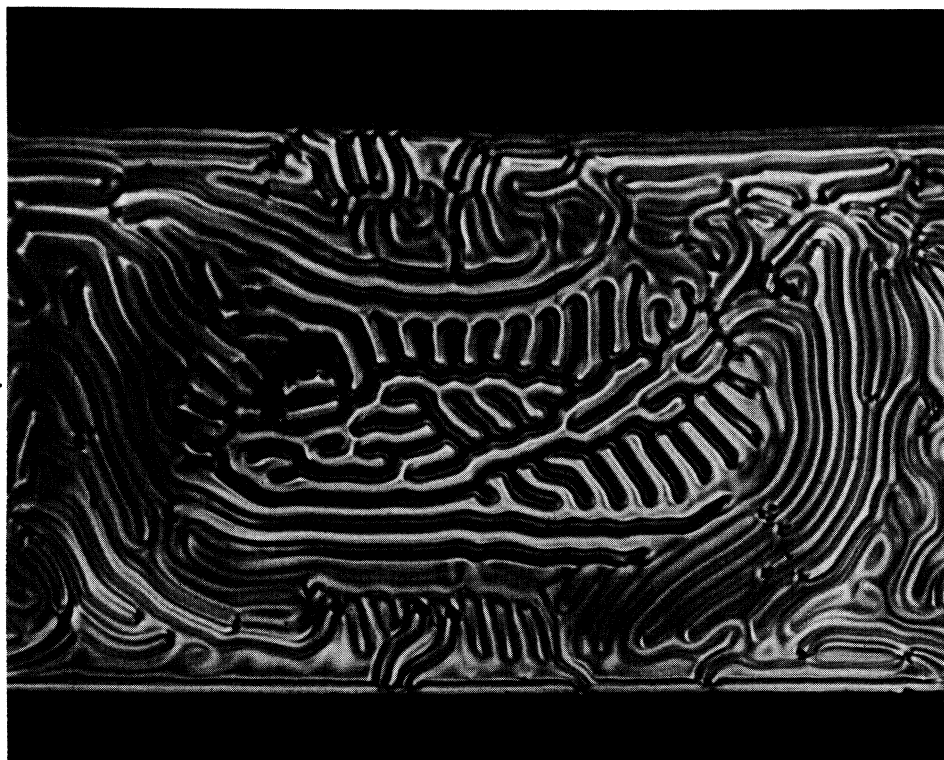


PLATE 1.—Finger-print texture in the cholesteric mesophase.

polarized, passed through the sample film, and then observed and photographed in a microscope through a second, crossed polarizer.

3. RESULTS

At temperature below 326.5 K the microphotographs show that the sample is shaped as “*gouttes à gradin*”² as expected for a smectic A phase. In the temperature range 326.5–344.5 K the finger-print textures characteristic of cholesteric phases^{1,5} (plate 1) are observed.

Up to a probe concentration of 1.25 mmol dm⁻³ the electron resonance spectrum presents, at temperatures within the nematic range, the three sharp lines expected from a nitroxide in a nematic phase. However, upon increasing the probe concentration, the spectrum shows from 2.5 mmol dm⁻³ a five-line pattern consistent with the helical distribution of the director present in an induced cholesteric.

Similar concentrations of probe (I) in other nematic solvents with comparable elastic constants, *e.g.* MBBA and Phase IV, give a normal three-line spectrum, which seems to indicate a stronger chiral interaction in our case. The linewidths observed in the isotropic phase are essentially the same throughout the concentration range employed. This indicates that intermolecular broadening mechanisms are not important: they will accordingly be neglected in the following treatment.

By reducing the temperature and thus approaching the smectic phase, the spectra change, as would be expected for the cholesteric helix unwinding (*cf.* section 4). The inner diameter of the sample tube, 4 mm, is sufficient to ensure that we are actually looking at a bulk-induced cholesteric. This should be true unless we are very near to the smectic transition. In fact, even though the pitch diverges near the transition, strong boundary effects are only expected for sample thickness comparable or lesser than $P_0/2$.¹⁶ We further checked the relative unimportance of surface boundary effects by changing the tube diameter. The same type of spectra were still obtained.

4. SPECTRAL SIMULATION

The e.s.r. spectrum of a radical dissolved in a uniaxial liquid crystal with a non-uniformly aligned director is given by

$$S(B) = \int S(B, \gamma) P(\gamma) d\gamma \quad (1)$$

where $S(B, \gamma)$ is the spectrum resulting from regions with the director at an angle γ with respect to the magnetic field, while $P(\gamma)$ is the director distribution, assumed to be static over the experimental time-scale. For a cholesteric $P(\gamma)$ can be obtained from continuum theory.¹⁻³ If it is assumed that the helix is perfectly aligned perpendicular to the field B but partially unwound by the field itself it is found that

$$P(\gamma) = (1 - k^2 \cos^2 \gamma)^{-1/2} \int_0^{2\pi} (1 - k^2 \cos^2 \gamma)^{-1/2} d\gamma, \quad (2)$$

where the parameter k , related to the sharpness of the distribution, is given in terms of material constants through the equation

$$k = \frac{B}{B_c} E(k) \quad (3)$$

$$= \frac{P_0 B}{\pi^2} \left(\frac{\Delta\chi}{K_{22}} \right)^{1/2} E(k) \quad (4)$$

where B_c is the critical field for unwinding, P_0 is the pitch of the unperturbed helix, $\Delta\chi$ is the diamagnetic susceptibility and K_{22} is the scalar twist constant.^{1,3} The quantity $E(k)$ is an elliptic integral of the second kind

$$E(k) = \int_0^{\pi/2} (1 - k^2 \sin^2 \gamma)^{1/2} d\gamma.$$

The pitch of the undistorted helix P_0 appearing in eqn (4) can be written in terms of elastic constants as

$$P_0 = 2\pi K_{22}/K_2 \quad (5)$$

where K_2 is the pseudoscalar twist constant of the mixture. Since we only have a very small molar fraction, c , of chiral solute ($c \ll 1$) we can write the elastic constants in terms of those of the solvent,¹⁷ here indicated by the superscript \circ

$$K_{22} = K_{22}^\circ + \left(\frac{\partial K_{22}}{\partial c} \right)_0 c + \dots \approx K_{22}^\circ \quad (6)$$

$$K_2 = K_2^\circ + \left(\frac{\partial K_2}{\partial c} \right)_0 c + \dots \approx \left(\frac{\partial K_2}{\partial c} \right)_0 c. \quad (7)$$

Thus, while K_{22} can be approximated by the solvent twist elastic constant K_{22}° , K_2 , which vanishes in the nematic phase, is strictly a solute-solvent property. The coefficient $(\partial K_2/\partial c)_0$ is linked to the twisting power, β , for the solute in the particular nematic employed.¹⁸

The linewidths in the spectrum $S(B, \gamma)$ for a cholestane probe are determined by two main contributions: rotational spin relaxation and inhomogeneous broadening due to unresolved hyperfine structure. Let us consider the spin-relaxation process first. In general a slow tumbling simulation approach^{19a} could be used to calculate $S(B, \gamma)$ at any rate of reorientation. This method gives spectra reducing in the proper limit to rigid or fast-motion ones. On the other hand this approach is time-consuming, even though numerical techniques faster than the traditional ones have been recently proposed.^{19b} The complications of a slow-tumbling simulation can be even more severe for our type of problem, where a spectrum $S(B, \gamma)$ should be calculated for every angle γ needed for the integration and for every choice of static and dynamic parameters determining the spectrum. Thus, if possible, and if the aim is not specifically a detailed study of the reorientation, a less general but drastically simpler approach should be used. This is the case when the reorientational motion can be considered to be fast in the Redfield sense.²⁰ In this limit the spectrum at every angle can be considered to be a sum of three lineshape functions competing with the three transitions with nuclear spin quantum number $m = 0, \pm 1$. The predicted spin-relaxation lineshape is a lorentzian, $\mathcal{L}[B - B_m(\gamma), T_{2m}^{-1}(\gamma)]$, having a width

$$T_{2m}^{-1}(\gamma) = A(\gamma) + B(\gamma)m + C(\gamma)m^2. \quad (8)$$

The linewidth coefficients $A(\gamma)$, $B(\gamma)$ and $C(\gamma)$ can be calculated using the strong-collision or diffusional model of reorientation by employing the theory developed in a previous paper.²¹ If the strong-collision model is employed, the microscopic parameters determining the spectrum are, for a probe with effective cylindrical symmetry, in a frame which also diagonalizes the magnetic tensors \mathbf{A} and \mathbf{g} , the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$, and the orientational correlation times τ_0 and τ_2 .

This is essentially the case for our probe if the molecular frame which has the z axis at an angle of 111° from the N—O bond is chosen.²² Here τ_0 refers to long-axis reorientation. The time τ_2 refers instead essentially to a reorientation about the cylindrical-symmetry axis, provided that this process is faster than the long-axis reorientation process. Since in the Redfield limit we are reduced to calculating the spectrum as a sum of analytic functions, the simulation, even with the integration over γ , is rather fast. Fortunately in our case it is reasonable to assume that the Redfield limit holds. This is suggested by the relatively narrow linewidth (*ca.* 0.18 mT) and symmetrical appearance of the spectrum, in particular of the central $m = 0$ line.

Moreover, the cholestane-probe spectrum has a very strong inhomogeneous broadening contribution²³ which makes the relaxation contribution important but not dominant in our temperature range. This means that the general sensitivity of the spectrum to the relaxation parameters has to be verified, as we shall do later. We shall therefore assume henceforth that the relaxation contribution is well-approximated by the Redfield treatment. However, to obtain a good simulation it is important to account fully for the effect of inhomogeneous broadening. A straightforward approach is that of adding linearly or quadratically an angle-dependent residual linewidth to the relaxation linewidth.^{24,25} This does not change the lorentzian lineshape and does not seem sufficient in the present case. We have thus chosen to take into account hyperfine broadening by convoluting the spin-relaxation lorentzian with an inhomogeneous broadening function.^{25,26} We thus have

$$S(B, \gamma) = \sum_m V_m[B, B_m(\gamma), T_{2m}^{-1}(\gamma), X(\gamma)] \quad (9)$$

where

$$V_m[B, B_m(\gamma), T_{2m}^{-1}(\gamma), X(\gamma)]$$

$$= \int_{-\infty}^{\infty} \mathcal{L}[B - B', T_{2m}^{-1}(\gamma)] \mathcal{G}[B' - B_m(\gamma), X(\gamma)] dB' \quad (10a)$$

$$= \frac{T_{2m}^{-1}(\gamma)}{2\sqrt{\pi}X(\gamma)^2} \int_{-\infty}^{\infty} \left[\left(\frac{T_{2m}^{-1}(\gamma)}{\sqrt{2}X(\gamma)} \right)^2 + \left(t + \frac{B_m(\gamma) - B}{\sqrt{2}X(\gamma)} \right)^2 \right]^{-1} \exp(-t^2) dt \quad (10b)$$

where $B_m(\gamma)$ is the resonant field for the m th transition and $X(\gamma)$ is an angle-dependent inhomogeneous linewidth. This expression is relatively general and contains the case of additive residual linewidth when $\mathcal{G}[B' - B_m, X(\gamma)]$ is taken to be a lorentzian broadening. However, in our case it is more reasonable to assume \mathcal{G} to be a gaussian broadening, as appropriate for a static or very slow modulation.²⁷ When we make this hypothesis the lineshape $V_m[B, B_m, T_{2m}^{-1}(\gamma), X(\gamma)]$ becomes a convolution of a gaussian and lorentzian, the so-called Voigt function.²⁸ This function, known and studied in many branches of physics, has the nice property of moving continuously from a gaussian to a lorentzian as the relative contribution of the two processes changes.

In our simulation we have employed the Voigt lineshape form and assumed

$$X(\gamma) = X_{\parallel} \cos^2 \gamma + X_{\perp} \sin^2 \gamma. \quad (11)$$

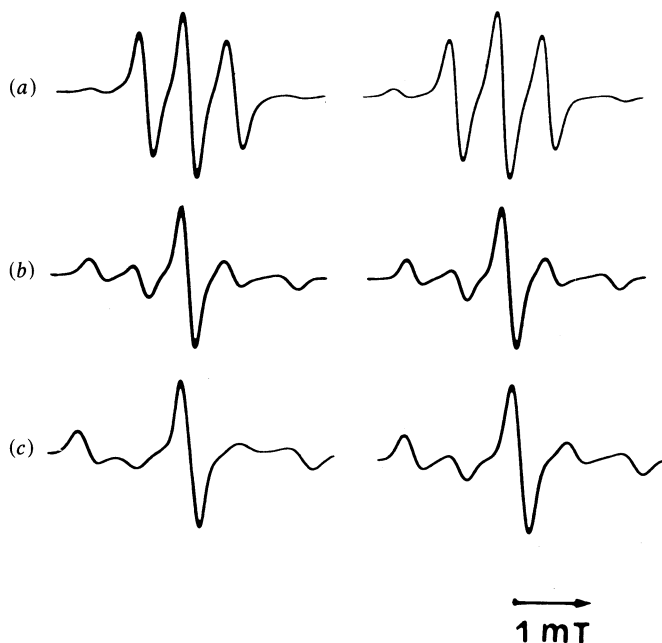


FIG. 1.—Experimental (left-hand column) and simulated (right-hand column) spectra of (I) in a 10 mmol dm^{-3} solution of HEPTAB. Spectra (a), (b) and (c) correspond to a temperature difference ($T - T_{sm}$) of 0.7, 1.7 and 4.6 K, respectively. Parameters for the simulations are given in table 1.

In fig. 1 we present three experimental spectra and their simulation using the helical distribution for $P(\gamma)$ [eqn (1)] and the Voigt lineshape. The spectra were obtained as described in the Experimental section by raising the temperature from the smectic phase to the values reported in the legend.

The magnetic parameters employed in all simulations were, in the molecular frame discussed earlier,

$$g^{2,\pm 2} = -0.0032; \quad g^{2,0} = 0.0007; \quad g_{\parallel} = 2.0056$$

$$A^{2,\pm 2} = 1.3247 \text{ mT}; \quad A^{2,0} = -1.08152 \text{ mT}; \quad a_{\parallel} = 1.498 \text{ mT}$$

and

$$X_{\parallel} = X_{\perp} = 0.12 \text{ mT}.$$

The parameters giving the best fit for the three spectra shown and three other temperatures studied in detail are given in table 1.

5. DISCUSSION

The optical observations (*cf.* plate 1) confirm that the chiral radical (I) induces a cholesteric phase. The e.s.r. spectra indicate that the helical director distribution is partially distorted by the spectrometer's magnetic field. The helix is further unwound as we approach the smectic phase of HEPTAB. For this compound the

TABLE 1.—ORDER PARAMETERS $\langle P_2 \rangle$, $\langle P_4 \rangle$ EMPLOYED IN SPECTRAL SIMULATIONS FOR (I) IN HEPTAB AT VARIOUS TEMPERATURES T ABOVE THE SMECTIC TRANSITION TEMPERATURE T_{sm}

The molecular biaxiality parameter $\langle D_{02}^2 \rangle$ was equal to zero. The helix distortion parameter k obtained is also tabulated together with its estimated deviation σ_k . In this temperature range it was found unnecessary to change the correlation times τ_0 and τ_2 , which were therefore set to $\tau_0 = 2 \times 10^{-5}$ s rad $^{-1}$ and $\tau_2 = 2 \times 10^{-10}$ s rad $^{-1}$, respectively.

$(T - T_{sm})/K$	$\langle P_2 \rangle$	$\langle P_4 \rangle$	k	σ_k
0.7	0.84	0.57	0.999 98	2×10^{-5}
1.0	0.84	0.57	0.998	2×10^{-3}
1.3	0.84	0.57	0.992	2×10^{-3}
1.5	0.84	0.57	0.982	2×10^{-3}
1.7	0.82	0.53	0.840	2×10^{-3}
1.9	0.80	0.50	0.63	2×10^{-2}
4.6	0.76	0.42	0.3	2×10^{-1}

nematic-smectic transition is a weak first-order one,²⁹ with a small variation in entropy ($\Delta S = 0.50$ J K $^{-1}$ mol $^{-1}$). Pretransitional effects, with a building up of some smectic positional order, are thus expected and have been demonstrated in the divergence of the twist and bend elastic constants as the transition is approached from above.³⁰ In such a situation Alben¹² has suggested that the elastic energy, and thus the pitch and its temperature dependence, should be considered as a sum of a stiffness term and a rotary term.

It has been proposed that it is the first term, *i.e.* the stiffening of the elastic constant, that changes dramatically near the transition. The rotary contribution is assumed instead to vary smoothly. A closer investigation requires a microscopic expression for the elastic constants, at least for the intrinsic or rotary term. Such an expression, proposed by various authors,⁹ relates elastic constants to order parameters and intermolecular interaction coefficients. Without going into detail, essentially two types of theory have been proposed. In the first type^{9b} chirality can also be associated with effective cylindrical symmetry. The temperature dependence of the pitch follows from the variation of $(\langle P_4 \rangle / \langle P_2 \rangle)^2$. The effect of deviation from cylindrical symmetry,³¹ although not essential, can also provide a temperature-dependent contribution.¹⁰

In the second type of model^{9a} the existence of a cholesteric is associated with molecular biaxiality, which implies $\langle D_{0q}^2 \rangle \neq 0$ for $q \neq 0$.

In our case we find that a chiral phase is obtained from a solute whose ordering matrix is essentially cylindrically symmetric,²² *i.e.* $\langle D_{02}^2 \rangle = 0$ within experimental error. The order parameters $\langle P_4 \rangle$ are well-predicted from the $\langle P_2 \rangle$ value by using the Maier-Saupe theory. This is reasonable, since for order parameters $\langle P_2 \rangle \approx 0.8$ every pseudopotential has an asymptotic expansion equivalent to that of the Maier-Saupe, model itself.³² In this region we find, in agreement with Alben's model, that the temperature dependence of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ is very weak, while the distortion parameter k varies dramatically.

At this stage it is useful to comment on the accuracy of the parameters obtained from the simulation. We notice first that the spectra are particularly sensitive to the distortion parameter k when this approaches its limiting value of one. This is shown by the estimated errors, σ_k , in table 1. Thus the e.s.r. technique can provide an effective way of following helix unwinding. Note that in our simulation we have

assigned a unique value of k to the spectrum at a given temperature. This may seem surprising at first since, as shown by eqn (2), k varies with the magnetic field and thus may change as the field is swept from B_{\min} to B_{\max} to record the spectrum. However, for a nitroxide ($B_{\max} - B_{\min}$) ≈ 3 mT, and the effect on k is normally negligible. More specifically, we find, for example, that $k_{\max} = 0.900$ when $k_{\min} = 0.895$, $k_{\max} = 0.999$ when $k_{\min} = 0.996$, and $k_{\max} = 0.99999$ when $k_{\min} = 0.99684$. These values represent equilibrium values obtained by supposing that the director distribution has had time to respond to the field variation. However, we also find that within *ca.* 2 K of the smectic transition, director rearrangements are slower by several orders of magnitude with respect to the sweep time, *i.e.* typically an hour compared with a few tenths of a second. On the one hand this confirms the validity of assigning a single k value near the transition: on the other the slowing down represents an interesting effect in its own right, and will be examined in greater detail in a future publication.

As regard to uncertainty in the order parameters, there is a difference between the cases of $\langle P_2 \rangle$ and $\langle D_{02}^2 \rangle$, which depend essentially on line positions, and that of $\langle P_4 \rangle$, which depends on linewidths. Thus, while we can place an uncertainty of *ca.* 3% on $\langle P_2 \rangle$ and $\langle D_{02}^2 \rangle$, a much greater one of *ca.* 30% can affect $\langle P_4 \rangle$. This large uncertainty stems from the important linewidth contribution caused by unresolved proton splitting, which in turn limits the sensitivity of $\langle P_4 \rangle$. A similar inaccuracy affects correlation times. The spectrum is more sensitive to changes in τ_2 than τ_0 . The values obtained confirm the validity, for our purposes, of using a fast-motion analysis.

Finally we wish to comment on possible improvements.

The spectral simulations reported in fig. 1 show that the best agreement is obtained for temperatures intermediate between those of spectra (a) and (c). A less satisfactory agreement is obtained very near [fig. 1(a)] or further away from [fig. 1(c)] the smectic transition. The simulated spectrum, fig. 1(a), seems to overestimate the number of molecules perpendicular to the director. In other words the distribution seems to deviate from a helical one. The reason for this behaviour might be ascribed to the effect of the pitch becoming comparable to the tube diameter.¹⁶ It has in fact been found that a complex sequence of director configurations arises in this temperature region, with differences in the heating and cooling cycle. In particular, heating from the smectic to a temperature slightly above the transition to the cholesteric ($T - T_{\text{sm}} \approx 1$ K) in tubes of diameter 50–400 μm produces a compression effect on the cholesteric spiral. In our case this effect may account for imperfect simulations very near to T_{sm} , while the decrease in pitch obtained by further heating quickly makes our sample behave as a bulk one. We can therefore understand the success of simulations for temperatures >1 K above T_{sm} . In the other limiting situation, for higher temperatures [spectrum (c)] the simulation is again not satisfactory. The comparison between simulated and experimental spectra seems to indicate this time that the number of molecules parallel to the director is overestimated. This can be understood if the helix alignment is not perfectly perpendicular to the director. Similar behaviour was found by Luckhurst and Smith^{3b} in their investigation of MBBA doped with cholesteryl chloride. They found that for concentrations of cholesteryl chloride of *ca.* 10% the spectrum could be simulated by assuming a distribution of perfectly formed helices. The imperfect helix alignment was in turn attributed to a reduction in the range of pairwise correlations. In our experiment the concentrations are much smaller, which seems to indicate once more a larger value of the chiral solute–solvent interaction.

6. CONCLUSIONS

We have shown that the e.s.r. technique can be used to study cholesteric phases induced by a suitable chiral spin-probe. We believe this to be the first example of such a phase which is not unwound in the 330 mT range of an e.s.r. spectrometer at X band while being generated with a probe concentration still so low as to allow a normal e.s.r. study. The information obtained includes order parameters of the chiral solute and distortion parameter k for the director helix. It seems likely that these studies, when coupled with information on the nematic solvent order parameters, will be able to provide precise information on chiral intermolecular interactions. The use of e.s.r. spectrometers operating at lower fields may prove a useful way of extending the applicability of the technique to other radicals and nematic hosts.

We thank Prof. G. F. Pedulli for various stimulating discussions and Drs. S. Faetti and L. Fronzoni for help with the optical observations. We are grateful to the C.N.R. and Ministero P. I. (Rome) for financial support.

- ¹ S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977).
- ² P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974).
- ³ (a) G. R. Luckhurst and H. J. Smith, *Mol. Cryst. Liq. Cryst.*, 1973, **20**, 319. (b) G. R. Luckhurst and H. J. Smith, *Mol. Phys.*, 1975, **29**, 317.
- ⁴ (a) J. E. Adams and W. E. L. Haas, *Mol. Cryst. Liq. Cryst.*, 1971, **15**, 27. (b) T. Nakagiri, H. Kodana and K. K. Kobayashi, *Phys. Rev. Lett.*, 1971, **27**, 564.
- ⁵ (a) A. Saupe, *Mol. Cryst. Liquid Cryst.*, 1973, **21**, 211. (b) G. Gottarelli, B. Samorì and C. Stremmenos, *Chem. Phys. Lett.*, 1976, **40**, 308.
- ⁶ G. Durand, L. Leger, F. Rondelez and M. Veysie, *Phys. Rev. Lett.*, 1969, **22**, 227.
- ⁷ J. J. Wysocki, J. E. Adams and W. E. L. Haas, *Phys. Rev. Lett.*, 1968, **20**, 1024.
- ⁸ S. Meiboom, L. C. Snyder and E. Sackmann, *J. Am. Chem. Soc.*, 1967, **89**, 5981.
- ⁹ (a) H. Schröder, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray (Academic Press, New York, 1979), p. 121. (b) B. W. van der Meer and G. Vertogen, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray (Academic Press, New York, 1979), p. 149 and references therein.
- ¹⁰ (a) B. W. van der Meer and G. Vertogen, *Phys. Lett.*, 1979, **74A**, 242. (b) B. W. van der Meer, G. Vertogen, A. J. Dekker, J. G. J. Ypma, *J. Chem. Phys.*, 1976, **65**, 3935.
- ¹¹ W. J. A. Goosens, *J. Phys. (Paris)*, 1979, **40**, C3-158.
- ¹² R. Alben, *Mol. Cryst. Liq. Cryst.*, 1973, **20**, 231.
- ¹³ G. F. Keana, S. B. Keana and D. Beethan, *J. Am. Chem. Soc.*, 1967, **89**, 3055.
- ¹⁴ J. Van der Veer, W. H. de Jeu, A. H. Groblen and J. Boven, *Mol. Cryst. Liq. Cryst.*, 1972, **17**, 291.
- ¹⁵ S. Faetti and L. Fronzoni, *Solid State Commun.* 1978, **25**, 1087.
- ¹⁶ P. E. Cladis, A. E. White and V. F. Brinkman, *J. Phys. (Paris)*, 1979, **40**, 325.
- ¹⁷ K. Rottley and A. Saupe, *Mol. Phys.*, 1978, **35**, 1405.
- ¹⁸ G. Gottarelli, G. F. Pedulli and C. Zannoni, *Chem. Phys.*, in press.
- ¹⁹ (a) C. F. Polnaszek and J. H. Freed, *J. Phys. Chem.*, 1975, **79**, 2283. (b) G. Moro and J. H. Freed, *J. Phys. Chem.*, 1980, **84**, 2837.
- ²⁰ G. R. Luckhurst in *Electron Spin Relaxation in Liquids*, ed. L. T. Muus and P. W. Atkins (Plenum Press, New York, 1972).
- ²¹ G. R. Luckhurst and C. Zannoni, *Proc. R. Soc. London, Ser. A*, 1977, **353**, 87.
- ²² S. G. Carr, S. K. Khoo, G. R. Luckhurst and C. Zannoni, *Mol. Cryst. Liq. Cryst.*, 1976, **35**, 7.
- ²³ E. Meirovitch and J. H. Freed, *J. Phys. Chem.*, 1980, **84**, 2459.
- ²⁴ (a) C. Zannoni, G. F. Pedulli, L. Masotti and A. Spisni, *J. Magn. Reson.*, 1981, **43**, 141. (b) G. R. Luckhurst, M. Setaka, R. N. Yeates and C. Zannoni, *Mol. Phys.*, 1979, **38**, 1507.
- ²⁵ J. Talpe, *Theory of Experiments in Paramagnetic Resonance* (Pergamon Press, New York, 1971).
- ²⁶ (a) K. V. S. Rao, C. F. Polnaszek and J. H. Freed, *J. Phys. Chem.*, 1977, **81**, 449. (b) M. K. Bowman, H. Hase and L. Kevan, *J. Magn. Reson.*, 1976, **22**, 23.
- ²⁷ R. Kubo, in *Stochastic Processes in Chemical Physics*, ed. K. E. Shuler (Wiley, New York, 1969).
- ²⁸ R. Armstrong, *J. Quant. Spectrosc. Radiat. Transfer*, 1967, **7**, 61.

- ²⁹ W. H. de Jeu, *Solid State Commun.*, 1973, **13**, 1521.
- ³⁰ W. H. de Jeu and W. A. P. Claasen, *J. Chem. Phys.*, 1977, **67**, 3705.
- ³¹ (a) G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Mol. Phys.*, 1975, **30**, 1345. (b) C. Zannoni, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray (Academic Press, New York, 1979).
- ³² G. R. Luckhurst, M. Setaka and C. Zannoni, *Mol. Phys.*, 1974, **48**, 49.

(PAPER 1/646)