Molecular Orientation in Uniaxial Liquid Crystal Phases as Studied by Electron Paramagnetic Resonance

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The electron paramagnetic resonance spectra of 3β-doxyl-5α-cholestane dissolved in five liquid crystals have been recorded as a function of temperature in the isotropic and mesogenic phases. From these spectra the order parameter $\langle P_2 \rangle$ has been determined. The results have been compared with the data obtained from the optical birefringence measurements and from the polarized absorption spectra of the dichroic dye dissolved in liquid crystal host.

Key words: Liquid Crystal; EPR; Order Parameter.

I. Introduction

Electron paramagnetic resonance (EPR) spectroscopy cannot be applied directly to liquid crystals because they are diamagnetic. The application of this technique becomes possible however, if the liquid crystal is doped with a small amount of a paramagnetic solute, commonly called a spin probe. Nitroxide spin probes have proved to be extremely valuable for studies of the long range orientational order and molecular dynamics of a wide variety of liquid crystalline materials [1 - 9]. It should be kept in mind that the doped substance reflects only indirectly the properties of the host system. The probe can disturb the solvent, and *vice versa* the solvent can more or less deform the dissolved probe. However, Humphries *et al.* [10] have shown that the orientational order in binary systems can be determined if the quantity of solute is very small or its molecular shape is similar to the shape of the liquid crystalline host molecule. The former condition may be easily fulfilled because of the high sensitivity of EPR method, whereas the latter requires the choice of an appropriate spin probe.

In this paper we describe investigations of the orientational order obtained from EPR spectra for five liquid crystals in the nematic and smectic A phases by using 3β-doxyl-5α-cholestane as spin probe. This nitroxide has an elongated form, similar to the liquid crystals investigated and contains a single unpaired electron interacting with the ^{14}N magnetic nucleus having the spin $I = 1$. Both particles possess magnetic moments, which can interact. This coupling is known as a hyperfine interaction and its effect is to split the single line into $2I + 1 = 3$ equally spaced components. The spacing between the lines changes on passing from the isotropic phase to the mesophase, which allows to calculate the order parameter as a function of temperature.

II. Materials and Methods

The molecular structure and the phase transition temperatures of the liquid crystals investigated are gathered in Table 1. These substances were synthesized in the Laboratory of Prof. R. Dąbrowski, Military Academy of Technology, Warsaw and were used without further purification.

The paramagnetic probe, 3β-doxyl-5α-cholestane (**1**) was bought from Aldrich Chem. Co and dissolved in the liquid crystals at a concentration of $5 \cdot 10^{-4}$ M/l. It was found that at so small a concentration of the probe the phase transition temperature of the mixture and the molecular alignment, determined on the basis of absorption measurements [11], are within the experimental uncertainties the same as for pure liquid crystals. Figure 1 shows the molecular structure of the compound **1** and the local principal axes for the nitrogen hyperfine tensor **A**.

Table 1. The molecular structure and the phase transition temperatures for the liquid crystals investigated.

Liquid crystal	Molecular structure	Phase transition temperatures / °C		
		Cr → N or Cr → Sm A	Sm A → N	N → I
6CHBT	C_6H_{13}—⬡—◯—NCS	28.8	-	42.8
6CB	C_6H_{13}—◯—◯—CN	14.5	-	29.1
6OCB	$C_6H_{13}O$—◯—◯—CN	58.0	-	76.5
8CB	C_8H_{17}—◯—◯—CN	21.8	33.5	40.6
8OCB	$C_8H_{17}O$—◯—◯—CN	54.5	67.0	80.0
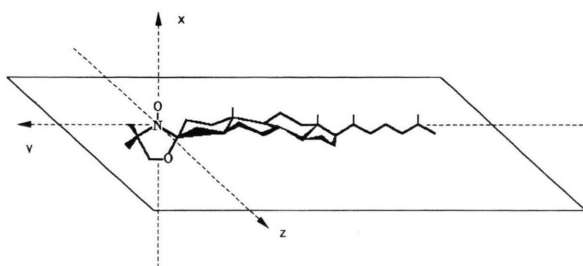
Fig. 1. The molecular structure of 3β-doxyl-5α-cholestane (**1**) and the local principal axes for the nitrogen hyperfine tensor.

The X-band EPR spectra of the liquid crystals doped with the spin probe were recorded as a function of temperature both in the isotropic and liquid crystalline phases by means of a RADIOPAN SE/X-2547 (9.4 GHz) spectrometer with TM_{110} cylindrical cavity and 100 kHz magnetic field modulation. The measurements were made in capillaries with a diameter of 2 mm by cooling the sample. The temperature was regulated in the range from 100 to 20 °C and controlled with an accuracy of ±0.1 °C.

III. Orientational Order in Uniaxial Phases

The long range orientational order of anisotropic systems can be characterized by an orientational distribution function $f = f(\alpha, \beta, \gamma)$, where α, β, γ are the Eulerian angles. In the case of liquid crystals this function gives the probability of finding a molecule at a particular orientation to the director. If there is a cylindrical symmetry about the director, then only two Eulerian angles β and γ are necessary to specify this

orientation. Moreover, if one assumes that the liquid crystal molecules are cylindrically symmetric, which is true for many mesogenic substances, the rotation around the molecular symmetry axis (angle γ) should not modify the distribution function and a consideration of an abbreviated orientation distribution $f(\beta)$ is sufficient, where β is the angle between the long molecular axis and the director. From $f(\beta)$ a set of order parameters for the anisotropic matrix,

$$\langle P_L \rangle = \frac{\int_0^{\pi/2} P_L(\cos\beta) f(\beta) \sin\beta \, d\beta}{\int_0^{\pi/2} f(\beta) \sin\beta \, d\beta}, \quad (1)$$

can be derived [12], where $P_L(\cos\beta)$ are the Legendre polynomials.

The second rank order parameter

$$\langle P_2 \rangle = \frac{1}{2}\langle 3\cos^2\beta - 1 \rangle \quad (2)$$

is of greatest interest, because it can be easily determined from experiments [13, 14].

In the following we restrict our attention to the nitroxide spin probe and ascribe to it the Cartesian coordinate system as follows: the x axis is in the direction of the N-O bond and the z axis in the direction of the nitrogen $2p\pi$ orbital. The direction of the y axis correspods to a right-handed coordinate system (see Figure 1). The local x, y, z system is the principal axes system of the spin Hamiltonian parameters of the unpaired nitroxide electron with g_{xx}, g_{yy}, g_{zz} and A_{xx}, A_{yy}, A_{zz} principal values. These values can be determined from a rigid phase (single crystal, frozen solution) EPR spectrum, where the molecular motions are hindered. In liquid crystalline phases the anisotropic molecular motions produce rapid fluctuations of the angle between nitroxide axes and the external magnetic field direction. The motions are rapid in the EPR time-scale and the EPR spectrum reflects an average nitroxide molecule orientation. The time averaged **g** and **A** tensors have an axial symmetry with the symmetry axis along the magnetic field and $g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$ principal values. The order parameter $\langle P_2 \rangle$ can easily be found from the experimental $A_\parallel$ and $A_\perp$ values as [7]:

$$\langle P_2 \rangle = \frac{A_\parallel - A_\perp}{A_{zz} - A_{xx}} \left[\frac{1}{2}\langle 3\cos^2\xi - 1 \rangle \right]^{-1}, \quad (3)$$

where ξ is the angle, the nitrogen $2p\pi$ orbital (local z axis) makes with the long molecular axis. Equation (3) is valid for the uniaxial case, i. e. when the

Fig. 3. The temperature dependence of the order parameter $\langle P_2 \rangle$ for 6CHBT determined from the EPR spectra of **1** (squares), the optical birefringence (crosses) [16] and the polarized absorption spectra of the dichroic dye (circles) [20].
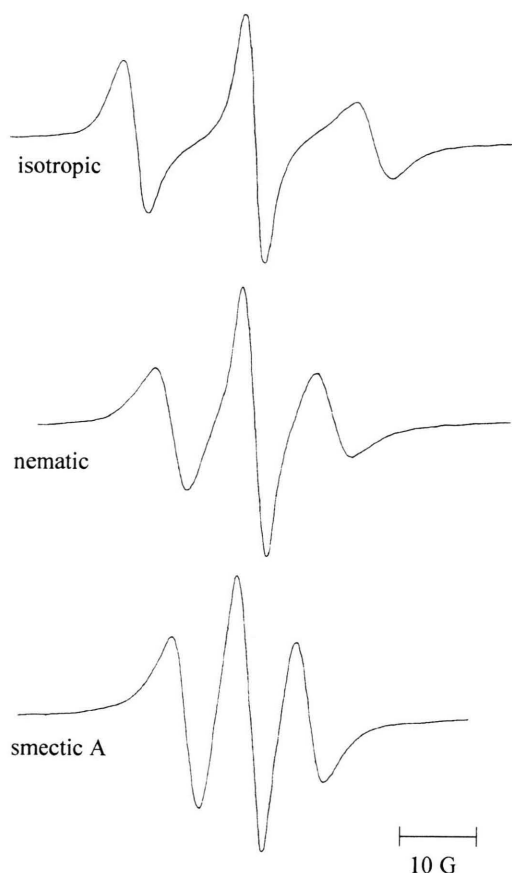

Fig. 2. The electron resonance spectra (ν = 9.4 GHz) of **1** in the isotropic and liquid crystalline phases of 8CB.

order parameter tensor has axial symmetry and when $A_{xx} = A_{yy}$, which is approximately fulfilled for most nitroxide compounds [7].

IV. Results

Figure 2 presents the exemplary EPR spectra for the compound **1** dissolved in the liquid crystal 8OCB in the isotropic, nematic and smectic A phases, recorded when the director was parallel to the magnetic field. It is seen that there is a marked difference in the hyperfine spacing for these three phases. From the line separation in the isotropic phase the value of A_{iso} was determined, whereas the measurements in the liquid crystalline phases allow to obtain the values of $A_{\|}$. On the basis of these values the order parameter $\langle P_2 \rangle$ was calculated from (3), taking into account the following data:
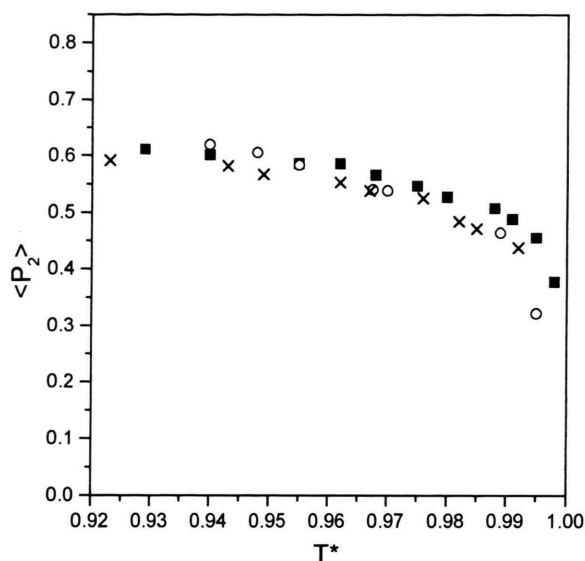
Fig. 4. The temperature dependence of the order parameter $\langle P_2 \rangle$ for 6CB determined from the EPR spectra of **1** (squares), the optical birefringence (crosses) [17] and the polarized absorption spectra of the dichroic dye (circles) [20].
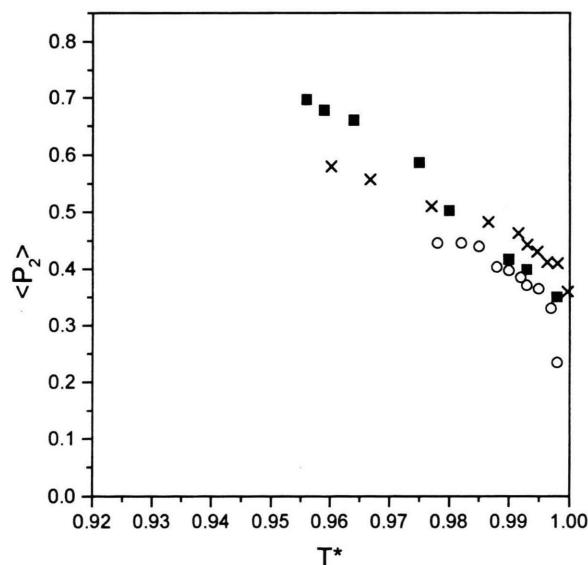
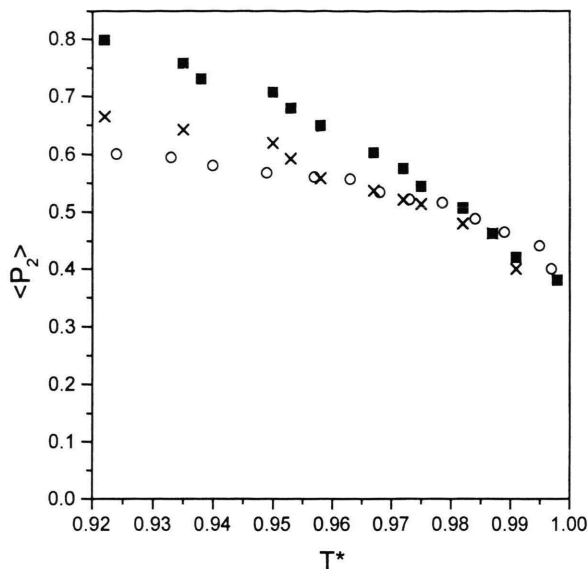1) the diagonal elements of the hyperfine tensor **A** for **1** are [15]

Fig. 5. The temperature dependence of the order parameter $\langle P_2 \rangle$ for 6OCB determined from the EPR spectra of **1** (squares), the optical birefringence (crosses) [18] and the polarized absorption spectra of the dichroic dye (circles) [21].

Fig. 7. The temperature dependence of the order parameter $\langle P_2 \rangle$ for 8OCB determined from the EPR spectra of **1** (squares), the optical birefringence (crosses) [19] and the polarized absorption spectra of the dichroic dye (circles) [21].
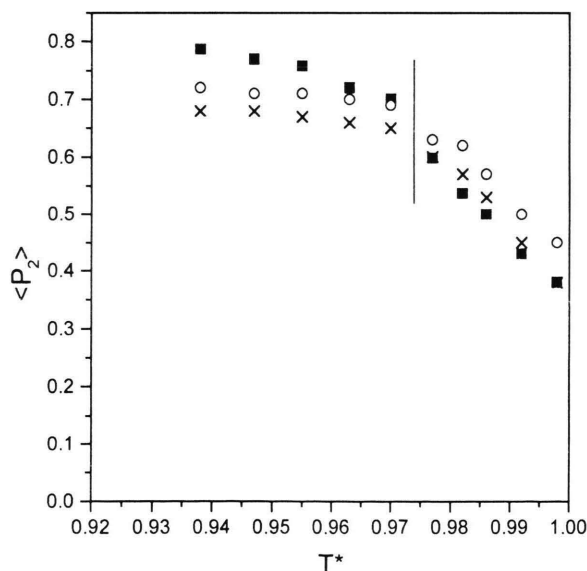
2) the $2p\pi$ orbital makes an angle $\xi = 90°$ with the long molecular axis of **1**,

3) the component $A_\perp$ can be calculated from the relation

$$A_{\text{iso}} = \frac{1}{3}(A_\parallel + 2A_\perp). \tag{4}$$

Figures 3 - 7 present the order parameter $\langle P_2 \rangle$ as a function of the reduced temperature $T* = T/T_{\text{NI}}$ for **1** in the liquid crystals investigated. T_{NI} is here the nematic-isotropic transition temperature. For comparison, in these figures, the values of $\langle P_2 \rangle$ determined on the basis of the optical birefringence measurements [16 - 19] as well as from the polarized absorption spectra of the dichroic dye (guest) dissolved in the liquid crystalline host [20 - 22] are also shown.

V. Discussion

From the results presented in Figs. 3 - 7 it is seen that for the five liquid crystals investigated the character of the changes of the order parameter is similar: with rising temperature $\langle P_2 \rangle$ becomes smaller and jumps to zero at the clearing point. At the nematic - smectic A transition a small discontinuity is observed (Figs. 6 and 7), which demonstrates the first-order
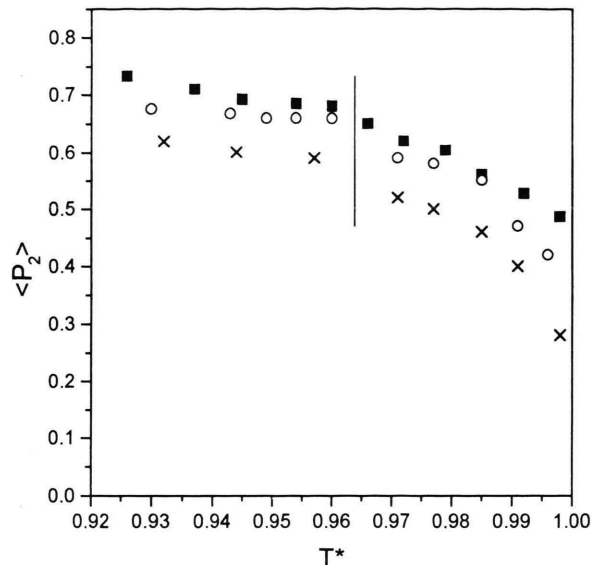

Fig. 6. The temperature dependence of the order parameter $\langle P_2 \rangle$ for 8CB determined from the EPR spectra of **1** (squares), the optical birefringence (crosses) [19] and the polarized absorption spectra of the dichroic dye (circles) [22].

$$A_{xx} = 5.85 \pm 0.1 \text{ G}, \ A_{yy} = 6.32 \pm 0.1 \text{ G},$$
$$A_{zz} = 31.90 \pm 0.02 \text{ G},$$

character of this transition. The results obtained for 8CB and 8OCB from EPR spectra in the smectic A phase are in good agreement with those reported previously by Luckhurst and Poupko [23], whereas for the data in the nematic phase some differences become visible, what can be connected with the experimental conditions.

The comparison of the $\langle P_2 \rangle$ values obtained from EPR spectra with those determined by using other methods demonstrates that agreement within the error limits occurs only for 6CHBT, while for the other liquid crystals sometimes even large discrepancies occur. There can be many reasons of such a behaviour of $\langle P_2 \rangle$. For example, the assumption that a solute (spin probe, dichroic dye) is neutral and a faithful indicator of the host orientation must be treated carefully and critically. This is very distinctly seen in the case of 8OCB: the order parameter for the solute-liquid crystal mixtures (EPR, polarized absorption) is larger in the whole range of temperature than $\langle P_2 \rangle$ for pure host, obtained from the optical birefringence. Such an effect has also been observed previously [21, 24 - 26] and explained in terms of the tendency of the guest molecules to improve the molecular orientation of the host. It is seen also for 1 in 6CB, 6OCB, and 8CB at the low temperatures, although here the $\langle P_2 \rangle$ values can be overestimated due to a systematic error in the $A_{\parallel}$ determination from less resolved (than at higher temperatures) overlaping resonance lines. Another reason for differences in $\langle P_2 \rangle$ can be connected

right with the method used, e. g. with the assumptions made in order to obtain the appropriate formula for the order parameter. Finally, the way of the sample orientation (magnetic or electric field, rubbing process) plays also some role. At any rate, all the methods allow to ascertain and to compare the orienting ability of various liquid crystals investigated, which is a very important information from the technological point of view.

VI. Conclusions

The temperature dependence of the orientational order of a nitroxide spin probe dissolved in five liquid crystals by using electron paramagnetic spectroscopy has been presented. It has been ascertained that the NO spin probe can easily detect phase transition temperatures. Moreover we can conclude tha,t even if the assumption about the cylindrical symmetry of the nitrogen hyperfine tensor around the rotation axis is valid only in first approximation and the spin probe molecule cannot be strictly treated as uniaxial [4], there exists satisfactory agreement between the order parameter obtained from the EPR spectra and that determined on the basis of other methods.

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