EPR Study of the Nematic Liquid Crystals: PEBAB and EBRA *

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By EPR two nematic liquid crystals PEBAB and EBBA were investigated. The experimental variation of the order parameter with temperature is corroborated with theory. In EBBA a spectrum reminiscent of glassy nature is observed at $-60\,^{\circ}C$.

Introduction

The study of molecular ordering and molecular motion in liquid crystals through EPR spectroscopy is a well established technique. We report in this paper on the order parameter σ in two liquid crystals: N-(p-ethoxy benzylidene)-p-amino benzonitrile (PEBAB) and N-(p-ethoxy benzylidene)-p-n-butyl aniline (EBBA). Vanadyl Acetyl Acetonate (VAAC), a paramagnetic molecule, was used as a probe in studying the nature of the nematic phase of these liquid crystals. The dielectric anisotropy in EBBA is $-$ve, while it is highly $+$ve in PEPAB. This prompted us to take up this study.

Experimental

The transition temperatures and phases were determined with a polarising microscope and by DTA techniques. The transitions in PEBAB and EBBA are as follows:

PEBAB: $C_2H_5O-C_6H_4-CH=N-C_6H_4-C\equiv N$

$$\text{isotropic} \underset{}{\overset{125\,^{\circ}C}{\rightleftharpoons}} \text{nematic} \overset{105\,^{\circ}C}{\rightleftharpoons} \text{solid}$$

EBBA: $C_2H_5O-C_6H_4-CH=N-C_6H_4-C_4H_9$

$$\text{isotropic} \overset{76\,^{\circ}C}{\rightleftharpoons} \text{nematic} \overset{32\,^{\circ}C}{\rightleftharpoons} \text{solid}$$

A speck of VAAC and liquid crystal were packed in a quartz tube, heated to the corresponding isotropic temperature and stirred continuously until VAAC was homogeneously mixed with the liquid crystal. The molar concentration of VAAC did not exceed 10^{-3}.

EPR spectra of both PEBAB and EBBA were recorded with a Varian E-12 X-band spectrometer. The temperature of the samples was controlled with a Varian E-257 variable temperature accessory and recorded with a copper constantan thermocouple inside the quartz tube.

Theory

The EPR spectrum of VAAC ($S=1/2$ and $I=7/2$) consists of eight well resoved hyperfine lines around $g=2$. When VAAC is aligned in a nematic host matrix and is tumbling freely, the alignment is measured by an order parameter σ (Fryburg et al. [1])

$$\sigma = \frac{1}{2}\langle 3\cos^2\Theta - 1\rangle = \frac{1}{2}\left[\frac{\langle a\rangle - a}{a - A_\perp}\right], \qquad (1)$$

where Θ is the angle between the direction of the director and the $V=0$ direction of the VAAC molecule.

$\langle a\rangle$ is the average hyperfine coupling constant in the nematic phase. Complete ordering of the liquid crystal in the magnetic field would correspond to an order parameter $\sigma = -0.5$.

Results and Discussion

PEBAB:

By lowering the temperature from 130 °C to 125 °C the width of the eight lines of the spectrum did narrow continuously. At 125 °C the order parameter did rise sharply from -0.02 (isotropic phase) to -0.18 (nematic phase) indicating the transition to be of first order. With a further lowering of the temperature the order parameter did again increase continuously (cf. Figure 1).

Figure 5 shows the variation of the order parameter σ with reduced temperature ($T_c - T$) in PEBAB over a wide range of temperature. The order parameter is well below the theoretical curve given

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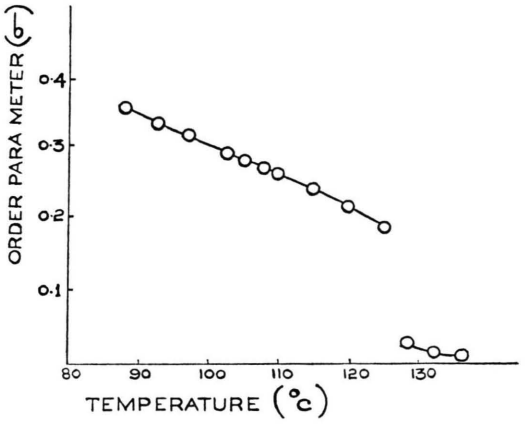

Fig. 1. Variation of order parameter σ with temperature in PEBAB.

by Humphries et al. [2]. Hence higher order terms of the molecular potential have to be included in the HJL theory in such a way that $U_4 = -\lambda U_2$ where λ is still smaller than -0.116, the value obtained for diethoxy azoxy benzene. A smaller value of λ means that the molecular potential in PEBAB is nearer to spherical symmetry.

EBBA:

The variation of the order parameter σ with temperature is shown in Figure 2. The σ value in the nematic phase at the isotropic to nematic transition is -0.153 and increases to -0.437 at 12 °C. Table 1 presents the comparison between values of EBBA obtained here with those obtained from NMR measurements [3].

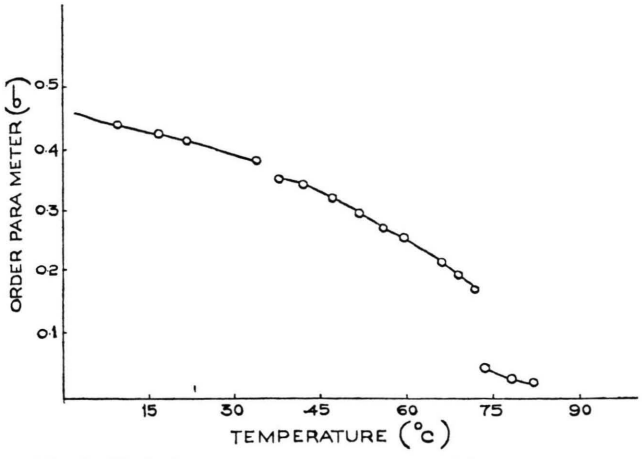

Fig. 2. Variation of order parameter σ with temperature in EBBA.

Table 1. Comparison of σ values in EBBA from EPR and NMR measurements [3].

Temperature °C	Order parameter σ from EPR	(2σ) EPR	Order parameter S from NMR
22	0.409	0.818	0.840
26	0.400	0.800	0.790
40	0.353	0.706	0.710
48	0.317	0.634	0.652
52	0.300	0.600	0.630
56	0.280	0.560	0.583

However, it is to be noted that values obtained from EPR should be doubled for comparison with those of order parameter values obtained by any other technique.

The interesting observation in EBBA is a sudden discontinuity in the slope of the curve $\sigma = f(T)$ around $T = 30$ °C.

To explain this, it may be pointed out that there can be hindered motions of VAAC molecules different from that of tumbling. Hindered motion should cause asymmetry of the eight line spectrum which is not observed even at 10 °C as shown in Figure 3. Apart from this the viscosity and order

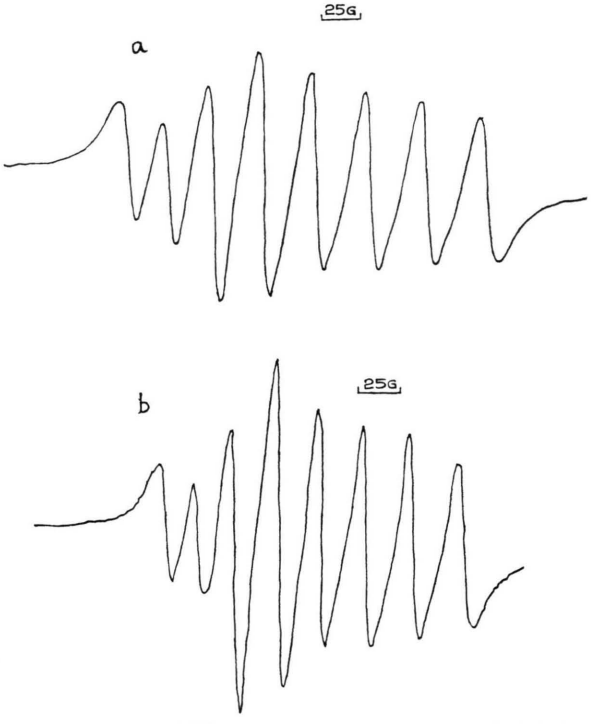

Fig. 3. Spectra of VAAC in the nematic phase of EBBA, (a) at 73 °C; b) at 12 °C.

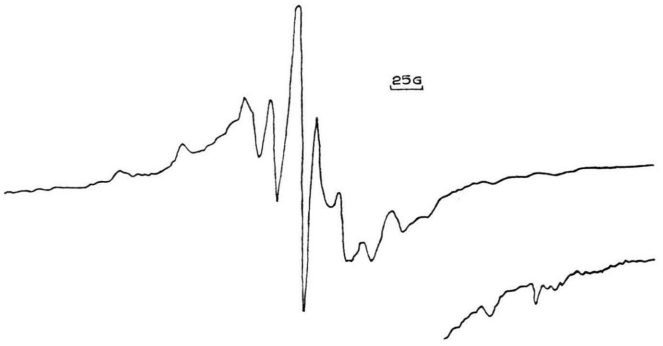

Fig. 4. Spectrum of VAAC in EBBA at $T = -60\,^{\circ}C$ showing glassy nature spectrum.

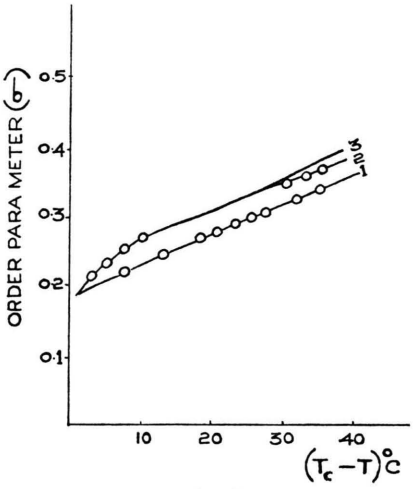

Fig. 5. Variation of order parameter σ with reduced temperature $(T_c - T)$ in: (1) PEBAB, (2) EBBA, (3) Calculated from HJL theory.

parameter are smoothly varying functions [4]. Hence the possibility of hindered motion of VAAC molecule is ruled out. It is therefore felt that some other mechanism is responsible for this discontinuity at $T = 30\,^{\circ}C$. To explain the discontinuity further studies are being taken up.

At $8\,^{\circ}C$, there is slight asymmetry in the line shape. At $-60\,^{\circ}C$ a spectrum reminiscent of glassy nature was recorded and is shown in Figure 4. EBBA was not reported having glassy nature previously, even if the cooling rate was 500 K/minute [5]. Good correspondence between theoretical and experimental curves $\sigma = f(T_c - T)$ is found (see Figure 5).

Conclusions

1. In PEBAB, higher order terms for the molecular potential are to be included to explain the discrepancy of experimental and theoretical curves $\sigma = f(T_c - T)$.
2. Other than viscosity, there is some mechanism responsible for the discontinuity around $T = 30\,^{\circ}C$ in the slope of the order parameter curve in EBBA.
3. A spectrum reminiscent of glassy nature is observed in EBBA at $-60\,^{\circ}C$.

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