

EPR Study of the Molecular Ordering in the Liquid Crystal: HBT *

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Ordering of molecules is observed in the nematic and smectic-B phases of the liquid crystal HBT below 74 °C. In the S_B phase there is a considerable decrease in the intensity without increase in the width of the EPR lines. This unusual behaviour is believed to be due to a order-disorder state with layers coupled by strong forces.

Introduction

N-(p-hexoxy benzylidene)-p-n-methyl aniline, HBT, exhibits nematic and smectic-B phases when the temperature is lowered below ~74 °C.

All smectic phases are layered systems with translational order which is less pronounced than that of a solid. Three smectic phases appear frequently: smectic-A, smectic-C and smectic-B. The smectic-B phase is not well characterised.

Sackmann and Demus [1] have classified the smectic phases in their X-ray diffraction and optical studies. De Gennes [2] felt that smectic-B has flat layers and is reminiscent of a plastic crystal. Smectic-B need not to be classified as a smectic phase, since it has long range crystalline order: Molecules are ordered in a three-dimensional lattice together with a certain amount of orientational disorder. This analogy with a plastic crystal [3] would account for the large heat of transition observed at the transition solid → S_B. The heat of transition affects the mono-domain structure and leads to multi-domain structure with a reduced orientational order parameter. Another model of the smectic-B phase [4] claims strong forces inside each layer (favouring a two-dimensional solid like arrangement) and weak forces between the layers. At low temperatures HBT behaves as a conventional crystal.

A crucial test is known to distinguish the phases by X-ray diffraction techniques [5]. Through EPR measurements on solid → S_B phase, Dvoleitsky et al.

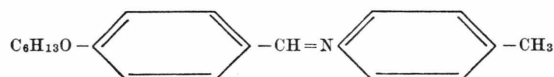
[6] concluded the presence of melting of aliphatic chains in the compound.

In this paper we report molecular ordering of HBT in the nematic and S_B phases with a view to interpret the type of S_B formed at the transition nematic → smectic B.

Vanadyl Acetyl Acetonate, VAAC, was used as a probe in studying HBT by EPR-technique (X-band). Experimental details and the theory involved were reported recently [7].

Results and Discussion

Transition temperatures and phases were assigned by use of the polarising microscope and by DTA techniques. The transitions of HBT



are:

$$\text{isotropic} \rightleftharpoons \text{nematic} \rightleftharpoons \text{smectic-B} \rightleftharpoons \text{solid}.$$

The isotropic system becomes nematic at 73.7 °C. The nematic phase (m. p. = 57 °C) was undercooled to 52.9 °C. The crystallization of the undercooled smectic phase B was observed at 49 °C. The angular variation of the average coupling constant is given by

$$\langle a \rangle = a + \frac{b}{3} \sigma (3 \cos^2 \alpha - 1), \quad (1)$$

where $b = A_{\parallel} - A_{\perp}$ and α is the angle between director and the magnetic field in the smectic phase.

The recorded EPR spectra of HBT in the nematic and smectic phases are shown in Figure 1. In the isotropic phase at 90 °C, $\langle a \rangle$ is -107 G. As the temperature is lowered there is ordering of molecules. At 74 °C a sudden compression of the spec-

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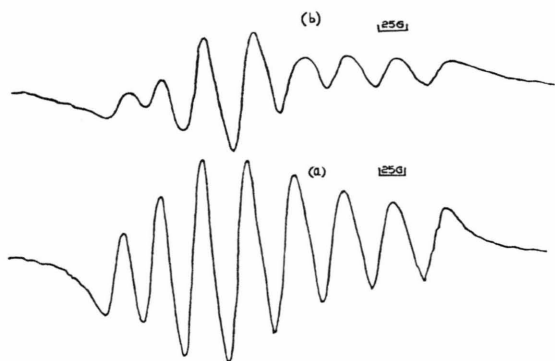


Fig. 1a. Spectrum of VAAC in the nematic phase of HBT at 55°C. — 1b. Spectrum of VAAC in the smectic-B phase of HBT at 50°C.

trum is observed indicating ordering of the molecules; the order parameter is -0.184 . This is due to a first order transition from the isotropic to the nematic phase. By further lowering of T down to 52°C the order parameter rises to -0.325 . Under a magnetic field of 3.3 kG at 51°C a complex spectrum is observed. Thereby the intensity of the spectrum has decreased considerably without any increase in the line width of the lines as shown in Figure 1(b). All eight lines have nearly the same line width as observed for the nematic phase. However, the lines are slightly asymmetric. Phase S_B (melting point 57°C) was undercooled and thereby retained the nematic order. σ increases from -0.325 at 52°C to -0.330 at 50°C. When the sample is cooled in the presence of a magnetic field as high as 9.8 kG an increase of the order parameter from -0.325 at 52°C to -0.350 at 50°C (S_B phase) is found. The variation of the order parameter with temperature is shown in Figure 2. The experimental points taken for the S_B phase are limited due to its very narrow range. When the temperature is decreased further from 50°C to 48°C, HBT has gone into a solid phase whereby the order parameter decreases and the line-width increases showing a multi-domain formation in the crystalline state.

Table 1 compares the order parameter (σ) obtained here through EPR technique with those obtained from refractive index measurements [8]. Note that the σ -values obtained from EPR must be doubled for comparison with those obtained by other techniques.

The reduction of the intensity of the lines in the S_B phase is interesting. In general the nematic \rightarrow

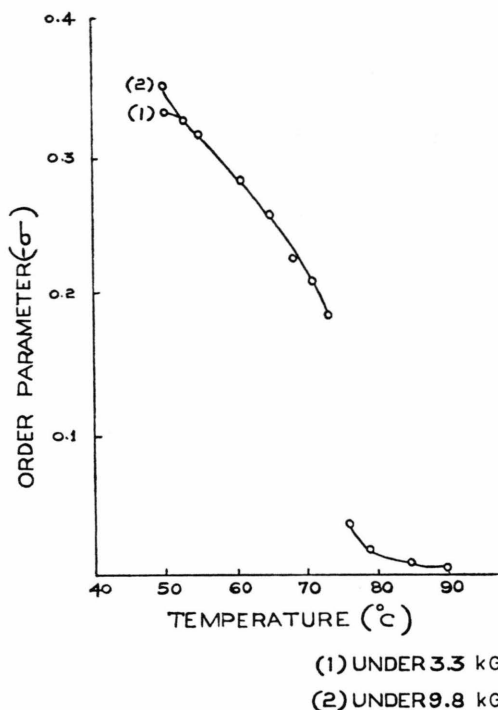


Fig. 2. Variation of order parameter σ with temperature in HBT.

Table 1. Comparison of σ values in HBT from EPR and refractive index measurements [8].

Temperature °C	2σ from EPR	Order parameter (S) from refractive index measurements
69	0.450	0.450
64	0.520	0.500
59	0.540	0.520
54	0.640	0.580

The error involved in σ values is ± 0.002 .

smectic B ($n \rightarrow S_B$) transition is of first order with a decrease in the order parameter. Bahadur *et al.* [9] indicated a first order transition at $n \rightarrow S_B$ through magnetic susceptibility measurements. The present observation indicates no change in the ESR spectrum at the $n \rightarrow S_B$ transition, possibly due to mono-domain formation.

The reduction of the line intensity is attributed to the formation of a solid type S_B phase where VAAC molecules are twodimensionally fixed in layers whereas the direction $V=0$ may still have freedom to rotate due to orientational disorder. It thus re-

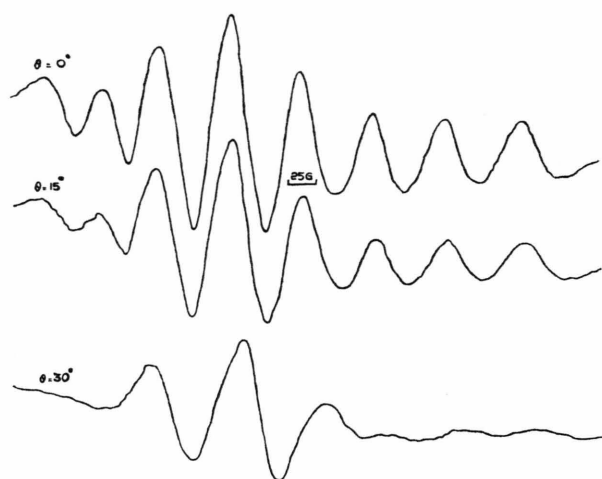


Fig. 3. Angular rotation of VAAC in the smectic-B phase of HBT at 50°C.

presents the order-disorder state of S_B where there is orientational disorder within an ordered crystal-line state.

It became difficult to perform an angular variation in the S_B phase due to a sudden disappearance of the end lines after an B angular rotation of 30° . This is shown in Figure 3. This observation is in favour of assuming layers coupled by strong forces; otherwise it would have been possible to carry out angular rotation.

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