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## Molecular Crystals and Liquid Crystals

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## Refractive Indices, Density and Order Parameter of Some Liquid Crystals

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# Refractive Indices, Density and Order Parameter of Some Liquid Crystals

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The temperature variation of the refractive indices ( $n_o$ ,  $n_e$ ) and density are reported for two liquid crystals. The order parameter is evaluated by both Vuks' and Neugebauer's approaches. The possible sources of error in evaluating the order parameter from refractive indices measurements have been discussed. The contradictory behavior of  $\Delta n$  and  $\Delta \chi$  during the nematic-smectic *B* phase transition of HBT has been explained on the basis of polydomain formation and the order parameter in the  $S_2$  phase is estimated. The order parameter of two liquid crystals, HBT and OBT, is also evaluated by NMR measurements, confirming the polydomain formation in the  $S_2$  phase of HBT.

## INTRODUCTION

The order parameter of a liquid crystal is one of the most important parameters which determine its physical properties and therefore any tensorial property such as refractive index, magnetic and electric susceptibility, elastic constant etc. can in principle be used to determine the order parameter of liquid crystals.<sup>1-5</sup> The order parameter thus determined from bulk properties and referred to as the macroscopic

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order parameter  $Q$ , differ among themselves and also from the microscopic order parameter  $S$ .<sup>1-6</sup> This discrepancy is essentially due to the effect of the local field on tensorial properties. Assuming the validity of a given local field model, it is possible to determine the microscopic order parameter  $S$  from the knowledge of the macroscopic properties such as refractive index, magnetic susceptibility etc.<sup>2,4,6,7</sup> Alternatively,  $S$  can be evaluated directly from microscopic techniques such as NMR, EPR etc. In the first part of this paper we are reporting the refractive indices and order parameter of two liquid crystals: MBAMPD and NPOB. MBAMPD is a Schiff base while NPOB is an ester.

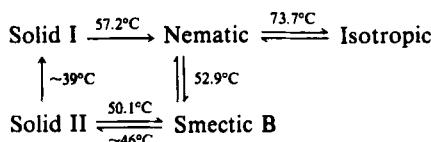
Recently Madhusudana<sup>8</sup> has drawn some theoretical conclusions about the reliability of some experimental measurements (viz. density and refractive indices) used for evaluating the order parameter. The second part of this paper essentially examines the validity of such conclusions based on our density and refractive indice measurements on some samples (HBT, OBT, MBAMPD and NPOB). The measurements on HBT and OBT have already been reported by us<sup>1</sup>). The formation of a polydomain structure in the  $S_B$  phase of HBT, leading to an erroneous value of order parameter, has also been confirmed by our NMR measurements and photographs taken during birefringence measurements. A method is suggested to evaluate the order parameter in such cases by refractive indices measurements.

## EXPERIMENTAL

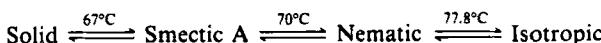
### Materials

NPOB and MBAMPD were provided to us by Dr. D. Demus (GDR) and Dr. W. H. de Jeu (Netherlands) respectively in pure form and were used as such. HBT and OBT obtained from M/S. E. Merck (Germany) were further purified before use. The transition temperature of these liquid crystals are listed below:

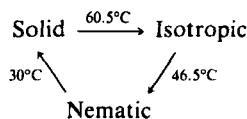
#### (i) HBT, *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine



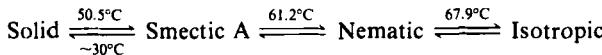
#### (ii) OBT, *N*-(*p*-octyloxybenzylidene)-*p*-toluidine



(iii) MBAMPD, *p*-methoxybenzylidene amino-*p'* (2 methyl phenyl) decanoate



(iv) NPOB, *p*-nitrophenyl-*p*-*n*-octyloxybenzoate



### Refractive Indices measurements

The refractive index in the isotropic phase ( $n$ ) and the ordinary refractive index ( $n_o$ ) in nematic phase were measured using an Abbe refractometer.<sup>1</sup> The birefringence ( $\Delta n$ ) was measured using a modified wedge technique<sup>1</sup> from relation  $\Delta n = \Delta x / \Delta x'$  where  $\Delta x$  is the separation between two consecutive Fizeau fringes in the air gap of the wedge and  $\Delta x'$  is the separation between two birefringence fringes in the portion of the wedge occupied by the liquid crystal. This method obviates the need for measurements of the wedge angle and is therefore more accurate and is free from the uncertainties involved in the measurement of the wedge angle.  $n$ ,  $n_o$  and  $\Delta n$  are accurate up to 0.1%, 0.1% and 0.5% respectively. The temperature regulation was better than 0.1°C. All the refractive indices measurements were carried out at  $\lambda = 5893 \text{ \AA}$ .

### Density measurements

Density was measured using a specially constructed sensitive dilatometer having two uniformly bored capillary arms of length  $\sim 30$  cms above the bulb (Figure 1). The volume of the dilatometer bulb and the volume of the capillary bore per cm were determined by calibrating it with freshly distilled water,<sup>9</sup> benzene<sup>9</sup> and mercury<sup>9</sup> and were found to be 3.23915 cc and 0.00993 cc/cm respectively. The level of the fluid in both the capillary arms was recorded using two travelling microscopes (least count =  $\pm 0.001$  cm). The temperature variation of the volume of the dilatometer was recorded and corrections were made for it. All the weighings were done on a sensitive Mettler balance (sensitivity = 0.00005 gm). The temperature regulation was  $\pm 0.1$ °C. The relative values of the density are accurate to  $\pm 0.01\%$  but absolute values may be correct up to  $\sim 0.2\%$  due to uncertainties in calibration (i.e. density of the standard material etc.).

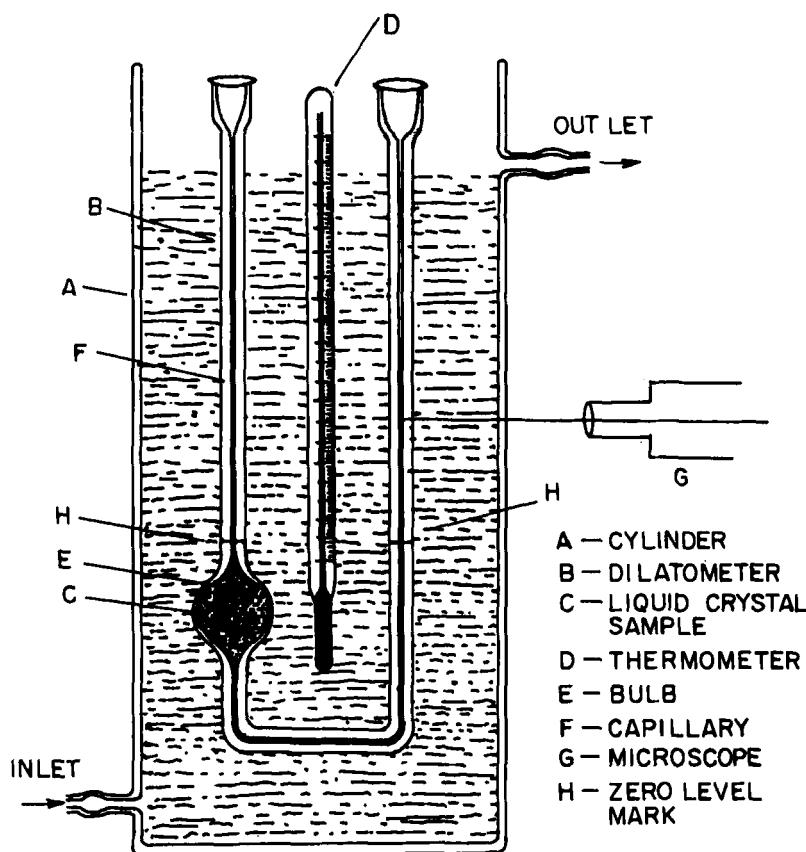


FIGURE 1 Experimental set up for measurement of density of liquid crystals.

### NMR measurements

The wide line NMR spectra were recorded on a Varian 4200-B spectrometer operated at 15.98 MHz. The temperature of the sample was controlled with a Varian V-4540 variable temperature accessory with a sensitivity of  $\pm 0.2^\circ\text{C}$ . The order parameter of liquid crystals HBT and OBT were evaluated using the relations,<sup>10,11</sup>

$$\delta H = 4\alpha(\frac{1}{2} \cos^2 \gamma - \frac{1}{2})(\frac{1}{2} \cos^2 \phi - \frac{1}{2})S$$

where  $\gamma$  is the angle between the director and magnetic field,  $\phi$  is the angle between the molecular long axis and the interproton vector.  $\alpha$  is equal to  $\frac{1}{2}\mu_H r_{H-H}^3$  for proton dipole-dipole interaction. In these types of molecules, the major doublet splitting arises from dipole-dipole in-

teractions between the ortho proton pairs of the benzene rings. The distance between ortho protons ( $r_{H-H}$ ) is taken to be 2.45 Å. Although the value of  $\phi$  in HBT and OBT is not exactly known yet it is certain that it is not zero and using the molecular models one may assume it to be 10°.<sup>10,12</sup>

### Magnetic susceptibility

We have already reported the magnetic susceptibility data.<sup>13</sup> Using this data and the extrapolation procedure the order parameter is obtained.

## RESULTS AND DISCUSSION

The temperature variation of  $n$ ,  $n_o$ ,  $n_e$  and  $\Delta n$  for NPOB and MBAMPD are shown in Figures 2 and 3 respectively. Variation of density with temperature for these two liquid crystals is shown in Figures 4

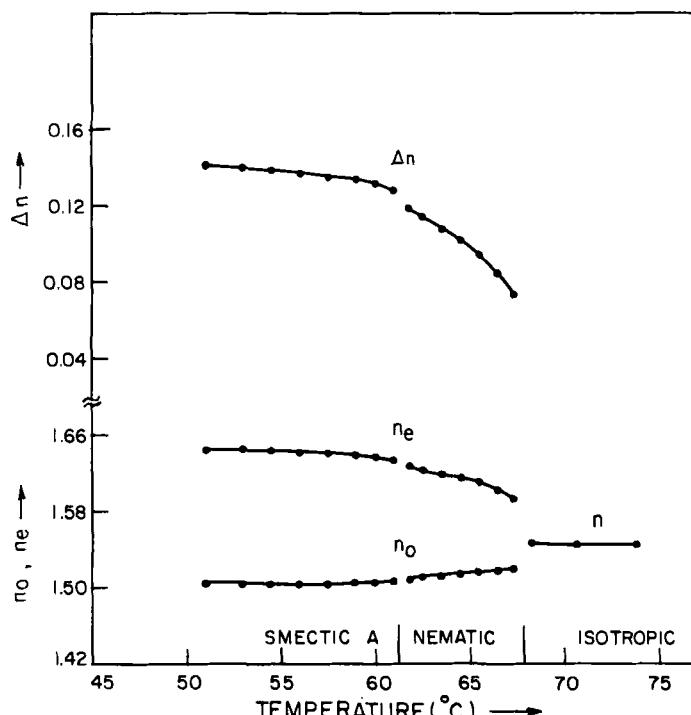


FIGURE 2 Temperature variation of the refractive indices ( $n_o$ ,  $n_e$ ) and birefringence ( $\Delta n$ ) of NPOB ( $\lambda = 5893$  Å).

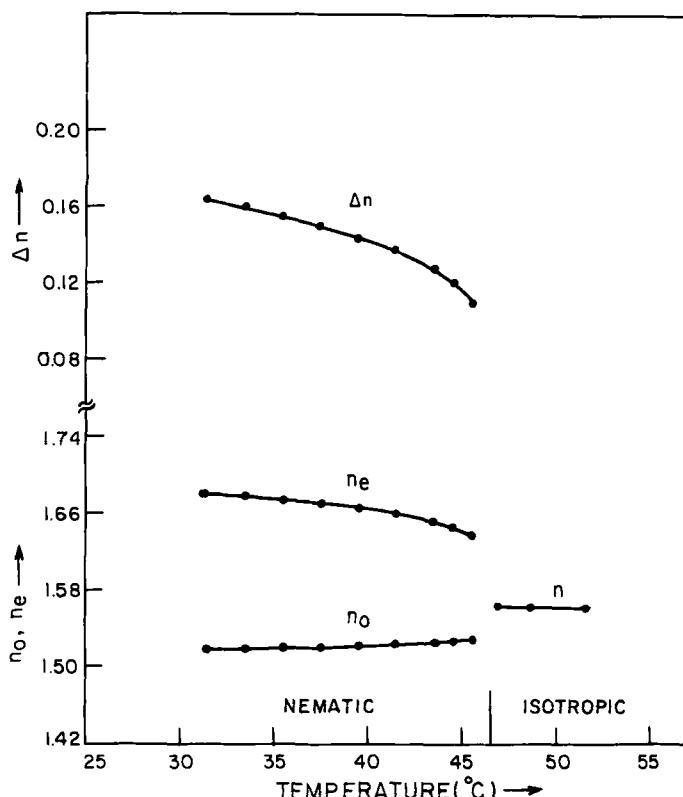


FIGURE 3 Temperature variation of the refractive indices ( $n_o$ ,  $n_e$ ) and birefringence ( $\Delta n$ ) of MBAMPD ( $\lambda = 5893 \text{ \AA}$ ).

and 5 respectively. The density of both the liquid crystals exhibits the normal behavior i.e. it increases with decrease in temperature. Abrupt jumps were observed in the vicinity of the nematic-isotropic transition temperature indicating that this transition is a first order transition. In the case of NPOB, which also exhibits a nematic-smectic A transition, the volume jump at the  $N-S_A$  transition is found to be very small indicating it to be a very weak first order transition. The pretransitional variations in density are observed on both sides of the transition though it is more pronounced on the nematic side.

Using refractive indice and density data, the order parameter was evaluated using both Vuks' and Neugebauer's approaches.<sup>1,14,15</sup> The temperature dependence of the order parameter of NPOB and MBAMPD are shown in Figures 6 and 7. The order parameters of HBT and OBT evaluated from NMR and magnetic susceptibility mea-

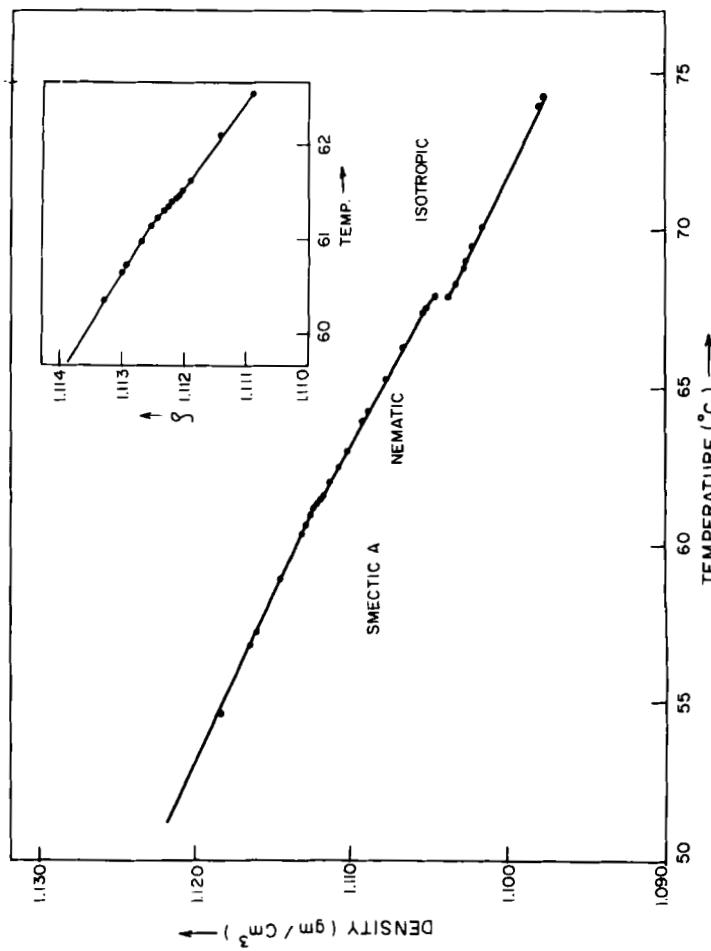


FIGURE 4 Temperature variation of the density of NPOB.

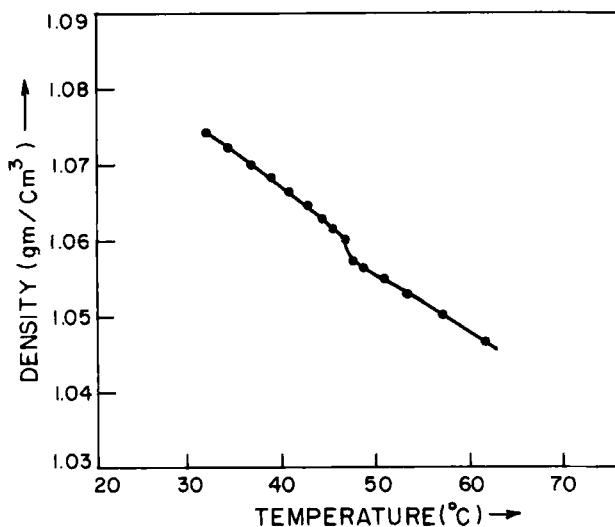


FIGURE 5 Temperature variation of the density of MBAMPD.

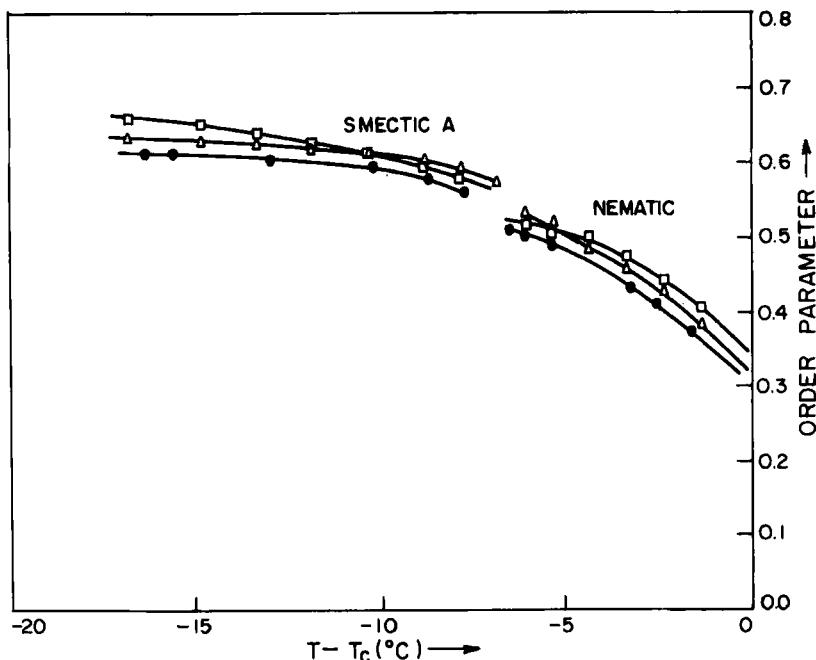


FIGURE 6 Temperature variation of the order parameter of NPOB ---△---△---△--- using Vuks approach; ---□---□---□--- using Neugebauer's approach; ---●---●---●--- from  $\Delta\chi$ .

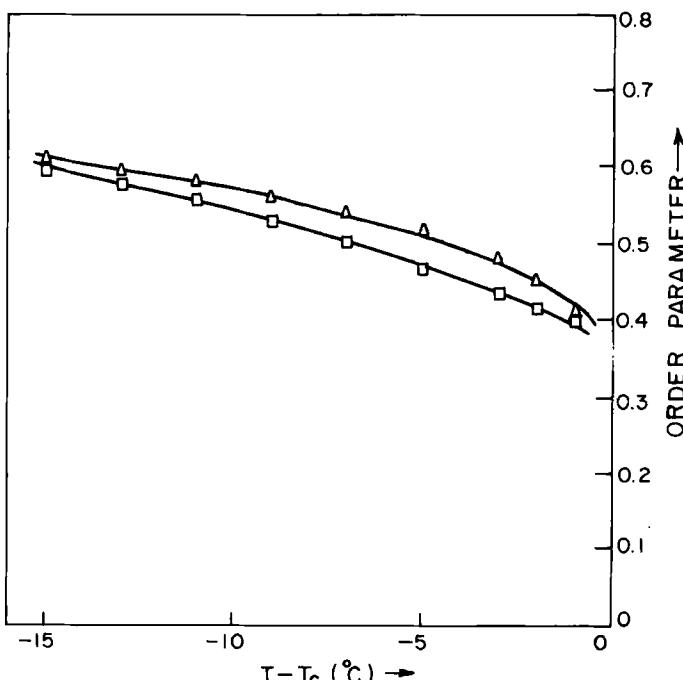


FIGURE 7 Temperature variation of the order parameter of MBAMPD —Δ—Δ— using Vuks approach; —□—□—□— using Neugebauer's approach.

surements are compared with those obtained from birefringence measurements and are shown in Figures 8 and 9.

In the light of measurements reported here and in Ref. 1, we would like to make few comments. The order parameter  $S$  of these liquid crystals determined by the two approaches, namely Vuks' and Neugebauer's, in general agree well. However, there are minor differences and these are more marked in the smectic phases (see Ref. 1 also). To find out the cause of the discrepancies in  $S$ , let us examine the possible sources of error/limitations in the measurements. Four measurements are required: (i)  $n_o$  (ii)  $n_e$  or  $\Delta n$  (iii)  $(\alpha_{\parallel} - \alpha_{\perp})$  and (iv)  $\rho$ . The reliability of  $n_o$  measurements by using Abbe refractometer is well established.  $(\alpha_{\parallel} - \alpha_{\perp})$  is normally not determined directly and is evaluated from an extrapolation technique which has a limitation of 10%.<sup>16,17</sup>  $\rho$  measurements are also very accurate (relative accuracy 0.01% and absolute accuracy 0.2%) as described in the density measurement section. To remove the doubts of some workers<sup>8</sup> about the reliability of density data, let us examine the sensitivity of density measurements and its effect on

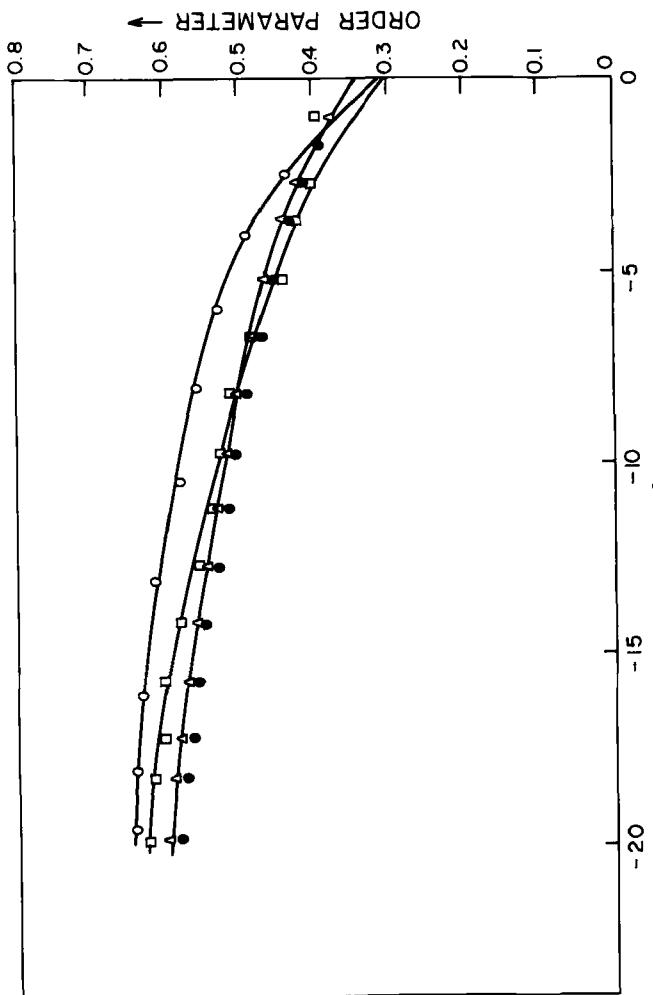


FIGURE 8 Temperature variation of the order parameter of HBT. —△—△—△— using Vuk's approach; —○—○—○— using Neugebauer's approach; —●—●—●— from NMR;

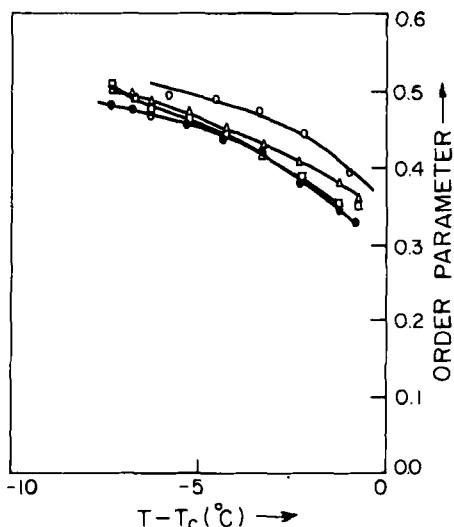


FIGURE 9 Temperature variation of the order parameter of OBT,  $-\Delta-\Delta-\Delta-$  using Vuks' approach;  $-\square-\square-\square-$  using Neugebauer's approach;  $-\circ-\circ-\circ-$  from NMR;  $-\bullet-\bullet-\bullet-$  from  $\Delta\chi$ .

the order parameter. In Vuks' approach  $S \propto (\alpha_e - \alpha_o) \propto (n_e + n_o) \Delta n / \rho(n^2 + 2)$ , so the uncertainties or deviation of  $\rho$  will affect  $S$  by the same %. In the case of Neugebauer's approach  $(\alpha_e - \alpha_o)$  is very sensitive to density since the values of  $\alpha_{e,o}$  also depend on density. Madhusudana<sup>8</sup> has shown that at a particular temperature 1% change in the value of density in PAA changes  $(\alpha_e - \alpha_o)$  and thus  $S$  by 1% in Vuks' and  $\sim 11.5\%$  in Neugebauer's approach and thought that this might be the reason for large difference in  $S$  value in smectic phases of HBT and OBT. However, it is not so. Such a large deviation in the value of density at a particular temperature is not possible since relative measurements are accurate up to 0.01%. 1% relative error would mean a change of height of fluid meniscus by  $\sim 1.8$  cm in each arm in case of HBT (at 54°C) which when viewed even by naked eye cannot escape attention of any observer. The reliability and accuracy of meniscus reading by microscope is obviously much better ( $\sim 1000$  times). Even if we assume a systematic error of 1% in density in the entire temperature range (including the isotropic phase) due to some error in calibration,  $(\alpha_e - \alpha_o)$  and therefore  $S$  values do not change by more than 1 or 2% even in Neugebauer's approach. Madhusudana has obtained a large change in  $(\alpha_e - \alpha_o)$  in Neugebauer's approach by changing the value of density by 1% at a particular temperature in the

mesomorphic phase because he has omitted the corresponding changes in density in the isotropic phase. It leads to an erroneous value of  $\alpha$  in the isotropic phase which affects  $(\alpha_e - \alpha_o)$  considerably. It is clear from these arguments that our density measurements are very much more accurate and reliable and cannot be the reason for discrepancies in the values of  $S$ .

We may now discuss the reliability of  $\Delta n$  or  $n_e$  measurements and its effect on the order parameter. There are two major sources of error: (i) in the determination of the wedge angle and (ii) misalignment. In our procedure the inaccuracy due to measurement of wedge angle has been eliminated.<sup>1</sup> The alignment is good in nematic phase i.e. the liquid crystal is observed in monodomain form with a maximum tilt angle of  $\sim 2^\circ$ . In smectic phases perfect homogeneous alignment is difficult to achieve. The situation becomes more complex with higher ordered smectic phases, viz.  $S_B$ ,  $S_E$ ,  $S_H$  etc., especially when the heat of transition is large (as in the case of HBT where the heat of transition at nematic-smectic transition is 1.94 k cal/mole). It seems that in HBT the monodomain structure of the nematic phase is not converted to the

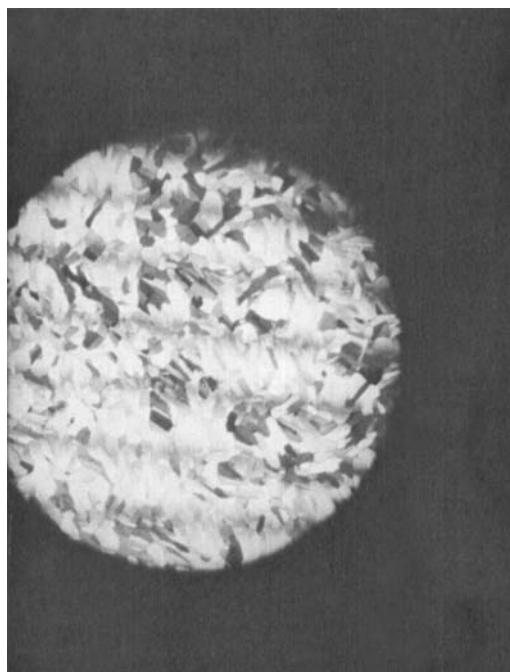


FIGURE 10 Micrograph of the birefringence pattern in the smectic *B* phase of HBT.

monodomain smectic *B* phase even in the presence of strong aligning forces (surface forces or magnetic field) due to evolution of a large amount of latent heat. A photograph of the birefringence pattern in the  $S_B$  phase of HBT (Figure 10) clearly shows the polydomain structure (mosaic texture). The NMR lines in the  $S_B$  phase of HBT (Figure 11) are also indicative of the polydomain structure. In a polydomain structure each of the domains possesses the characteristic high order of the  $S_B$  phase but the director orientation differs from one to the next domain. It is also significant to note that the birefringence fringes are seen (for obvious reasons) on the white mosaics. Thus the birefringence data obtained from the white domains having nearly the same orientation refers essentially to a monodomain structure of the  $S_B$  phase. However, magnetic susceptibility anisotropy data refers to an entire polydomain specimen with molecular orientation different in different

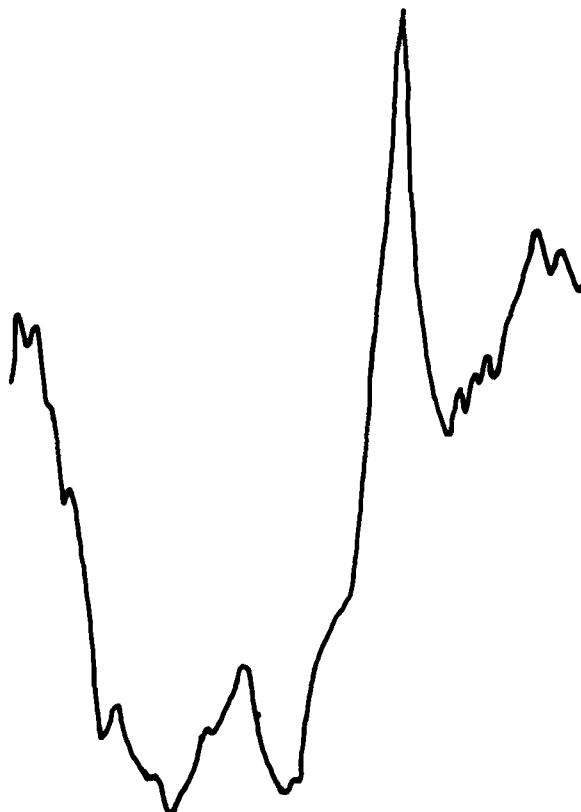


FIGURE 11 NMR spectra in smectic *B* phase of HBT.

domains. It is thus not surprising that magnetic susceptibility anisotropy decreases on crossing over  $N$ - $S_B$  transition<sup>13</sup> and  $\Delta n$  increases across the same phase transition.<sup>1</sup> Although the gross value of  $\Delta n$  and therefore  $n_e$  are slightly lower than their true values (because of slight misalignment of the white domain), refractive indice measurements may be used to estimate a rough value of  $S$  whereas other measurements like magnetic susceptibility fail entirely. Further, very good estimation of  $n_e$ , and therefore  $(\alpha_e - \alpha_o)$  and  $S$ , in smectic phases can be obtained from  $n_o$  in the smectic phase and  $\bar{\alpha}$  in the nematic or isotropic phase, assuming  $\bar{\alpha}$  to be constant in all the phases. Proceeding this way, in  $S_B$  phase of HBT,  $S$  is found to be 0.78 from Neugebauer's approach and 0.80 from Vuks' approach, whereas the previous experimental data<sup>1</sup> gave 0.68 from Vuks' and 0.85 from Neugebauer's approach. In the case of OBT,  $S$  in  $S_A$  phase (68.5°C) is found to be 0.65 from both the Vuks and Neugebauer approaches whereas previous experimental data<sup>1</sup> gave 0.58 from Vuks' and 0.69 from Neugebauer's approaches. In misaligned samples the order parameter is affected to nearly the same extent in both the Vuks and Neugebauer approaches but in opposite directions: in Vuks' it decreases whereas in Neugebauer's it increases. The average of the two gives nearly the actual value.

Concluding, it appears that both the Vuks and Neugebauer approaches in general give nearly equal values of the order parameter but since the two approaches are based on entirely different assumptions regarding the local field, it is not essential that they should lead to exactly the same value of order parameter. Besides the extrapolation procedure itself has an inherent inaccuracy of about 10%.

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