

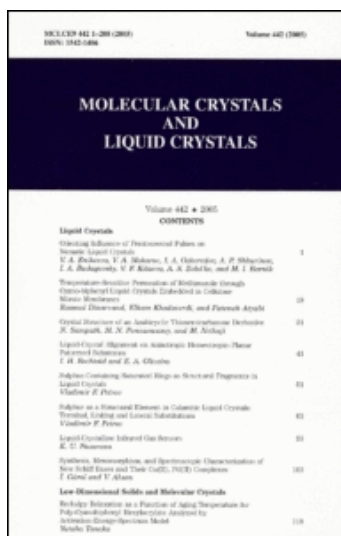
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## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644168>

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First published on: 01 January 1979

**To cite this Article** Sarna, R. K. , Bahadur, B. and Bhide, V. G.(1979) 'Refractive Indices, Density and Order Parameter of Two Liquid Crystals HBT and OBT', *Molecular Crystals and Liquid Crystals*, 51: 1, 117 – 135

**To link to this Article:** DOI: 10.1080/00268947908084697

**URL:** <http://dx.doi.org/10.1080/00268947908084697>

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# Refractive Indices, Density and Order Parameter of Two Liquid Crystals HBT and OBT

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*(Received May 11, 1978; in final form September 21, 1978)*

The temperature variation of refractive indices ( $n_e$ ,  $n_o$ ), birefringence ( $\Delta n$ ), density ( $\rho$ ) and order parameter ( $S$ ) of two liquid crystals, namely, *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine (HBT) and *N*-(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) are reported in the smectic ( $S_A$  in OBT and  $S_B$  in HBT), nematic and isotropic phases. For accurate measurement of  $\Delta n$ , the wedge method was modified to eliminate the need to measure the wedge angle. Density measurements indicate that the smectic–nematic and nematic–isotropic phase transitions in these materials are of first order. Using refractive index values and the density data, the internal field factors ( $\gamma_e$ ,  $\gamma_o$ ), the ratio of principal polarizabilities  $f (= \alpha_e/\alpha_o)$ , and the order parameter,  $S$ , have been evaluated and their temperature dependence discussed in the light of molecular geometry. The order parameter has been determined using the isotropic internal field model (Vuks approach<sup>1,2</sup>) and the anisotropic internal field model (Neugebauer's approach<sup>3,4</sup>). The  $S$  values determined using these two models agree in the nematic phase but differ considerably in the smectic phase.

## INTRODUCTION

The single most important parameter of a liquid crystal which governs nearly all its physical properties is its order parameter.<sup>5–8</sup> According to de Gennes,<sup>5–7</sup> any of the bulk tensorial properties like electric and magnetic susceptibilities, elastic constants, refractive indices etc. can be used to determine the order parameter which is referred to as the macroscopic order parameter  $Q$ . In contrast, the microscopic order parameter  $S$  is defined as  $S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$  where  $\theta$  is the angle between the long axis of the molecule and the director.<sup>8</sup> Because of the differential effects of the local fields on various tensorial properties, the macroscopic order parameter,  $Q$ , determined using these properties differ among themselves and from the microscopic order parameter,  $S$ .<sup>5–9</sup> Assuming the validity of a given local field model, it is possible to determine the microscopic order parameter,  $S$ , from the

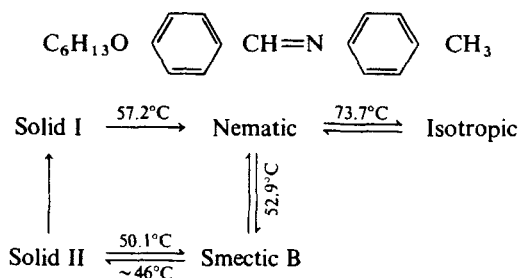
knowledge of the macroscopic tensorial properties.<sup>5,9</sup> Of all the tensorial properties, the optical anisotropy measurements yield direct and accurate values of  $S$ . In recent years, the order parameter of a number of nematogens<sup>9-13</sup> determined using optical anisotropy data have been reported. In this paper, we report the variation of refractive indices ( $n_e$ ,  $n_o$ ), density ( $\rho$ ) and the order parameter ( $S$ ) with temperature for two liquid crystals which belong to the same homologous series and exhibit nematic and smectic phases. The density measurements, besides being essential for the determination of  $S$ , provide useful information on the nature of the phase transitions.<sup>14</sup>

## EXPERIMENTAL

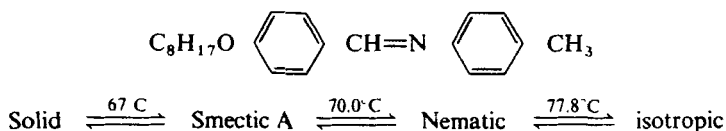
### a. Materials

The liquid crystals used in the present investigation, namely, *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine (HBT) and *N*-(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) are Schiff bases and belong to the same homologous series. Their phase transitions are as under:

#### 1) *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine (HBT)<sup>15</sup>



#### 2) *N*-(*p*-octyloxybenzylidene)-*p*-toluidine (OBT)<sup>16</sup>



### b. Refractive indices measurements

The refractive index ( $n$ ) of these liquid crystals in their isotropic phases was measured (with an accuracy of 0.1%) using Abbe refractometer having a dense glass prism. In the mesomorphic phases, the same technique was used

to determine the ordinary refractive index ( $n_o$ ) with the addition of a polarizer to block the extraordinary beam which improves the contrast at the boundary line. However, this method cannot be used to determine the extraordinary refractive index,  $n_e$ , as  $n_e$  in these liquid crystals is greater than the refractive index of the prism material. The most widely used method to determine  $n_e$  and  $\Delta n$  is the wedge method.<sup>9-13</sup> However, this method, as used by the previous workers, suffers from the following two main drawbacks: 1) the homogeneous alignment induced by unidirectional rubbing generally deteriorates with time, temperature and particularly with temperature cycling, 2) the wedge is formed by placing a Mylar strip or any other spacer in between two optically flat glass or quartz plates. The wedge angle thus formed is determined either from the knowledge of the spacer thickness or by employing optical goniometry. It is assumed that this angle is constant over the duration of measurement and at various temperatures. It has been observed that although the temperature cycling in the mesomorphic and isotropic phases has very little effect on the wedge angle, crystallization affects it considerably and irreversibly. Quantitatively this variation is unpredictable. Besides, the accuracy reported in the determination of the wedge angle is about 1%.<sup>10,13</sup> Consequently,  $\Delta n$  cannot be determined with an accuracy better than this.

The wedge method has been modified in the present investigation to improve the overall accuracy in the determination of  $n_e$  and  $\Delta n$ . The wedge is formed by placing a  $80\mu$  thick Mylar spacer in between two optically flat circular (4 cm diameter) or rectangular (4 cm  $\times$  2 cm) glass plates. The wedge thus formed is partially filled with liquid crystal material aligned parallel to the edge of the wedge (edge of the Mylar spacer). The liquid crystal wedge thus formed acts as a wedge of a uniaxial crystal with its optic axis parallel to the edge of the wedge. The remaining portion of the wedge has air as the medium separating the two glass plates (Figure 1).

On viewing the portion of the wedge with an air gap in the reflection geometry under a normally incident monochromatic light of wavelength  $\lambda$ , equidistant Fizeau interference fringes are seen. If the distance between the two consecutive fringes is  $\Delta x$ , then it can be shown that  $\tan \varphi$ , where  $\varphi$  is the wedge angle, is given by<sup>17</sup>

$$\tan \varphi \sim \varphi = \lambda/2\Delta x \quad (1)$$

Under the same conditions of viewing and illumination, very faint interference fringes are observed in the part of the wedge filled with liquid crystal. If, however, a polarizer is placed above the wedge (Figure 1) with its axis at an angle of  $45^\circ$  to the edge of the wedge, clear equidistant fringes are seen. In this situation we are observing a wedge of a uniaxial crystal under polarized light, polarized at an angle of  $45^\circ$  to the edge of the wedge. These fringes are

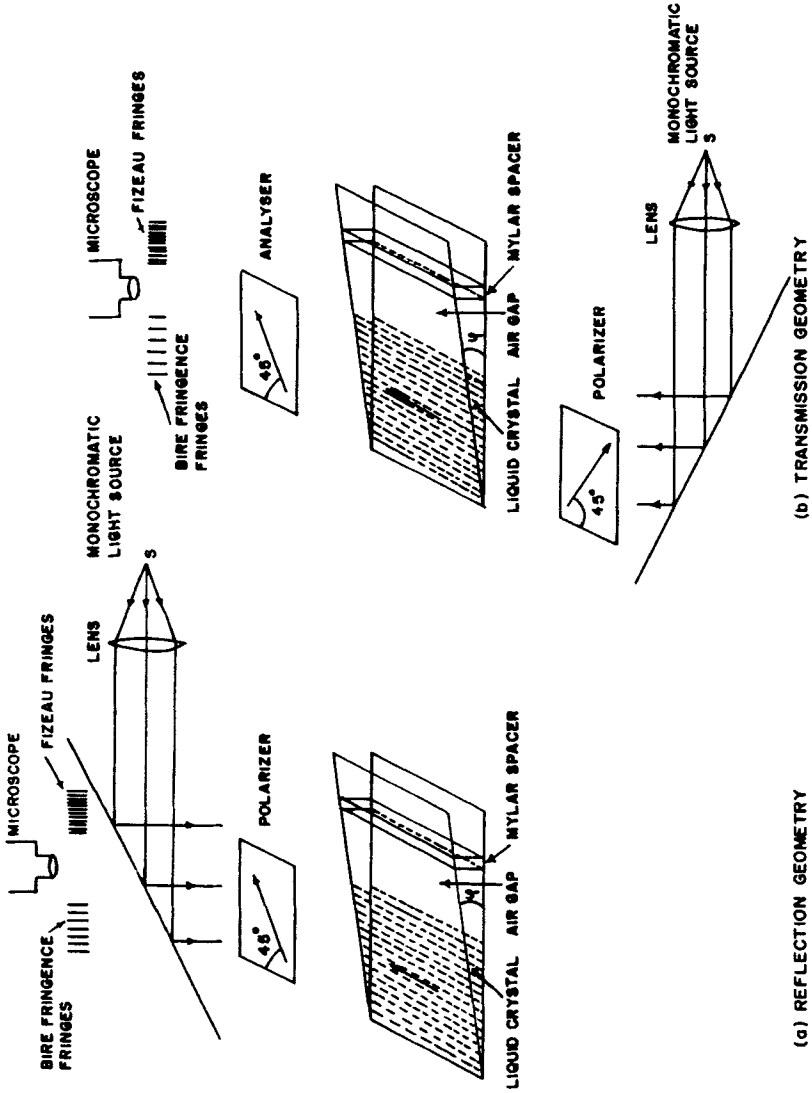


FIGURE 1 Experimental arrangement for measurement of birefringence ( $\Delta n$ ).

due to birefringence and it can be shown that the distance between the two consecutive fringes,  $\Delta x'^{17}$  is

$$\Delta x' = \lambda/2\varphi \cdot \Delta n \quad (2)$$

where

$$\Delta n = n_e - n_o$$

Thus by measuring the distance between two consecutive Fizeau fringes in the air gap,  $\Delta x$ , and the birefringence fringes,  $\Delta x'$ , in the part of the wedge filled with liquid crystal, one can determine  $\Delta n$ , given by

$$\Delta n = \frac{\Delta x}{\Delta x'} \quad (3)$$

Both the Fizeau fringes in the air gap and the birefringence fringes in the portion of the wedge filled with liquid crystal can also be observed in the transmission geometry. In the transmission geometry, the Fizeau fringe pattern is complimentary to the fringe pattern seen in the reflection geometry with the same separation between the two consecutive fringes.<sup>17</sup> To observe the birefringence fringes, it is necessary to place the wedge in between two crossed polarizers with their axes at an angle of  $45^\circ$  to the edge of the wedge. In this case it can be shown that the separation between the two consecutive birefringence fringes,  $\Delta x''$ ,<sup>13,17</sup> is

$$\Delta x'' = \lambda/\varphi \cdot \Delta n \quad (4)$$

Thus in the transmission geometry

$$\Delta n = 2 \frac{\Delta x}{\Delta x''} \quad (5)$$

It is possible to clearly see in the air gap some 100–200 fringes whereas one can see clearly 20–50 birefringence fringes in the reflection geometry and 10–25 fringes in the transmission geometry.  $\Delta x$ ,  $\Delta x'$  and  $\Delta x''$  are measured over a number of fringes with the help of a travelling microscope (least count = 0.0001 cm) and their average values are used to determine  $\Delta n$ . The values of  $\Delta n$  determined in the reflection geometry agree extremely well with those determined using the transmission geometry.

The present method to determine  $\Delta n$  obviates the need to measure the wedge angle† directly and any variation in the wedge angle with time, temperature etc. does not affect the values of  $\Delta n$  because both  $\Delta x$  and  $\Delta x'$  (or  $\Delta x''$ ) are measured at each temperature. The accuracy obtainable in the

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† The wedge angle in our method can be determined if necessary with great accuracy using equation 1 from the knowledge of  $\Delta x$  and the wavelength  $\lambda$ . Since  $\Delta x$  is determined from the spacing of the interference fringes by averaging over at least  $100 \pm 0.1$  fringes, the wedge angle can be determined with very great accuracy (better than 0.1%). The accuracy involved in the determination of  $\Delta x'$  (and  $\Delta x''$ ) is better than 0.5%. Thus in our method  $\Delta n$  can be determined with an accuracy of about 0.5%.

TABLE I  
 $\alpha_e$ ,  $\alpha_0$ ,  $\gamma_e$ , and  $\bar{\alpha}$  of MBBA

Temperature ( $T - T_c$ ) in °C	$\alpha_e \times 10^{24} \text{ cm}^3$		$\alpha_0 \times 10^{24} \text{ cm}^3$		$\gamma_e$		$\bar{\alpha} \times 10^{24} \text{ cm}^3$	
	Present work	Literature <sup>4</sup> value	Present work	Literature <sup>4</sup> value	Present work	Literature <sup>4</sup> value	Present work	Literature value
3.0	41.73	41.68	32.86	32.97	3.91			
5.0	42.56	42.31	32.45	32.66	3.78	3.77		
7.0	42.95	42.83	32.25	32.40	3.73			
10.0	43.60	43.58	31.93	32.02	3.66		35.82	34.7 <sup>10</sup>
13.0	43.81	43.96	31.82	31.83	3.66			35.87 <sup>4</sup>
16.0	44.00	44.17	31.73	31.73	3.67			
19.0	44.25	44.44	31.60	31.59	3.66			

determination of  $\Delta n(0.5\%)$  using this method is much better than that achieved by previous workers. The most accurate measurements reported so far are due to Haller *et al.*<sup>13</sup> and Hanson *et al.*<sup>9</sup> They measured the spacing of the interference fringes by averaging over  $20 \pm 0.1$  fringes giving the accuracy in the measurement of the spacing of the interference fringes of about 0.5%. In order to obtain the value of  $\Delta n$  in their method, it is necessary to know besides the fringe spacing, the value of the wedge angle. Thus the inaccuracy in  $\Delta n$  measurement in their set up is determined by the inaccuracy in the measurement of fringe spacing and the inaccuracy involved in the determination of the wedge angle; the latter being much greater ( $\sim 1\%$ <sup>13</sup>). Our modification obviates the need to measure the wedge angle and therefore yields far more accurate values of  $\Delta n$ .

A stable homogeneous alignment unaffected by temperature cycling was induced in the present case by coating the glass plates with a thin film of polyvinyl alcohol (concentration 0.5 to 1% in water) and then unidirectionally rubbing repeatedly. In some cases, homogeneous alignment was induced by coating the glass plates with SiO at an angle of 30°. This surface treatment is extensively used and is very stable.<sup>18</sup> We found that PVA coating also serves the same purpose in the temperature range we are interested in and is much more convenient. To check that the PVA coating does not affect the  $\Delta n$  values, we determined  $\Delta n$  of MBBA without PVA coating but rubbing the glass plates unidirectionally and then with a PVA coating and rubbing the plates unidirectionally. The values of  $\Delta n$  determined following these two surface treatments agree extremely well.

The temperature of the sample in the wedge was regulated using a regulated thermostat U-10 (M/s VEB MLW Prufgerate-Werk, Medingen, DDR) and was measured with a thermocouple placed in the close vicinity of the sample. The temperature uniformity in the entire sample was better than  $\pm 0.1^\circ\text{C}$  while the relative changes in the temperature could be determined with even better accuracy.

To evaluate the accuracy of the method,  $\Delta n$  of MBBA was measured at various temperatures and various parameters such as principal and average polarizabilities and anisotropic field factors were evaluated. The results obtained agree very well with those reported earlier and are summarized in Table I. The accuracy in  $\Delta n$  measurement is  $\pm 0.5\%$  whereas  $n_o$  and  $n$  could be determined with an accuracy better than 0.1%.

## DENSITY MEASUREMENTS

The density of the liquid crystals at various temperatures was measured using a U shaped dilatometer and a travelling microscope (least count  $\pm 0.001$  cm) to read the fluid level in the limbs of the dilatometer. The



thermal expansion of the dilatometer was taken into consideration in determining the density of the liquid crystals. The accuracy in the density measurements was better than  $\pm 0.01\%$ .

## RESULTS AND DISCUSSIONS

The temperature variation of the ordinary and the extraordinary refractive indices ( $n_o$ ,  $n_e$ ) and the birefringence ( $\Delta n$ ) of the liquid crystals HBT and OBT are shown in Figures 2 and 3 respectively. In the isotropic phase, the refractive index ( $n$ ) of both HBT and OBT decreases with an increase in temperature as in normal organic liquids.<sup>19</sup> The variation in the density of these liquid crystals with temperature in their smectic, nematic and isotropic phases is shown in Figure 4. Except in the vicinity of the smectic-nematic and nematic-isotropic phase transitions, the density of these liquid crystals

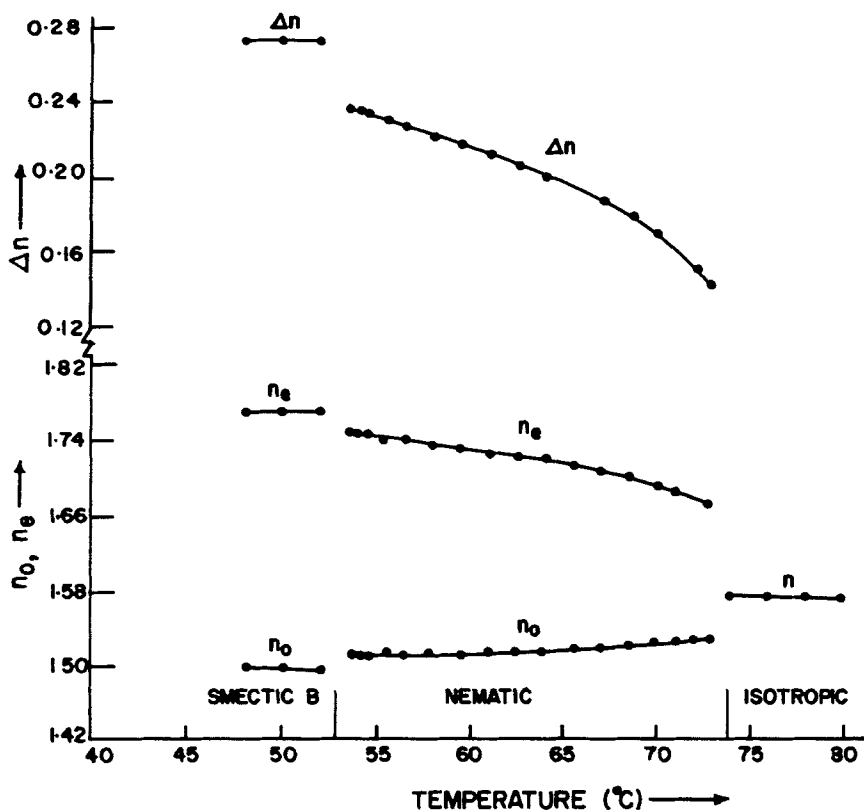


FIGURE 2 Temperature variation of the refractive indices ( $n_o$ ,  $n_e$ ) and birefringence ( $\Delta n$ ) of HBT. ( $\lambda = 5893 \text{ \AA}$ )

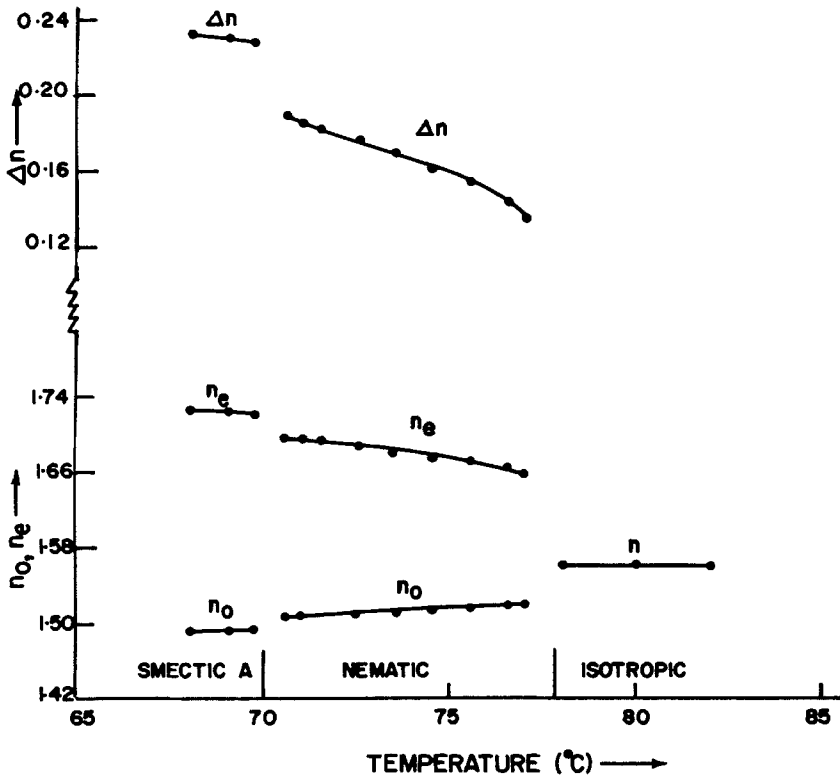


FIGURE 3 Temperature variation of the refractive indices ( $n_o$ ,  $n_e$ ) and birefringence ( $\Delta n$ ) of OBT. ( $\lambda = 5893 \text{ \AA}$ )

decreases almost linearly with increase in temperature. The density of these liquid crystals changes abruptly at both the phase transitions. The change at the smectic–nematic phase transition (1.5% in HBT and 0.55% in OBT) is much greater than that at the nematic–isotropic phase transition (0.39% in HBT and 0.36% in OBT). Relatively large change in the density at the nematic–smectic B phase transition in HBT as compared to that at the nematic–smectic A phase transition in OBT indicates that the smectic B phase of HBT is more well packed than the smectic A phase of OBT. This inference is further strengthened by the fact that in the smectic B phase of HBT, the density does not change appreciably with temperature. The pre-translational variation in the density occurs mainly on the low temperature side of the transition, although there is some indication of its occurrence on the higher temperature side as well.

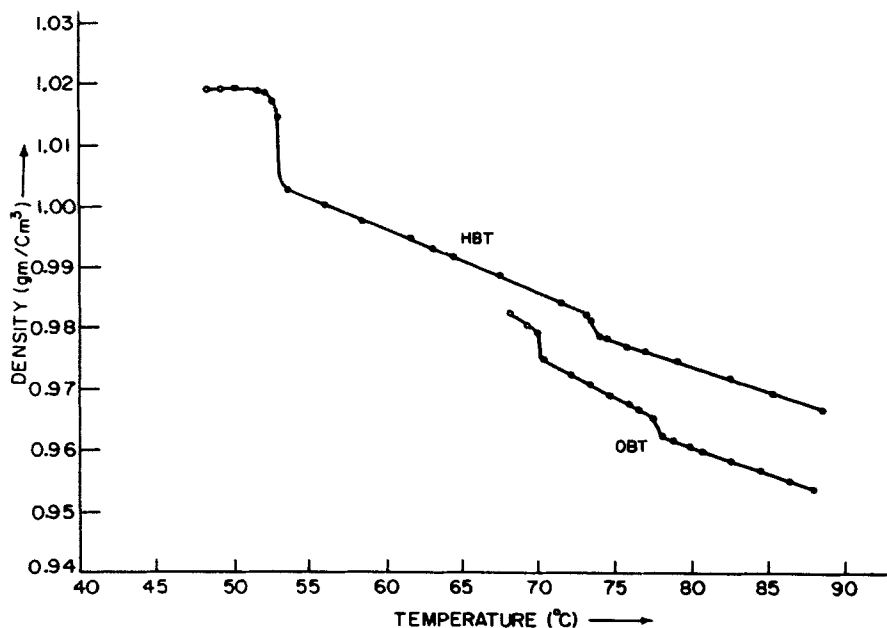


FIGURE 4 Temperature variation of the density ( $\text{gm}/\text{cm}^3$ ) of HBT and OBT.

The order parameter  $S$  can be expressed as<sup>8,11</sup>

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \quad (5)$$

where  $\alpha_e$  and  $\alpha_o$  are the principal polarizabilities in the mesomorphic phases and  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the principal molecular polarizabilities. As suggested by Haller *et al.*,<sup>10</sup>  $\alpha_{\parallel} - \alpha_{\perp}$  is assumed to be the value of  $\alpha_e - \alpha_o$  at absolute zero and is obtained by extrapolating  $(\alpha_e - \alpha_o)$  vs  $(T - T_c)$  curve to  $T = 0^\circ\text{K}$ .

It is thus seen that  $S$  can be determined and its temperature variation studied if  $\alpha_e$  and  $\alpha_o$  are known as a function of temperature.  $\alpha_e$  and  $\alpha_o$  can be derived from the knowledge of  $n_e$  and  $n_o$  (the extraordinary and the ordinary refractive indices). The determination of  $\alpha_{e,o}$  from  $n_{e,o}$  would require the knowledge of the nature of the local field, particularly its anisotropy. If one assumes that the local field is isotropic as assumed in Vuks relations,<sup>1,2</sup> we have,

$$\alpha_{e,o} = \frac{3}{4\pi N} \frac{n_{e,o}^2 - 1}{n^2 + 2} \quad (6)$$

where  $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$  and  $N$  is the number of molecules per cc =  $N_A \rho / M$  where  $N_A$  is the Avogadro's number,  $\rho$  the density and  $M$  is the molecular

weight. Value of  $\alpha_{\parallel} - \alpha_{\perp}$  is obtained, as mentioned above, by extrapolating the linear portion of the curve  $\log(\alpha_e - \alpha_o)$  vs  $\log\{(T - T_c)/T_c\}$  in the nematic phase to  $T = 0^\circ\text{K}$  where  $T_c$  is the nematic-isotropic transition temperature.<sup>10,11</sup> Using this approach,<sup>1,2</sup> we have determined  $S$  for HBT and OBT. The order parameter,  $S$ , for both the liquid crystals as a function of temperature is plotted in Figure 7.

If, however, the local field is anisotropic as is indeed the case, one can use Neugebauer's relations<sup>3,4</sup>

$$n_{e,o}^2 - 1 = \frac{4\pi N\alpha_{e,o}}{1 - N\alpha_{e,o}\gamma_{e,o}} \quad (7)$$

where  $\gamma_e$  and  $\gamma_o$  are the internal field factors with  $\gamma_e + 2\gamma_o = 4\pi$ .

It can be seen that  $\alpha_{e,o}$  can be determined from  $n_{e,o}$  only if  $\gamma_e$  and  $\gamma_o$  are known. For a single crystal with the known crystal structure, it is possible to determine the internal field factors. In the case of liquid crystals because of the change in the order parameter with temperature, the internal field factors are themselves temperature dependent. But since  $\gamma_e + 2\gamma_o = 4\pi$ , Eq. 7 can be written in the form

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3} \left[ \frac{n_e^2 + 2}{n_e^2 - 1} + \frac{2(n_o^2 + 2)}{n_o^2 - 1} \right] \quad (8)$$

In the isotropic phase

$$\gamma_e = \gamma_o = \frac{4\pi}{3}, \quad n_e = n_o = n \quad \text{and} \quad \alpha_e = \alpha_o = \bar{\alpha}$$

Assuming that the mean polarizability  $\bar{\alpha}$  remains the same in all the phases, we have

$$\alpha_e + 2\alpha_o = 3\bar{\alpha} = \frac{9}{4\pi N_i} \left( \frac{n^2 - 1}{n^2 + 2} \right) \quad (9)$$

where  $N_i$  is the number of molecules per cc in the isotropic phase. Using Eqs. 8 and 9,  $\alpha_e$  and  $\alpha_o$  can be determined from the knowledge of  $n_{e,o}$  and  $n$ . These are shown in Table II. As before,  $\alpha_{\parallel} - \alpha_{\perp}$  is determined by extrapolating  $\log(\alpha_e/\alpha_o)$  vs  $\log(T - T_c)$  curve to  $T = 0^\circ\text{K}$ .<sup>4</sup> Thus knowing the values of  $\alpha_e$ ,  $\alpha_o$  and  $\alpha_{\parallel} - \alpha_{\perp}$ , the value of  $S$  can be determined. It is equally possible to determine the internal field factors  $\gamma_{e,o}$  and  $\alpha_e/\alpha_o = f$ .

The temperature variation of  $f = \alpha_e/\alpha_o$  for both HBT and OBT is shown in Figure 5. The value of  $f$  increases gradually with decrease in temperature except at the nematic-smectic phase transition where  $f$  abruptly increases to higher value. The sudden increase in the value of  $f$  at nematic-smectic phase transition only shows that the anisotropy is more marked in the smectic

TABLE II  
 $\alpha_r$ ,  $\alpha_o$  of HBT and OBT

Temperature in °C	HBT				OBT			
	Vuks		Neugebauer's		Vuks		Neugebauer's	
	$\alpha_r \times 10^{24}$ cm <sup>3</sup>	$\alpha_o \times 10^{24}$ cm <sup>3</sup>	$\alpha_r \times 10^{24}$ cm <sup>3</sup>	$\alpha_o \times 10^{24}$ cm <sup>3</sup>	$\alpha_r \times 10^{24}$ cm <sup>3</sup>	$\alpha_o \times 10^{24}$ cm <sup>3</sup>	$\alpha_r \times 10^{24}$ cm <sup>3</sup>	$\alpha_o \times 10^{24}$ cm <sup>3</sup>
72.7	47.95	35.64	46.72	36.32	52.04	39.22	50.09	40.13
71.0	49.07	35.24	46.86	36.25	52.63	39.01	50.13	40.11
68.5	50.10	34.76	47.53	35.91	53.25	38.69	50.76	39.80
65.5	50.83	34.25	48.77	35.29	53.72	38.41	51.35	39.50
62.5	51.49	33.93	49.25	35.05	54.13	38.15	51.94	39.20
59.5	51.98	33.58	50.06	34.65	54.54	37.95	52.26	39.04
56.5	52.46	33.34	50.41	34.47	54.96	37.75	52.56	38.89
54.5	52.80	33.17	50.70	34.33	55.16	37.63	52.80	38.77
51.0	54.08	31.49	54.88	32.24	57.59	35.94	56.47	36.94

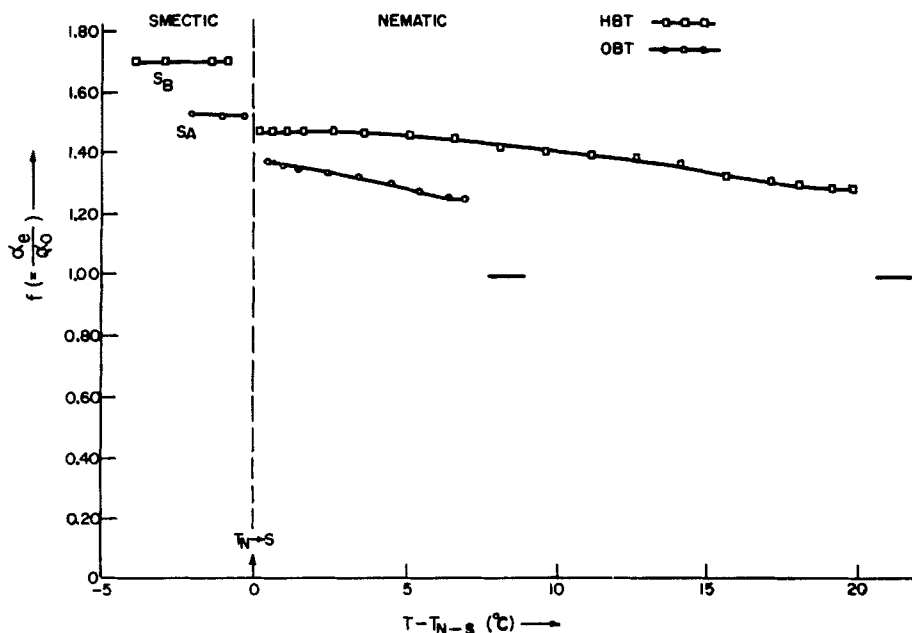


FIGURE 5 Temperature variation of  $f (= \alpha_e/\alpha_o)$  of HBT and OBT. Values of  $f$  in isotropic phase which is equal to 1 is also shown by solid line.

phase than in the nematic phase. It is equally of interest to note that in the smectic B phase of HBT, the value of  $f$  is practically independent of temperature and is much higher than its value in the smectic A phase of OBT. In nematic phase also,  $f$  in HBT is higher than that in OBT.

The variation of  $f$  is essentially due to two factors, namely, 1) the variation of the order parameter which is related to the orientation of the long molecular axis with respect to the director and 2) the buckling of the end alkyl groups in the molecules. In the fully extended zig-zag configuration, the  $\text{CH}_2$  groups of the alkyl chain contribute more to  $\alpha_e$  than to  $\alpha_o$ . As the buckling takes place, the difference in their contribution to  $\alpha_e$  and  $\alpha_o$  decreases. Krishnamurti *et al.*<sup>20</sup> have shown that the buckling of the end alkyl groups increases with increase in temperature thereby reducing  $\alpha_e/\alpha_o$ . Besides, the increase in  $\theta$  (i.e. decrease in the order parameter) with increase in temperature reduces  $\alpha_e$  and increases  $\alpha_o$  thereby reducing  $f$  further. In OBT, there are two more  $\text{CH}_2$  groups than in HBT. Assuming that in the buckled structure, the contribution of a  $\text{CH}_2$  group to  $\alpha_e$  is more or less equal to its contribution to  $\alpha_o$ , it is easy to see that  $\alpha_e/\alpha_o$  in OBT will be less than that in HBT. The relatively weaker temperature dependence of  $f$  in the smectic B phase of HBT and its higher value as compared to that in the smectic A phase of OBT

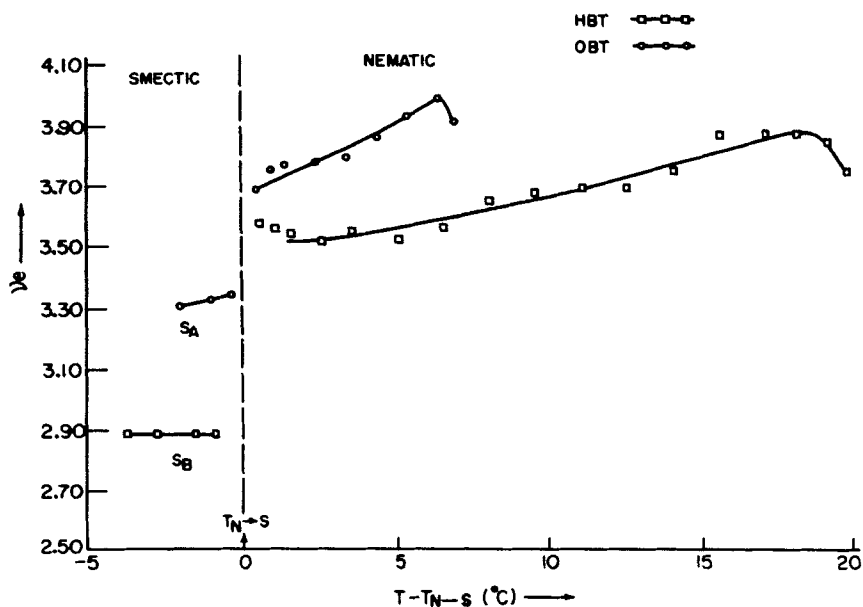


FIGURE 6 Temperature variation of  $\gamma_e$  of HBT and OBT.

shows that the  $S_B$  phase of HBT is more ordered than the  $S_A$  phase of OBT. This also indicates that in this phase, the aliphatic chains (as well as the core) of the molecules are more rigid.

The temperature variation of the internal field factor  $\gamma_e$  for both HBT and OBT is shown in Figure 6. As is indeed expected,  $\gamma_e$  in all the mesophases of OBT and HBT is less than  $4\pi/3$ , the value expected for an isotropic phase. The deviation of  $\gamma_e$  from  $4\pi/3$  is essentially due to the ordering of the molecules and indeed as the ordering improves on reducing the temperature, the value of  $\gamma_e$  decreases.  $\gamma_e$  has the least value in the smectic B phase of HBT indicating again that the  $S_B$  phase of HBT is the most ordered phase among all the mesophases of these materials. A few degrees below the nematic-isotropic transition temperature, the value of  $\gamma_e$  changes rather anomalously. As the temperature is reduced, the value of  $\gamma_e$  decreases sharply from its value of  $4\pi/3$  ( $= 4.19$ ) in isotropic phase. This sudden decrease in  $\gamma_e$  very close to the transition temperature is obviously due to the onset of ordering of the liquid crystal molecules. With a further decrease in temperature (about  $1-3^\circ\text{C}$  below nematic-isotropic transition temperature), a rather unusual slight increase in  $\gamma_e$  is observed in conformity with the observations of Krishna-murti *et al.*<sup>4</sup> and Haller *et al.*<sup>10</sup>  $\gamma_e$  decreases monotonically thereafter.

The variation of the order parameter  $S$  with temperature for HBT and OBT is shown in Figure 7 for the isotropic field model (Vuks approach) and

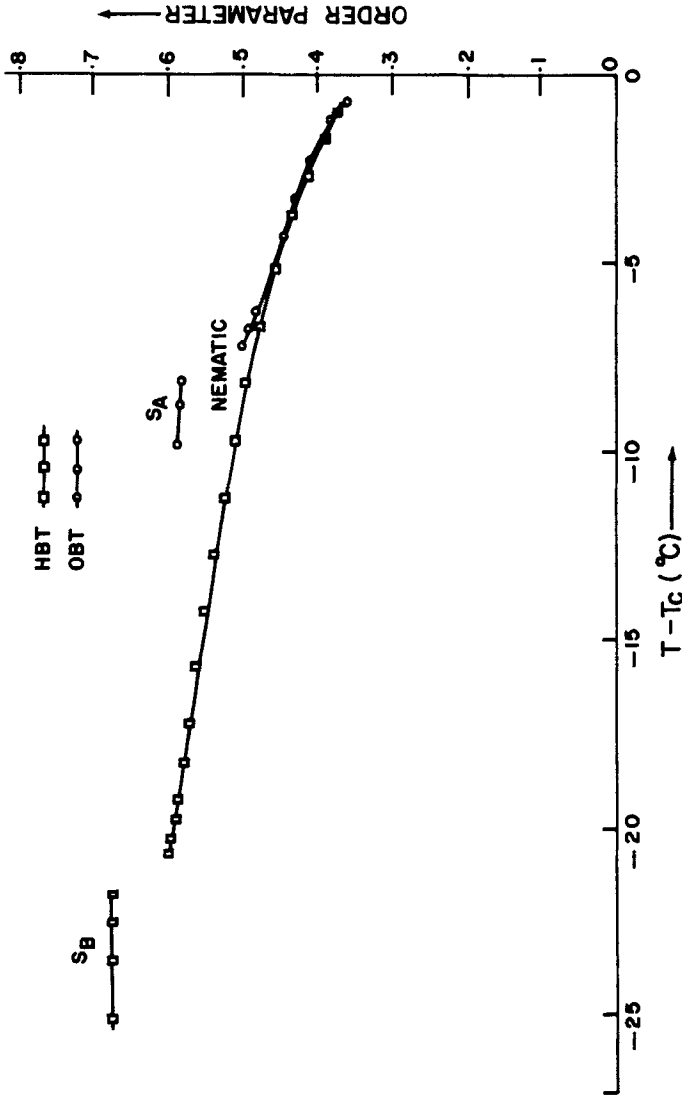


FIGURE 7 Temperature variation of the order parameter  $S$  of HBT and OBT calculated by Vuks approach.



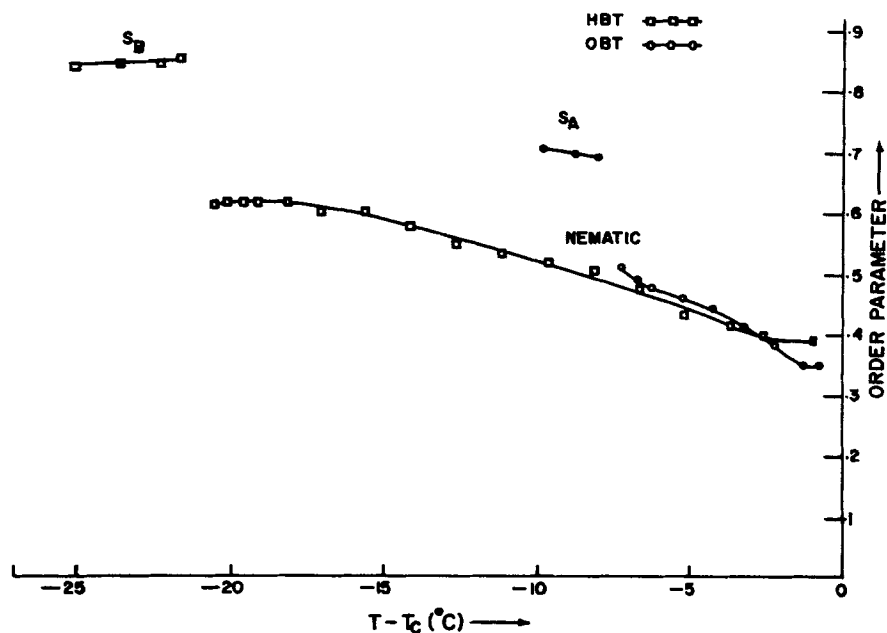


FIGURE 8 Temperature variation of the order parameter  $S$  of HBT and OBT calculated by Neugebauer's approach.

in Figure 8 for the anisotropic local field model (Neugebauer's approach).  $S$  increases with a decrease in temperature in the nematic phase. This is followed by a sudden jump at the nematic-smectic phase transition.  $S$  has a relatively stronger temperature dependence in the nematic phase as compared to that in the smectic phase; indeed  $S$  hardly varies with temperature in the  $S_B$  phase of HBT. The variation of  $S$  with temperature as described above is valid whether the isotropic or the anisotropic model is used.

It is well known that the order parameter can also be determined from the knowledge of  $\Delta\chi$ , the magnetic susceptibility anisotropy.<sup>5,11</sup> One would, therefore, expect that the polarizability anisotropy,  $\alpha_e - \alpha_o$ , would be linearly proportional to  $\Delta\chi$ . In Table III, the values of  $\alpha_e - \alpha_o/\Delta\chi$  are reported over the temperature range covering the smectic, nematic and isotropic phases. As expected, this ratio is reasonably constant in the nematic phases of HBT and OBT and in the smectic A phase of OBT. However, in the  $S_B$  phase of HBT, the ratio increases sharply. This is primarily due to the anomalous variation of  $\Delta\chi$  in this phase.<sup>15</sup>

The order parameter of these two liquid crystals is nearly the same in their respective nematic phases as is indeed expected for these long chain molecules. It may be noted that as reported for other homologous series,<sup>9</sup>

TABLE III  
 $(\alpha_o - \alpha_v)/\Delta\chi$  of HBT and OBT

		HBT			OBT						
Temp. in °C.	$\Delta\chi \times 10^7$ emu cgs gm <sup>-1</sup>	Vuks		Neugebauer's		Temp. in °C	$\Delta\chi \times 10^7$ emu cgs gm <sup>-1</sup>	Vuks		Neugebauer's	
		$(\alpha_v - \alpha_o) \times 10^{24}$ cm <sup>3</sup>	$\frac{\alpha_v - \alpha_o}{\Delta\chi}$	$(\alpha_o - \alpha_v) \times 10^{24}$ cm <sup>3</sup>	$\frac{\alpha_o - \alpha_v}{\Delta\chi}$			$(\alpha_v - \alpha_o) \times 10^{24}$ cm <sup>3</sup>	$\frac{\alpha_v - \alpha_o}{\Delta\chi}$	$(\alpha_o - \alpha_v) \times 10^{24}$ cm <sup>3</sup>	$\frac{\alpha_o - \alpha_v}{\Delta\chi}$
72.0	0.885	12.99	14.68	10.25	11.58	77.0	0.73	12.82	17.56	9.96	13.64
71.0	0.96	13.83	14.41	10.62	11.06	76.5	0.78	13.62	17.46	10.02	12.85
68.5	1.05	15.34	14.61	11.61	11.06	75.5	0.845	14.56	17.23	10.96	12.97
65.5	1.14	16.58	14.54	13.48	11.82	74.5	0.92	15.30	16.63	11.86	12.89
62.5	1.20	17.56	14.63	14.19	11.83	73.5	0.96	15.97	16.64	12.73	13.26
59.5	1.275	18.40	14.43	15.42	12.09	72.5	1.00	16.58	16.58	13.21	13.21
56.5	1.32	19.11	14.48	15.94	12.07	71.5	1.035	17.21	16.63	13.67	13.21
54.5	1.35	19.63	14.54	16.37	12.13	71.0	1.05	17.53	16.70	14.03	13.36
51.0	1.00	22.59	22.59	22.64	22.64	69.0	1.27	21.64	17.04	19.53	15.38

TABLE IV  
 $\bar{\alpha}$  and  $(\alpha_{\parallel} - \alpha_{\perp})$  of HBT and OBT

Material	$\bar{\alpha} \times 10^{24} \text{ cm}^3$		$(\alpha_{\parallel} - \alpha_{\perp}) \times 10^{24} \text{ cm}^3$		
	Experimental value in the isotropic phase	Calculated from bond polarizability <sup>4</sup>	Vuks approach	Neugebauer's approach	Calculated from bond polarizability <sup>4</sup>
HBT	39.79	40.02	32.2	26.6	25.4
OBT	43.45	43.71	35.5	28.5	27.6

the order parameter just below the nematic-isotropic transition in OBT is slightly lower than that in HBT.

The order parameter computed using isotropic local field model (Vuks approach) and the anisotropic local field model (Neugebauer's approach) agree fairly well for both the liquid crystals in their respective nematic phases. The order parameter determined using the isotropic field model, however, differs from the one determined using the anisotropic field model in the smectic phases. The agreement between the order parameter determined using the two approaches in the nematic phases may appear rather strange but this agreement is essentially due to the fact that the order parameter is the ratio of  $\alpha_e - \alpha_o$  and  $\alpha_{\parallel} - \alpha_{\perp}$ . It appears that although  $\alpha_e$  and  $\alpha_o$  vary with the model used, the ratio is not sensitive to the model.<sup>4</sup> In the smectic phases, the anisotropy is considerable because of the greater order and hence the two models give different order parameters.

Simple considerations will show that the Neugebauer's approach is more realistic than the Vuks approach as it takes into consideration the anisotropy of the local field factors. This inference is further strengthened by a comparison of the values of  $\bar{\alpha}$  and  $\alpha_{\parallel} - \alpha_{\perp}$  evaluated using both the models with those evaluated using bond polarizabilities<sup>4</sup> (Table IV). Further, the order parameter  $S$  derived for the smectic phases ( $S_A$ , 0.69;  $S_B$ , 0.85) of OBT and HBT using Neugebauer's relations appear more realistic than those derived from Vuks approach ( $S_A$ , 0.58;  $S_B$ , 0.68).

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