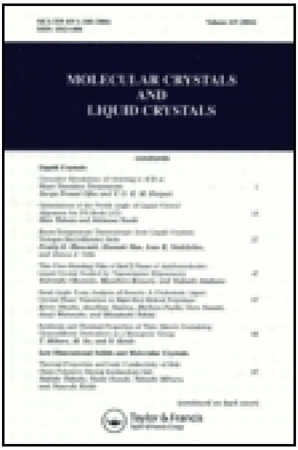

Molecular Crystals and Liquid Crystals

Optical and Dilatometric Properties of Binary Mixtures of HBT and OBT

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Optical and Dilatometric Properties of Binary Mixtures of HBT and OBT

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The nematic isotropic phase boundary, dilatometric properties and refractive indices of *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine (HBT), *N*-(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) and their mixtures are reported. The density measurements of HBT, OBT and their mixtures indicate that all the nematic to isotropic phase transitions are first order transitions. The refractive indices data, along with the density data, are used to calculate the mean polarizabilities of the various HBT/OBT mixtures and to calculate the differences between the effective polarizabilities of the mixtures using both the Vuks and Neugebauer descriptions of the local field. Using the polarizability anisotropies calculated from the bond polarizability data and the Vuks determined effective polarizability differences, the order parameters of HBT, OBT and their mixtures are determined and are all seen to have approximately the same values.

I. INTRODUCTION

The order parameters for *N*-(*p*-hexyloxybenzylidene)-*p*-toluidine (HBT) and *N*-(*p*-octyloxybenzylidene)-*p*-toluidine (OBT) have recently been determined from the refractive indices by Sarna *et al.*[1] The order parameters were calculated on the bases of both the Vuks model[2] in which the local field is taken to be isotropic and the Neugebauer model[3] in which the local field is anisotropic. Using the extrapolation method due to Haller *et al.*,[4] to find the polarizability anisotropies, Sarna *et al.* find that the order parameters obtained by the two models agree with each other. They also find that the order parameters for HBT and OBT have approximately the same values in their respective nematic phases. Their density measurements indicate that the nematic isotropic phase transitions in these two nematogen are both of first order. We would like to report in this paper, our measurements of the refractive indices and dilatometric properties of various binary mixtures of HBT and OBT.

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Similar studies of the optical and dilatometric properties of mixtures of *p*-azoxyanisole (PAA) and *p*-azoxyphenetole (PAP) and of 4-methoxybenzoic acid and 4-*n*-hexyloxybenzoic acid have been reported.[6] It was found that for both systems,[6,7] the order parameters of the mixtures (calculated on the basis of Vuks model) follow the additive relation

$$S_{\text{mix}} = \tau S_1 + (1 - \tau) S_2 \tag{1}$$

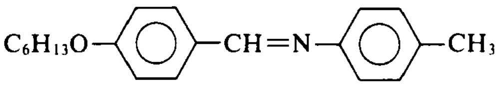
where τ is the mole fraction of constituent 1 having an order parameter S_1 and S_2 is the order parameter for constituent 2. For the PAA/PAP system,[7] it was seen that the mean (average) polarizabilities and the nematic isotropic transition temperatures of the binary mixtures also follow the additive rules.

II. EXPERIMENTAL PROCEDURES

A. Materials

The two pure nematogen constituents, whose structural formula and transition temperatures are

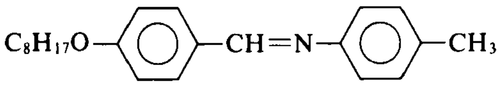
N-(4-hexyloxybenzilidene)-*p*-toluidine (HBT)



58° C nematic → 73.5° C isotropic

and

N-(4-octyloxybenzilidene)-*p*-toluidine (OBT)



69.5° C nematic → 77° C isotropic

were obtained from Merck (Darmstadt, Germany). The two liquid crystals were recrystallized twice from hexane-benzene solutions before their use. The mixtures of the two liquid crystals were prepared by mixing in the isotropic phase accurately weighed quantities of the two mesogenic components. The components were weighed to an accuracy of ±0.0001 gm.

B. Transition temperature measurements

The nematic-isotropic transition temperatures were determined by microscopic observation with a Reichert heating-stage microscope using a Mettler TM 16 thermometer to measure the temperature. The accuracy of these temperature measurements was ±0.1° C.

C. Dilatometric measurements

The densities of the liquid crystals at various temperatures were measured in a manner similar to that used by Sarna *et al.*[1] In our capillary dilatometer, the height change could be observed by a cathetometer with a precision of 0.001 cm. With a 0.002 cm^2 cross sectional area capillary and one gram samples, the accuracy of the density measurements was about ±0.0005 gm/cm^3. The temperatures of the samples were maintained by a Poly Science Corp. Model 80 constant temperature circulatory with a temperature stability of ±0.1° C.

D. Refractive indices measurements

The refractive indices for the 5893 Å sodium line were measured using the minimum deviation method of Pellet and Chatelain.[8] The values of the prism angle and minimum deviation angles were read from an AO Spencer Spectrometer (American Optical Corp., Scientific Instrument Division) to an accuracy of ±0.5 minute of arc. Using a prism angle of 200 minutes, the errors in the determination of the refractive indices are estimated to be ±0.4%. Determination of the temperatures at which the refractive indices were measured was only accurate to within ±0.5° C due to the arrangement of the prism on the heating stage.

III. RESULTS AND DISCUSSION

The nematic isotropic phase boundary of the HBT/OBT system is shown in Figure 1. As we see, our measured nematic isotropic transition temperatures for HBT and OBT are close to the values given in Ref. 1. The phase boundary for the HBT/OBT system deviates slightly from the linear phase boundary observed for the PAA/PAP system.[5] This slight deviation is similar to what is observed[9] in the nematic-isotropic phase boundaries of *p*-azoxyphenetole (PAP)/*p,p*-di-*n*-butyloxyazoxybenzene (PBAB) systems

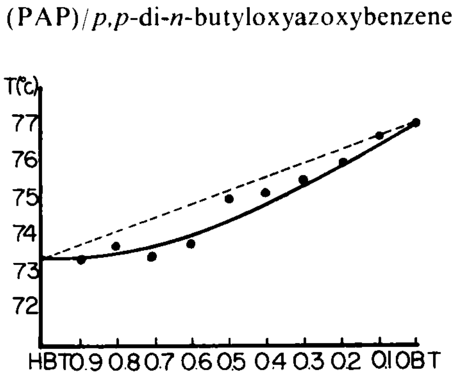


FIGURE 1 Nematic isotropic phase boundary for the HBT/OBT mixture.

and of *p,p*-di-*n*-propyloxyazoxybenzene (PDPAB)/*p,p*-di-*n*-pentyloxyazoxybenzene (PPAB) systems. It should be noted the deviations of the phase boundaries of other mixtures of the *p,p*-di-*n*-alkoxyazoxybenzenes[10] from the linear boundary become progressively larger[11] as the differences in the number of methylene (CH_2) groups in the alkoxy end groups of the two nematogens become greater.

We have plotted in Figure 2, the densities of HBT, OBT and their mixtures

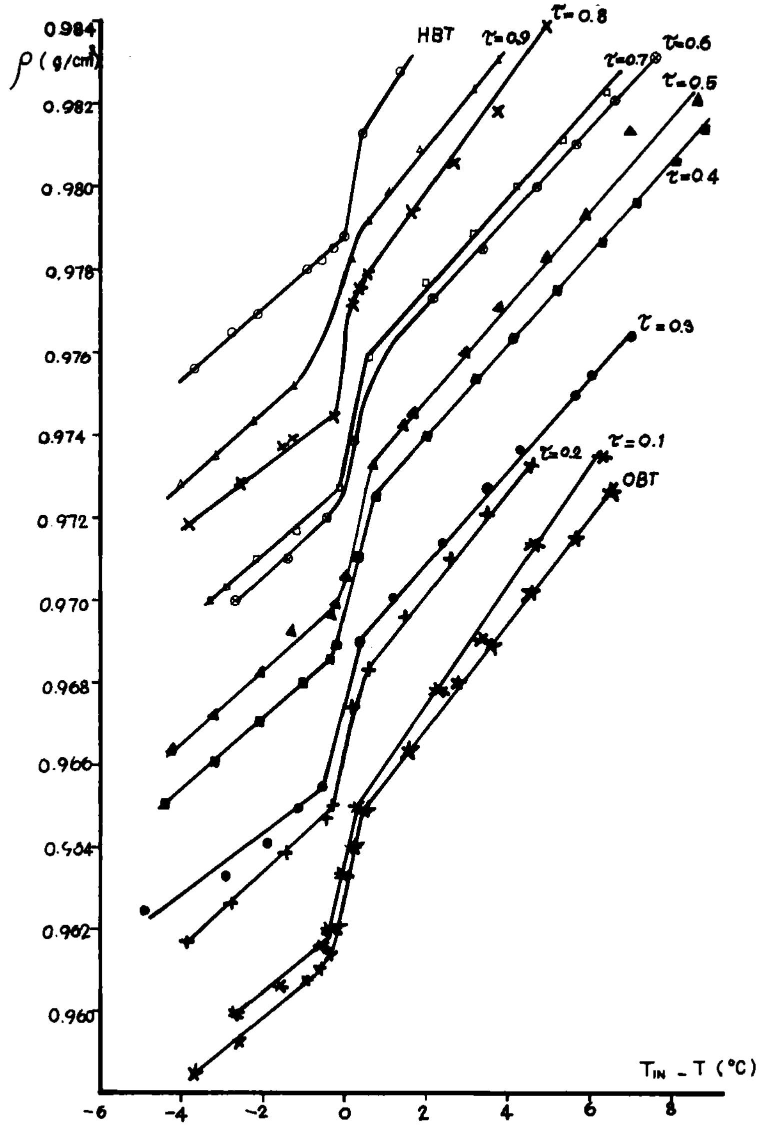


FIGURE 2 Density curves for the HBT/OBT mixtures. τ gives the mole fraction of HBT in the mixture.

in the nematic and isotropic phases. As can be seen, the densities are linear functions of the temperatures except in a small region of magnitudes 1.5° C just below the nematic isotropic transition. The discontinuities in these curves clearly indicate that the nematic isotropic transitions of all the binary mixtures are first order transitions. The coefficients of thermal expansion obtained from the slopes of the density curves are listed in Table I along with the numerical values of the densities. Our values for the pure nematogens HBT and OBT are in good agreement with the values obtained by Bahadur.[12]

In Figure 3, we have plotted the temperature dependence of n_0 (the ordinary refractive index), n_e (the extra ordinary refractive index) and n_i (the refractive index of the isotropic phase) for HBT, OBT and their mixtures. The observed behaviors of the refractive indices of the pure nematogens HBT and OBT are similar to those reported by Sarna *et al.*[1] (See Figures 2 and 3 of Ref. 1) and our measured values appear to be close to their values. Knowing the values of the refractive indices and the densities for the HBT/OBT systems, the mean polarizabilities α can be calculated from the Lorentz-Lorenz relation for the isotropic phase or from the Born relation for the nematic phase, i.e.,

$$\frac{4\pi}{3}\frac{N_0}{M}\bar{\alpha} = \left[\frac{1}{\rho}\frac{\bar{n}^2-1}{\bar{n}^2+2}\right]_{nematic} = \left[\frac{1}{\rho}\frac{n_i^2-1}{n_i^2+2}\right]_{liquid} \qquad (2)$$

TABLE I

The densities and the expansion coefficients of the mixtures of HBT and OBT. τ = mole fraction of HBT in the mixture.

Pure HBT			$\tau = 0.9$		
T(° C)	ρ(g/cm^3)	$\beta \times 10^4$(° C^{-1})	T(° C)	ρ(g/cm^3)	$\beta \times 10^4$(° C^{-1})
nematic phase			nematic phase		
65.95	0.9892		62.1	0.9903	
66.9	0.9884	10.3	64.0	0.9884	9.9
67.9	0.9872	10.6	65.95	0.9865	10.1
69.2	0.9859	10.6	67.9	0.9845	10.6
70.15	0.9849	11.6	69.35	0.9830	11.1
71.15	0.9837	11.6	70.0	0.9822	11.8
72.1	0.9826	13.9	71.3	0.9807	12.3
72.95	0.9813	16.5	72.0	0.9798	14.9
73.15	0.9809	57.5	72.45	0.9790	18.7
2 phases coexist			72.9	0.9782	47.5
73.4	0.9787	61.7	2 phases coexist		
isotropic phase			73.05	0.9762	56.3
73.55	0.9785	10.4	isotropic phase		
73.9	0.9782	9.5	73.3	0.9760	11.0
74.2	0.9779	9.5	73.55	0.9757	9.9
75.4	0.9768	8.8	74.2	0.9751	9.2
75.95	0.9764	8.3	75.2	0.9742	9.0
76.95	0.9755		76.1	0.9734	8.8
			77.0	0.9727	

TABLE I (*continued*)

$\tau = 0.8$			$\tau = 0.7$		
T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})	T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})
nematic phase			nematic phase		
64.0	0.9877		64.3	0.9856	
65.0	0.9868	9.4	66.35	0.9837	9.9
66.1	0.9857	10.1	67.8	0.9822	10.6
66.95	0.9848	10.5	68.9	0.9810	11.0
68.9	0.9828	10.4	69.9	0.9799	10.8
70.0	0.9817	11.3	71.0	0.9788	11.1
71.0	0.9805	11.9	72.0	0.9776	12.6
72.0	0.9793	13.8	73.05	0.9763	13.8
73.0	0.9775	14.4	73.4	0.9757	16.3
73.4	0.9772	64.2	73.9	0.9749	58.3
2 phases coexist			2 phases coexist		
73.7	0.9750	41.8	74.15	0.9727	41.9
isotropic phases			isotropic phase		
74.05	0.9745	9.9	74.55	0.9722	13.7
74.85	0.9739	8.8	74.6	0.9721	9.8
75.1	0.9736	9.8	75.2	0.9716	8.1
76.0	0.9728	8.0	76.15	0.9708	8.8
77.3	0.9717		76.8	0.9703	8.7
			77.25	0.9699	

TABLE I (*continued*)

$\tau = 0.6$			$\tau = 0.5$		
T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})	T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})
nematic phase			nematic phase		
65.6	0.9845		66.3	0.9820	
67.1	0.9829	10.6	67.9	0.9803	10.7
68.05	0.9820	11.4	68.95	0.9792	10.6
68.95	0.9809	11.7	70.0	0.9781	11.0
69.85	0.9799	10.7	71.0	0.9770	11.9
71.2	0.9785	10.8	71.9	0.9759	12.3
72.4	0.9772	12.0	73.15	0.9744	12.4
73.45	0.9758	17.1	73.3	0.9742	14.3
74.4	0.9739	34.4	74.05	0.9732	14.6
2 phases coexist			74.3	0.9728	15.8
74.55	0.9721	45.7	74.55	0.9724	57.5
isotropic phase			2 phases coexist		
74.85	0.9719	10.6	74.7	0.9706	87.9
75.1	0.9716	10.0	74.85	0.9698	28.8
75.8	0.9709	8.7	isotropic phase		
76.5	0.9704	9.2	75.0	0.9697	10.3
77.05	0.9698		76.0	0.9687	9.6
			76.7	0.9681	8.4
			77.8	0.9672	8.7
			78.8	0.9663	

TABLE I (*continued*)

$\tau = 0.4$			$\tau = 0.3$		
T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})	T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})
nematic phase			nematic phase		
66.35	0.9814		68.6	0.9763	
67.1	0.9806	10.8	69.5	0.9755	10.7
68.05	0.9795	11.4	69.9	0.9750	11.7
68.8	0.9786	10.7	71.1	0.9737	11.5
70.0	0.9775	10.7	71.9	0.9727	11.9
71.0	0.9763	11.7	73.1	0.9714	12.2
71.9	0.9753	12.2	74.15	0.9700	13.2
73.05	0.9739	13.2	74.95	0.9690	15.9
74.15	0.9724	15.1	75.15	0.9685	25.0
74.85	0.9712	36.6	75.3	0.9681	68.1
2 phases coexist			2 phases coexist		
75.15	0.9688	59.7	75.55	0.9658	53.8
isotropic phase			isotropic phase		
75.3	0.9686	10.4	75.8	0.9653	10.3
76.0	0.9680	9.2	76.5	0.9649	10.0
77.0	0.9671	9.0	77.3	0.9641	9.5
78.1	0.9661	8.8	78.2	0.9633	8.4
79.3	0.9651		79.2	0.9625	

TABLE I (*continued*)

$\tau = 0.2$			$\tau = 0.1$		
T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})	T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})
nematic phase			nematic phase		
71.1	0.9733		70.15	0.9724	
72.1	0.9721	12.4	71.1	0.9714	12.0
73.05	0.9709	12.8	71.9	0.9704	12.6
74.1	0.9696	13.6	73.05	0.9690	12.1
75.0	0.9683	17.3	74.1	0.9678	12.8
75.4	0.9674	44.0	75.0	0.9666	15.3
2 phases coexist			76.0	0.9650	24.9
75.8	0.9649	51.6	2 phases coexist		
isotropic phase			76.4	0.9632	49.0
75.95	0.9646	10.6	isotropic phase		
76.95	0.9637	9.5	76.65	0.9619	31.1
77.55	0.9632	9.3	76.95	0.9616	10.3
78.2	0.9626	8.8	77.95	0.9606	9.6
79.35	0.9616		79.05	0.9596	9.5
			79.8	0.9589	9.1
			80.75	0.9581	

TABLE I (*continued*)

Pure OBT		
T(°C)	ρ(g/cm^3)	$\beta \times 10^4$(°C^{-1})
nematic phase		
70.5	0.9725	
71.0	0.9714	12.3
72.1	0.9701	12.2
73.15	0.9689	12.8
73.9	0.9679	13.1
75.1	0.9664	15.3
76.0	0.9648	16.7
76.25	0.9645	14.3
76.5	0.9641	56.9
2 phases coexist		
76.7	0.9621	70.1
isotropic phase		
76.9	0.9614	24.7
77.1	0.9611	10.8
77.4	0.9609	9.6
78.05	0.9602	9.7
79.05	0.9593	9.1
80.05	0.9585	8.8
81.05	0.9576	

where N_0 is Avogradro's number; M, the molecular weight of the mixture; ρ, the densities in their respective phases and $\overline{n}^2 = (n_e^2 + 2n_o^2)/3$. The results of these calculations are shown in Figure 4. The small but clear deviation from a linear behavior seen in Figure 1 is not *clearly* evident in the compositional behavior of the mean polarizabilities of the mixtures. In Figure 1, we find the deviation from a linearity to be systemmatic while the deviation in Figure 4 of the mean polarizabilities from a linear behavior appears to be scattered (the experimental values lie both below and above the straight line). Since the deviation of the mean polarizabilities of the mixtures does not appear to be systemmatic, we are not able to conclude that mean polarizabilities of the mixtures follow a non additive rule.

We find the mean polarizability of HBT is 39.97×10^{-24} cc. while the mean polarizability of OBT is 43.45×10^{-24} cc. These values should be compared to the values 39.79×10^{-24} cc. obtained by Sarna *et al.*,[1] and the values 40.02×10^{-24} cc. and 43.71×10^{-24} cc. obtained from the bond polarizability data.[13] Our values for the mean polarizabilities indicate that each methylene group contributes the amount 1.75×10^{-24} cc. to the mean polarizability of the molecule while the bond polarizability data gives a contribution of 1.84×10^{-24} cc.

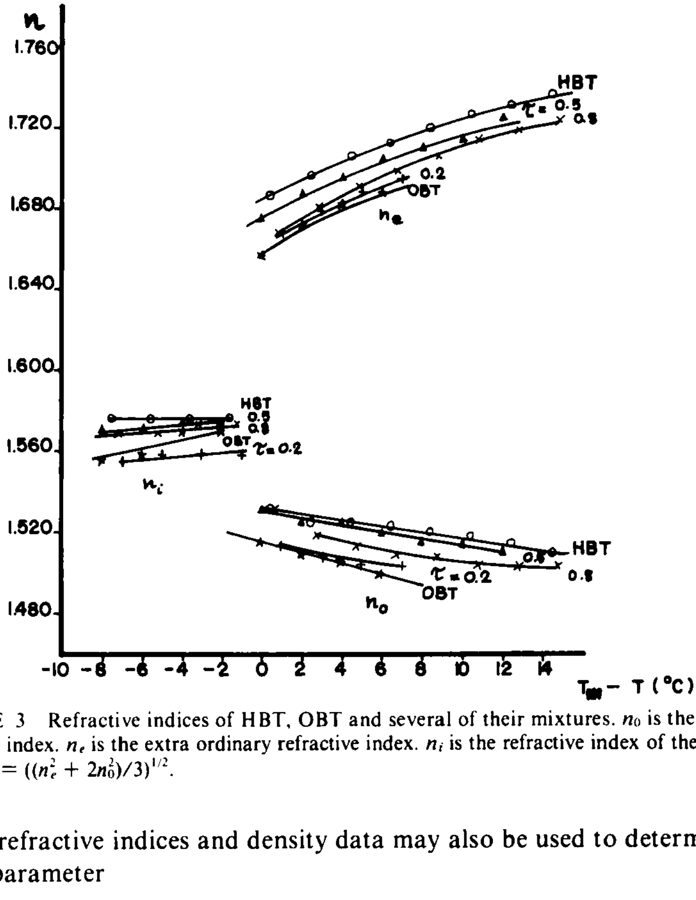


FIGURE 3 Refractive indices of HBT, OBT and several of their mixtures. n_0 is the ordinary refractive index. n_e is the extra ordinary refractive index. n_i is the refractive index of the isotropic phase. $\bar{n} = ((n_e^2 + 2n_0^2)/3)^{1/2}$.

The refractive indices and density data may also be used to determine the order parameter

$$S = \langle \tfrac{1}{2}(3\cos^2\theta - 1) \rangle \tag{3}$$

where θ is angle between the long axis of the molecule and the average direction of the molecular alignment, which is related to the polarizabilities through the relation[14]

$$S\Delta\alpha = (\alpha_e - \alpha_0) \tag{4}$$

where α_e and α_0 are the effective polarizabilities and $\Delta\alpha$ is the molecular polarizability anisotropy. In the Vuks model,[2] the difference between the effective polarizabilities (the RHS of Eq. (4) can be calculated from the relation

$$\alpha_e - \alpha_0 = \frac{3N_0M}{4\pi\rho}\left[\frac{n_e^2 - n_0^2}{\bar{n}^2 + 2}\right] \tag{5}$$

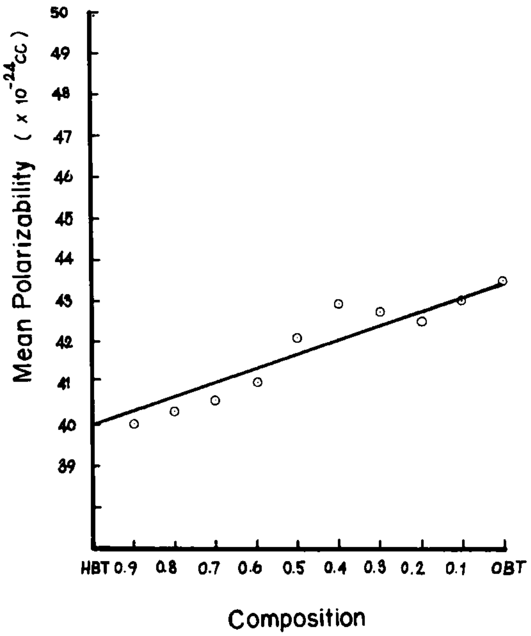


FIGURE 4 Compositional dependence of the mean polarizability.

In the Neugebauer model,[3] the differences can be obtained from the following equation derived by Horn,[15]

$$\alpha_e - \alpha_0 = \bar{\alpha}\,\frac{9}{4}\,B\left[\left(B^2 - \frac{10}{3}B + 1\right)^{1/2} + \frac{B}{3} - 1\right] \tag{6}$$

where

$$B = \frac{n_i^2 - 1}{n_i^2 + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\,\frac{n_0^2 + 2}{n_0^2 - 2}\right] \tag{7}$$

The results of these calculations are listed in Table II.

The order parameters of HBT, OBT and their mixtures can be calculated only if values of the polarizability anisotropies of HBT, OBT and their mixtures are known. Chandrasekhar and Madhusudana[7] obtained the values of the polarizability anisotropies for the PAA/PAP system from the solid state data of Chatelain and Germain.[6] In the absence of solid state data or other means of measuring the anisotropies, reasonable assumptions about the values of the anisotropies must be made. In their studies of the homologous series *p*-alkoxy-benzylidene butylaniline (which are closely related to the two nematogen HBT and OBT) Chang *et al.*,[16] assumed that the small variations in the chain lengths of the alkoxy $(Ch_3(CH_2)_{n-1}O)$ end groups in their liquid crystals do not cause an appreciable variations in the anisotropies of all the members of the homologous series and that the polarizability anisotropies of all the members of the series would have approximately the same value as the first member. Using this assumption, Chang *et al.*, were able to show the pres-

TABLE II

Differences between the effective polarizabilities calculated using Eqs. (7) and (9). $(\alpha_e - \alpha_0)_N$ are the differences when Neugebauer's model, Eq. (7), is used. $(\alpha_e - \alpha_0)_V$ are the differences in Vuks model.

Pure HBT

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
59	−0.04	16.10	19.16
61	−0.036	14.28	18.34
63	−0.03	13.01	17.75
65	−0.024	12.23	16.98
67	−0.018	11.13	16.22
69	−0.013	10.03	15.52
71	−0.008	10.37	14.69

$\tau = 0.9$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
59	−0.04	14.58	18.87
61	−0.036	14.79	18.10
63	−0.03	14.64	17.69
65	−0.024	14.46	17.24
67	−0.018	12.49	16.60
69	−0.013	10.74	15.49
71	−0.008	10.51	14.84

$\tau = 0.8$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
59	−0.043	18.32	19.57
61	−0.037	18.18	19.16
63	−0.031	18.04	18.75
65	−0.025	16.62	17.91
67	−0.02	16.65	17.28
69	−0.014	15.13	15.45
71	−0.008	13.69	14.24
73	−0.002	12.27	12.73

$\tau = 0.7$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
59	−0.042	15.29	18.98
61	−0.036	14.88	18.74
63	−0.03	14.97	18.13
65	−0.025	13.92	17.29
67	−0.019	13.01	16.80
69	−0.013	11.92	15.84
71	−0.007	11.46	14.75

TABLE II (*continued*)

$\tau = 0.6$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
61	−0.037	16.83	19.35
63	−0.031	14.91	18.25
65	−0.025	14.69	18.75
67	−0.02	14.51	17.43
69	−0.014	12.32	16.57
71	−0.008	12.98	15.44
73	−0.002	11.65	13.84

$\tau = 0.5$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
63	−0.034	17.10	19.26
65	−0.029	15.64	17.94
67	−0.023	15.45	17.52
69	−0.017	13.40	16.65
71	−0.011	11.65	15.29
73	−0.005	11.57	14.69

$\tau = 0.4$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
65	−0.029	14.04	19.06
67	−0.023	14.08	17.43
69	−0.018	13.86	17.00
71	−0.012	13.98	16.30
73	−0.006	13.00	14.30

$\tau = 0.3$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
67	−0.024	15.72	18.56
69	−0.019	15.95	16.67
71	−0.013	13.85	16.53
73	−0.007	10.25	15.40
75	−0.001	11.32	13.09

$\tau = 0.2$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
69	−0.02	13.41	17.74
71	−0.014	13.17	17.21
73	−0.008	11.16	15.85
75	−0.003	8.81	14.47

$\tau = 0.1$

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
69	−0.022	14.07	18.02
71	−0.016	14.11	17.30
73	−0.01	11.82	16.20
75	−0.004	12.13	15.30

TABLE II (*continued*)

Pure OBT

T(°C)	T_{reduced}	$(\alpha_e - \alpha_0)_N$	$(\alpha_e - \alpha_0)_V$
71	−0.017	17.02	17.76
73	−0.011	14.89	16.86
75	−0.006	13.05	15.39

ence of an even-odd effect in the homologous series *p*-alkoxybenzylidene butylanilines.

Haller *et al.*,[4] proposed that the extrapolation of the calculated $S\Delta\alpha$ values down to $T_{\text{red}} = -1$ (where T_{red} is the reduced temperature $(T\text{-}T_{\text{IN}})/T_{\text{IN}}$) and assuming that at $T = 0°$ K, S is equal to one, would give a value for $\Delta\alpha$. This procedure was used by Sarna *et al.*,[1] to obtain the polarizability anisotropies for HBT and OBT. The extrapolation using the $S\Delta\alpha$ calculated by the Vuks model yielded values which were different from those obtained by extrapolating the $S\Delta\alpha$ calculated by the Neugebauer model. Van Hecke *et al.*,[17] have pointed out that there can only be one molecular polarizability anisotropy per compound or mixture. Another difficulty with the extrapolation method is that when the method is applied to the refractive indice data of a whole homologous series, a set of scattered values for the anisotropies for the series is produced.[17,18] The lack of a general trend in the values of the polarizability anisotropies for the series has lead de Jeu and Classen[18] to discard a similar extrapolation method as a means of determining the magnetic susceptibility anisotropies for two homologous series.

Subramhanyam *et al.*,[13] proposed that the molecular polarizability anisotropies can be calculated from the bond polarizability data. This method produces an increasing polarizability anisotropy as additional methylene groups are added to the end chains. Van Hecke *et al.*,[17] finds that when this method is applied to their $S\Delta\alpha$ values calculated by the Vuks method, the order parameters of the homologous series trans-4-ethoxy-4′-*n*-alkanoyloxyazobenzenes exhibit the even-odd effect. Using this method on the data of Chang *et al.*,[16] we would find that the order parameters of the homologous series *p*-alkoxybenzylidene-butylanilines still exhibits the even-odd effect. We shall assume for the purpose of further analysis that the polarizability anisotropies of HBT and OBT have values close to those calculated from the bond polarizability data, i.e., 25.4×10^{-24} cc and 27.6×10^{-24} cc, respectively. We will assume that the polarizability anisotropies of the HBT/OBT mixtures behave in the same way as the polarizability anisotropies of the PAA/PAP mixtures (i.e., the anisotropies of the mixtures follow the additive rule).

The results of calculating the order parameters for HBT/OBT systems using the Vuks description of the local field are shown in Figure 5. Like Sarna *et al.*,[1] we find the order parameters for the two nematogens HBT and OBT (denoted by 0 and * in Figure 5, respectively) have nearly the same values in

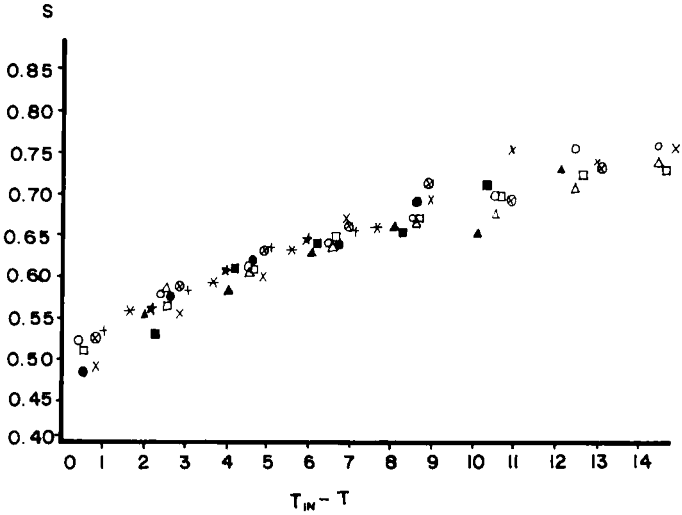


FIGURE 5 Order parameters calculated in the Vuks model. The order parameters were obtained by dividing $(\alpha_e - \alpha_0)_T$ (entries in Table II) by the polarizability anisotropies calculated according to the text.

○ HBT
△ $\tau = 0.9$
× $\tau = 0.8$
☐ $\tau = 0.7$
⊕ $\tau = 0.6$
▲ $\tau = 0.5$
■ $\tau = 0.4$
● $\tau = 0.3$
+ $\tau = 0.2$
✱ $\tau = 0.1$
★ OBT

their respective nematic phases although the values we obtained are different from those obtained by Sarna *et al.*,[1] The values which we obtained, between 0.45 and 0.50, are close to the values for HBT and OBT obtained by Bahadur[12] from his measurements of the specific volume changes at the nematic-isotropic transition temperatures of these two nematogen. Since the order parameters of HBT and OBT are nearly the same, the order parameters for the mixtures should also have the same values if the order parameters of the mixtures follow the additive rule, Eq. (1). As we see from Figure 5, the Vuks calculated order parameters lie more or less on the same curve.

Our calculations of the order parameters of HBT, OBT and their mixtures using the Neugebauer model appears to be contradictory in that the temperature dependence curves for the different mixtures intersect each other. This may be due to order parameters calculated in the Neugebauer model are very sensitive to errors in the density measurements. Madhusudana[19] has pointed out an one percent error in the density measurements gives rise to an eleven percent error in the order parameter when the Neugebauer approach is used but that the same density measurement error would result in only an one percent error in the order parameter when the Vuks approach is used. Because of the uncertainty of the temperatures at which the refractive indices were measured, the values for the densities used in the Neugebauer approach calculation may be in error. Thus the extreme sensitivity of the Neugebauer approach to errors in the densities, the Neugebauer calculated order parameters may be meaningless.

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