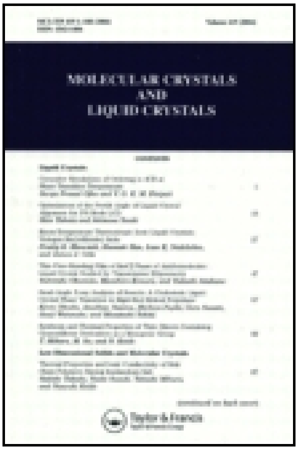

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Nematic Ordering in nOCB Series from Molecular Polarizabilities

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Nematic Ordering in nOCB Series from Molecular Polarizabilities

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The molecular polarizabilities (α_0, α_e) of the four members of the homologous series of cyano-alkyloxy-biphenyl ($C_nH_{2n+1}\cdot O\cdot\phi\cdot\phi\cdot CN$ for $n = 5$ to 8) in the nematic range have been calculated using two different internal field models. The additive rule of bond polarizabilities has been adopted to get the mean polarizability (α) and the principal molecular polarizability anisotropy ($\alpha_l - \alpha_t$) values for these compounds. The orientational order parameters have been calculated from these results. The ordering exhibits an odd-even alternation along the series. The results have been compared with different theories. Possible causes for deviation from the theories have been discussed. Besides the relative stabilities of the alkyloxy cyano biphenyls have also been discussed in terms of the molecular parameters.

Keywords: molecular polarizability, order parameter, odd-even effect

INTRODUCTION

The optical birefringence studies on liquid crystal materials are very important, because the anisotropy of the molecular polarizabilities plays a significant role in the intermolecular interaction. Measurements of refractive indices (n_0, n_e) of liquid crystals and densities can be analysed to get the informations about the polarizabilities as well as the degree of orientational order of the constituent molecules. The relationship between the refractive indices (n_0, n_e) and the molecular polarizabilities (α_0, α_e) is not straightforward. The intricate assumptions involved in defining the local electric field in an anisotropic medium like nematic is a subject of discussions. Different internal field models have been suggested so far for liquid crystals.[1–7] The present author used Vuks' isotropic[1] and Neugebauer's anisotropic[2] internal field models to calculate the molecular polarizabilities (α_0, α_e) from the refractive index and density data.

Different techniques based on different anisotropic properties of liquid crystals have been employed to determine the orientational order parameter $\langle P_2\rangle$ of several nematic liquid crystals. In most cases the reported order parameters do not follow the unique curve drawn from the mean field theory given by Maier and Saupe.[8]

This work has been reported in 14th Int. Liq. Cryst. Conf., Italy, 1992 (Abstract no. A-P12).

The experimental $\langle P_2 \rangle$ values deviates most from the mean field theory near nematic-isotropic transition temperature (T_c). Several possibilities have been proposed so far to explain such deviation. The present author reports here the nematic ordering in cyano-alkyloxy-biphenyns ($C_nH_{2n+1} \cdot O \cdot \phi \cdot \phi \cdot CN$, $n = 5$ to 8) from molecular polarizability calculations. The results show pronounced odd-even alternation along the series. Moreover, the stabilities of the alkyloxy cyano biphenyls have been discussed in terms of molecular interaction via anisotropic dispersion forces as well as rigid-body repulsions. The transition temperatures of the four compounds are given in Table I.

The data for refractive indices (n_0, n_e) of the four compounds have been taken from literature.[9] The refractive indices and the densities of 5OCB and 8OCB have already been reported[10,11] from our laboratory. Probably due to presence of trace impurities in the experimental 8OCB sample[11] they found a first order phase transition from smectic A to nematic, which was not found by others for pure 8OCB sample. There might be some errors in the values of refractive indices and densities for 8OCB as a pure sample. So the following procedure has been adopted here to get the density values of the four compounds.

The densities of 5OCB sample have been taken from literature.[10] The densities of the other three compounds at different temperatures have been evaluated with the help of the density data of nCB compounds reported by Dunmur and Miller.[12] The variation of density of nCB and nOCB with ($T_c - T$) is assumed to be similar. Figure 1 is given to justify this assumption for 5CB and 5OCB. The density of 5OCB at every ($T_c - T$) value is equal to the density of 5CB at the ($T_c - T$)

TABLE I

Transition temperatures of the four alkyloxy cyano biphenyls ($C_nH_{2n+1} - O \cdot \phi \cdot \phi \cdot CN$, $n = 5$ to 8)

Compounds	Transition temperatures* in °C		
	t_k	t_s	t_c
5OCB	48.0	—	68.0
6OCB	57.0	—	75.5
7OCB	54.0	—	74.0
8OCB	54.5	67.0	80.0

* t_k = solid ——> smectic A or nematic

t_s = smectic A ——> nematic

t_c = nematic ——> isotropic

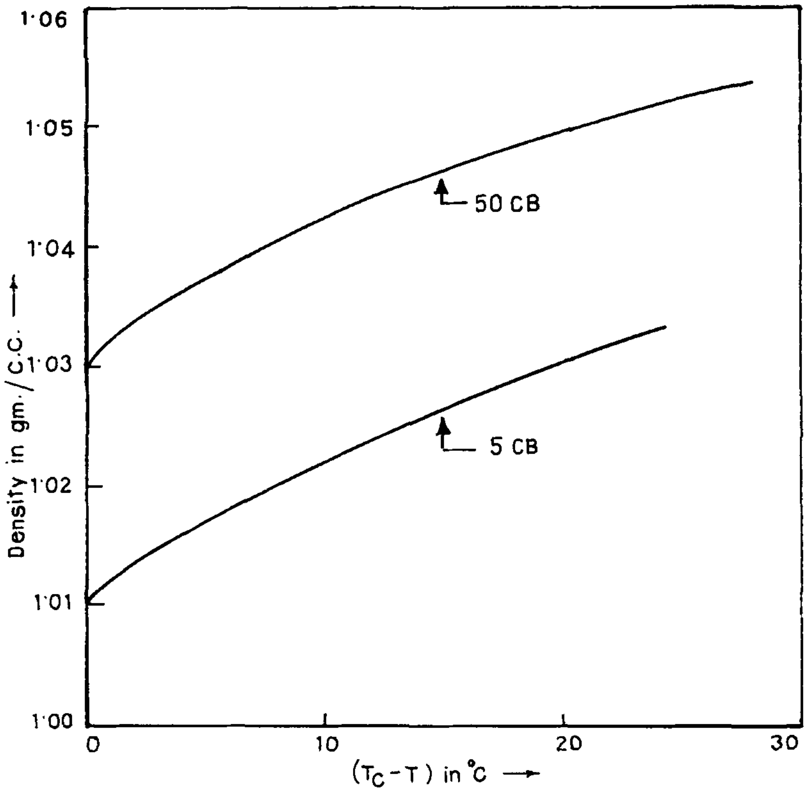

FIGURE 1 Variation of density of 5CB and 5OCB with $(T_c - T)$.

value plus 0.02 gm./c.c. So, for the other three compounds the relation used to calculate the densities at different temperatures is given below.

$$\rho_{\mathrm{nOCB}} = \rho_{\mathrm{nCB}} + 0.02$$

where ρ_{nOCB} and ρ_{nCB} stand for the densities of nOCB and nCB samples respectively corresponding to the same $(T_c - T)$ value.

THEORETICAL BACKGROUND

Polarizabilities

Chandrasekhar and Madhusudana[13] first applied Vuks' model to nematic liquid crystals. In this model, it is assumed that the internal field is isotropic even in an anisotropic medium. With this assumption the equations relating the molecular polarizabilities (α_0, α_e) and refractive indices (n_0, n_e) can be written as

$$\alpha_{e,0} = (3/4\pi)N(n_{e,0}^2 - 1)/(n^2 + 2) \qquad (1)$$

where N is the number density of molecules and $n[= \{(n_e^2 + 2n_0^2)/3\}^{1/2}]$ is the mean refractive index.

Following Neugebauer's model Saupe and Maier[14] supposed that the molecules in a nematic medium are distributed over a simple lattice. So they applied the anisotropy of internal field in a crystal as developed by Neugebauer to nematic liquid crystals. Neugebauer's relations for the liquid crystalline phase can be written as

$$(n_{e,0}^2 - 1) = 4\pi N\alpha_{e,0}(1 - N\alpha_{e,0}\gamma_{e,0})^{-1} \tag{2}$$

and

$$\gamma_e + 2\gamma_0 = 4\pi \tag{3}$$

$\gamma_{e,0}$ are the internal field constants corresponding to the refractive indices $n_{e,0}$. The relevant equations for calculating the polarizabilities (α_0, α_e) obtained from Equations (2) and (3) are

$$(1/\alpha_e + 2/\alpha_0) = (4\pi N/3)[n_e^2 + 2)/(n_e^2 - 1) + 2(n_0^2 + 2)/(n_0^2 - 1)] \tag{4a}$$

$$(\alpha_e + 2\alpha_0) = (9/4\pi N)[(n^2 - 1)/(n^2 + 2)] \tag{4b}$$

Order Parameter

The extra-ordinary and ordinary polarizabilities (α_0, α_e) corresponding to the electric vector parallel and perpendicular to the optic axis respectively in a uniaxial nematic liquid crystal are expressed by[15]

$$\alpha_e = \alpha + 2(\alpha_l - \alpha_t)\langle P_2\rangle/3 \tag{5a}$$

$$\alpha_0 = \alpha - (\alpha_l - \alpha_t)\langle P_2\rangle/3 \tag{5b}$$

where $\langle P_2\rangle$ is the orientational order parameter and α_l nad α_t are the molecular polarizabilities parallel and perpendicular to the molecular long axis. The average polarizability α is expressed by

$$\alpha = (\alpha_e + 2\alpha_0)/3 = (\alpha_l + 2\alpha_t)/3 \tag{6}$$

Combining Equations (5) and (6) we get

$$\langle P_2\rangle = (\alpha_e - \alpha_0)/(\alpha_l - \alpha_t) \tag{7}$$

RESULTS AND DISCUSSIONS

The molecular polarizabilities (α_0, α_e) calculated by using Vuks' isotropic and Neugebauer's anisotropic field models have been listed in Table II. Due to lack of refractive index data in the crystalline state the values of α_l and α_t were not calculated directly. In order to obtain $(\alpha_l - \alpha_t)$ the author has used the Haller's extrapolation procedure.[16] The additive rule of bond polarizabilities has been adopted to get the mean polarizability α and $(\alpha_l - \alpha_t)$ values for the four compounds. The bond polarizability values are available in the literatures.[17,18] When calculations are made assuming the molecules to be non-conjugated, it is found that there is a

TABLE II

Polarizabilities (α_0, α_e) and orientational order parameter $\langle P_2 \rangle$ of the four compounds for λ = 6328 Å

Temp. (°C)	Vuks' model			Neugebauer's model		
	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
			5OCB			
32.0	26.68	44.26	0.6833	29.68	42.26	0.6874
36.9	28.77	43.91	0.6640	29.74	41.97	0.6683
40.0	28.86	43.56	0.6447	29.80	41.68	0.6492
44.0	28.97	43.18	0.6232	29.87	41.37	0.6284
48.0	29.12	42.80	0.6000	29.99	41 07	0.6055
52.0	29.27	42.4.	0.5759	30.10	40.74	0.5814
54.0	29.38	42.16	0.5605	30.18	40.55	0.5661
56.0	29.50	41.89	0.5434	30.28	40.33	0.5492
58.0	29.67	41.60	0.5237	30.42	40.10	0.5295
60.0	29.85	41.24	0.4996	30.57	39.81	0.5055
62.0	30.09	40.78	0.4689	30.76	39.44	0.4743
64.0	30.35	40.24	0.4338	30.96	39.01	0.4393
66.0	30.80	39.38	0.3767	31.33	38.32	0.3820
66.5	30.97	39.08	0.3557	31.47	38.07	0.3606
67.0	31.16	38.71	0.3311	31.63	37.77	0.3355
67 5	31.42	38.12	0.2938	31.84	37.29	0.2978
67.8	31.69	37.47	0.2535	32.04	36.76	0.2574
67.9	31.82	37.16	0.2346	32.15	36.51	0.2383
			6OCB			
39.5	30.06	46.49	0.7067	31.10	44.41	0.7099
43.5	30.14	46.10	0.6865	31.15	44.09	0.6901
47.5	30.23	45.69	0.6649	31.20	43.75	0.6688
51.5	30.35	45.28	0.6422	31.28	43.41	0.6469
55.5	30.48	44.88	0.6194	31.38	43.08	0.6245
59.5	30.66	44.43	0.5923	31.52	42.72	0.5973
61.5	30.76	44.15	0.5763	31.59	42.49	0.5813

TABLE II (*Continued*)

Temp. (^{o}C)	Vuks model			Neugebauer's model		
	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
63.5	30.89	43.86	0.5578	31.69	42.25	0.5632
65.5	31.04	43.51	0.5368	31.81	41.97	0.5419
67.5	31.23	43.12	0.5114	31.96	41.65	0.5168
69.5	31.46	42.64	0.4804	32.15	41.26	0.4859
70.5	31.59	42.36	0.4632	32.25	41.04	0.4683
71.5	31.75	42.03	0.4422	32.38	40.77	0.4475
72.5	32.00	41.62	0.4138	32.59	40.44	0.4187
73.5	32.16	41.15	0.3862	32.71	40.05	0.3915
74.0	32.33	40.85	0.3665	32.85	39.81	0.3712
74.5	32.51	40.47	0.3419	33.00	39.50	0.3467
75.0	32.79	39.86	0.3041	33.22	39.00	0.3083
75.3	33.08	39.29	0.2671	33.46	38.53	0.2709
75.4	33.27	38.98	0.2455	33.61	38.29	0.2491
			7OCB			
38.0	32.10	48.18	0.6842	33.10	46.17	0.6879
42.0	32.17	47.82	0.6655	33.15	45.87	0.6695
46.0	32.26	47.46	0.6468	33.21	45.58	0.6511
50.0	32.36	47.10	0.6272	33.27	45.27	0.6321
54.0	32.48	46.73	0.6064	33.36	44.97	0.6110
58.0	32.63	46.30	0.5821	33.47	44.62	0.5868
60.0	32.71	46.06	0.5677	33.53	44.42	0.5731
62.0	32.83	45.78	0.5511	33.62	44.20	0.5563
64.0	32.98	45.48	0.5319	33.74	43.95	0.5374
66.0	33.18	45.12	0.5085	33.91	43.67	0.5137
68.0	33.68	44.73	0.4826	34.07	43.35	0.4879
70.0	33.66	44.18	0.4477	34.30	42.90	0.4526
71.0	33.87	43.82	0.4234	34.47	42.61	0.4284
72.0	34.15	43.27	0.3881	34.70	42.17	0.3926
72.5	34.37	42.86	0.3613	34.88	41.83	0.3698
73.0	34.62	42.38	0.3302	35.09	41.44	0.3342
73.5	34.97	41.59	0.2817	35.37	40.79	0.2853
73.8	35.32	40.86	0.2357	35.66	40.20	0.2389
73.9	35.52	40.46	0.2102	35.82	39.87	0.2137
			8OCB			
68.0	34.42	46.55	0.5060	35.15	45.09	0.5110
70.0	34.57	46.31	0.4902	35.27	44.90	0.4951

TABLE II (*Continued*)

Temp. (^{o}C)	Vuks model			Neugebauer's model		
	α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
72.0	34.74	46.04	0.4718	35.42	44.69	0.4766
74.0	34.96	45.70	0.4484	35.60	44.42	0.4535
76.0	35.26	45.24	0.4167	35.85	44.05	0.4211
77.0	35.45	44.97	0.3975	36.02	43.84	0.4021
78.0	35.68	44.61	0.3729	36.21	43.54	0.3774
78.5	35.86	44.32	0.3532	36.36	43.31	0.3573
79.0	36.09	43.97	0.3290	36.56	43.03	0.3332
79.5	36.40	43.45	0.2944	36.82	42.62	0.2977
79.8	36.70	42.90	0.2585	37.07	42.16	0.2617
79.9	36.91	42.49	0.2330	37.24	41.83	0.2360

α_o and α_e are in 10^{-24} cm^3 units.

sharp disagreement between the experimental and calculated values. This may be due to the enhancement of the bond polarizability values in the conjugated region. So the molecular polarizabilities have also been calculated using double bond polarizability values for the conjugated region ($-\phi\cdot\phi\cdot$CN).

To get the experimental ($\alpha_l - \alpha_t$) values for these compounds the following procedure was employed. For 5OCB, the ($\alpha_l - \alpha_t$) value was obtained from Haller's extrapolation procedure and this value corresponds well to the reported value.[10] As the alkyl chain increases the molecular polarizability anisotropy should increase slightly. The incremental part was obtained from the calculations made for additive rule of bond polarizabilities. For details the author refers to the earlier paper on nCB series.[19] Table III contains the values of experimental and calculated mean polarizability (α) and the principal molecular polarizability anisotropy ($\alpha_l - \alpha_t$) of the four compounds. From Table III it is clear that for this homologous series the double bond polarizability values for the conjugated region give much higher mean polarizability than the experimental one, but the calculated ($\alpha_l - \alpha_t$) values are quite close to the values obtained from Vuks' model. On the other hand, the assumption of a molecule to be non-conjugated gives lower α-values in comparison with the experimental results and this time the calculated ($\alpha_l - \alpha_t$) values are quite close to the Neugebauer's model.

The variation of order parameter $\langle P_2 \rangle$ with ($T_c - T$), T_c being the clearing temperature, for the four compounds has been displayed in Figure 2. The ordering exhibits a pronounced odd-even alternation along the series. To have a clear picture of the odd-even effect different molecular parameters, viz.; optical birefringence $\Delta n[= (n_e - n_0)]$, transitional order parameter $\langle P_2 \rangle_c$ and the internal field constant

TABLE III

Mean polarizability (α) and molecular polarizability anisotropy ($\alpha_l - \alpha_t$) of the compounds nOCB

Compounds	$\alpha \times 10^{24}$ cm^3			$(\alpha_l - \alpha_t) \times 10^{24}$ cm^3			
	Expt.	Calculated		Experimental		Calculated	
		Non-conjugated[*]	Conjugated[+]	Vuks's model	Neug. model	Non-conjugated[*]	Conjugated[+]
5OCB	33.60	32.31	36.68	22.80	18.30	20.60	22.60
6OCB	35.20	34.47	38.47	23.25	18.75	21.05	23.05
7OCB	37.20	36.26	40.26	23.50	19.00	21.30	23.30
8OCB	38.80	38.00	42.05	23.95	19.45	21.75	23.78

[*] Taking average of single and double bond polarizability values for the conjugated region.

[+] Taking double bond polarizability values for the conjugated region.

γ_e corresponding to the extra-ordinary ray at $(T_c - T) = 0.1$°C are listed in Table IV. The nematic-isotropic transition temperatures (T_c) of all the compounds are also included in Table IV. Figure 3 shows the odd-even alternation of ordering at $(T_c - T) = 0.1$°C along the number of carbon atoms (n) in the end chain. So the molecular flexibility plays also an important role in the stability of mesophases, via anisotropic interaction between the molecules. Dowell and Martire[20,21] have studied the effect of chain flexibility and chain length on the transition properties by assuming both attractive and repulsive forces taking part in the interactions. On the other hand, Marčelja[22] has presented a theory which accounts the anisotropic interaction between the rigid cores and the flexible chains. According to Marčelja's theory the orientational order parameter $\langle P_2 \rangle$ should depend significantly on the end chains and should also exhibit pronounced odd-even effect for a particular homologous series. The results of this paper may be interpreted within the framework of this model.

The variation of $\langle P_2 \rangle$ with temperature deviates from the Maier and Saupe (MS) mean field model. Near T_c the $\langle P_2 \rangle$ values for the four compounds lie between 0.21 to 0.25. But according to MS theory this value at T_c should be 0.43 for all nematogens. For nCB ($n = 5$ to 9) series[19] this type of deviation was found to be quite less than the nOCB series. So the temperature dependence of $\langle P_2 \rangle$ for these four compounds can not be explained by simple mean field theory. The author has also calculated the $\langle P_2 \rangle$ values at different temperatures using the modified mean field theory suggested by Humphries *et al.*[23] (HJL theory). The HJL theory too fails to explain the present results. Because the JHL curves are almost parallel to the MS curve, so the HJL theory can only fit the experimental $\langle P_2 \rangle$ values over a

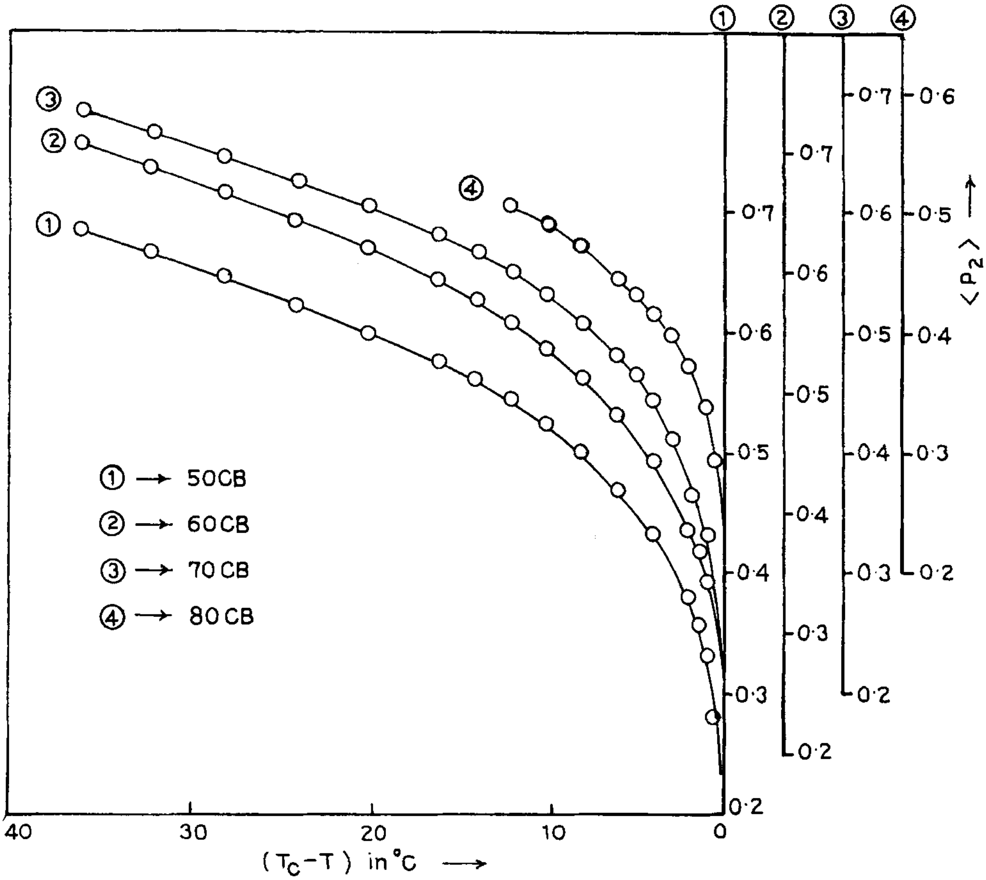

FIGURE 2 Plot of order parameter $\langle P_2 \rangle$ with $(T_c - T)$.

TABLE IV

Values of different molecular parameters at $T_c - T = 0.1°\text{C}$ and T_c of the four compounds to show odd-even effect

Compounds	$(\Delta n)_c$	$\langle P_2 \rangle_c$	γ_e	T_c
5OCB	0.0740	0.2346	3.996	68.0
6OCB	0.0745	0.2455	3.992	75.5
7OCB	0.0605	0.2102	4.030	74.0
8OCB	0.0647	0.2330	4.016	80.0

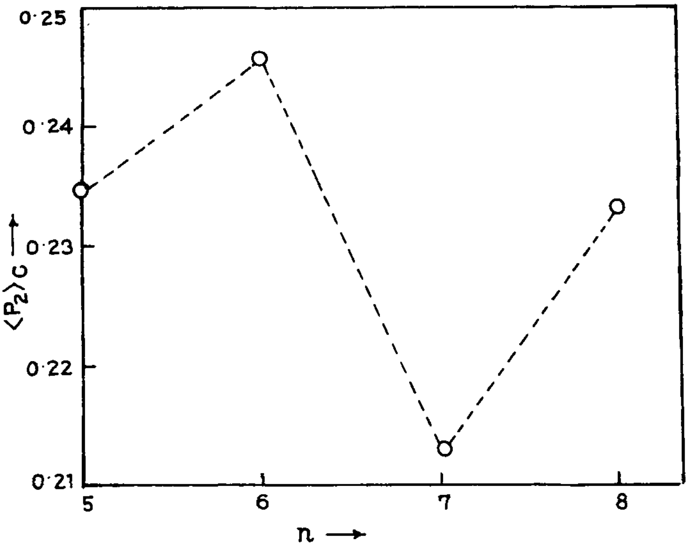

FIGURE 3 Variation of transitional order parameter $\langle P_2\rangle_c$ with the number of carbon atoms in the end chain.

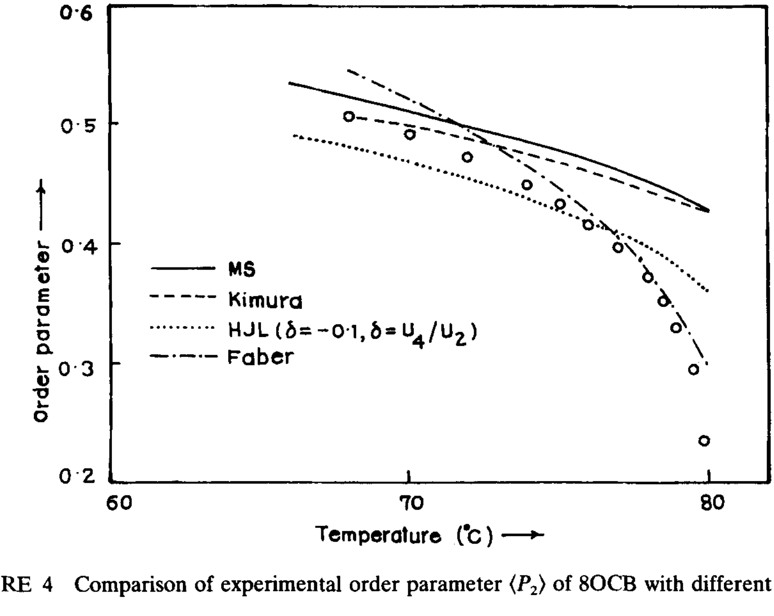

FIGURE 4 Comparison of experimental order parameter $\langle P_2\rangle$ of 8OCB with different theories.

limited temperature range. Figure 4 is given as a model picture to show these deviations for 8OCB.

The stability of the nematic phase in the alkyloxy cyano biphenyls can be understood by considering the intermolecular interactions. The molecular field theory given by Maier and Saupe for the existence of nematic phase is based on the anisotropic dispersive interaction between the rigid molecules. According to this theory the nematic-isotropic transition temperature T_c is given by,

$$T_c = A_{MS}/(4.54k_bV^2) \tag{8}$$

where k_b is Boltzmann's constant, A_{MS} is the substance constant which is related to the strength of the dispersive interactions and V is the molar volume at the clearing point. A linear relation between A_{MS} and $(\alpha_l - \alpha_t)^2$ can be established after some approximations. The relation is given by[24]

$$A_{MS} = (4\pi^2/135)(\alpha_l - \alpha_t)^2 I \tag{9}$$

Here I is the ionization potential. Figure 5 is plotted for A_{MS} vs. $(\alpha_l - \alpha_t)^2$ curve which is almost linear. So there is a good correlation between A_{MS} and the observed $(\alpha_l - \alpha_t)^2$ values. From Figure 5 it is clear that the value of I for these four compounds are more or less same i.e., I is mainly dependent on the aromatic π-electrons in the rigid part of the molecules.

The mean field model has been refined and extended by De Jeu *et al.*[25] and Kimura.[26] They assumed a hybrid model combining both attractive and repulsive interactions. The relevant equation or substance constant (A_K) given by Kimura is as follows:

$$A_K = k_bT_cV^2[4.54 - (5\pi/32)\Delta vn] \tag{10}$$

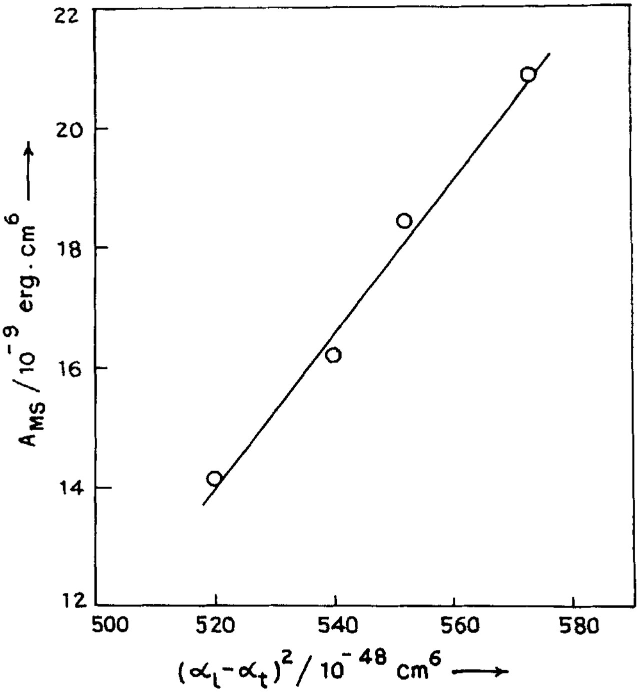

FIGURE 5 Variation of substance constant A_{MS} with $(\alpha_l - \alpha_t)^2$ for the four compounds.

where $\Delta v = 2DL^2[1 - (D/L)]^2$, D and L are the breadth and length of the molecules respectively, n is the number density.

In this case the value of D for all the samples is taken to be a 5 Å[27] and the molecular length of the molecules have been obtained by using stereo model unit. The results from Equation (1) suggest that the rigid body repulsive interaction makes a minor contribution to the stability of these four compounds since the length/breadth ratio is not so high.

The orientational order parameter $\langle P_2 \rangle$ values at different temperatures of the compounds have also been calculated following Kimura's model. According to this theory the expression for $\langle P_2 \rangle$ is given by

$$\langle P^2 \rangle = \frac{\int_0^{\pi/2} P_2(\cos\theta)\exp[\Gamma\langle P_2\rangle P_2(\cos\theta)]\, d(\cos\theta)}{\int_0^{\pi/2} \exp[\Gamma\langle P_2\rangle P_2(\cos\theta)]\, d(\cos\theta)} \tag{11}$$

where $\Gamma = A_K n^2/k_b T + (5\pi/32)\Delta v n$.

This theory also fails to explain the observed $\langle P_2 \rangle$ values for the four compounds. In Figure 4 the results for 8OCB is shown only.

The continuum theory of disorder in nematic formulated by Faber[28] has also been tested here. The values of elastic constants K_{ii}'s of 8OCB are available in the literatures.[29,30] But no such data are available for the other three compounds. The results of continuum theory for 8OCB have already been reported.[11] For comparison, this result is again plotted in Figure 4. From Figure 4 it is seen that Faber's continuum theory is closer to the experimental observations than the other mean field theories. Better agreement of Faber's theory with the experimental results has already been shown by Paul.[31]

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