Molecular Polarizabilities and Orientational Ordering of Two Mesogens

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The refractive indices (n_o, n_e) and densities of two mesogens have been measured in their liquid crystalline and liquid phases. The molecular polarizabilities (α_o, α_e) were evaluated by Vuks' and Neugebauer's relations. The polarizabilities thus obtained are compared with those estimated from the bond polarizabilities, and the orientational order parameters, $\langle P_2 \rangle$, are compared with the mean field theory of Maier and Saupe, the modified mean field theory of Humphries, James and Luckhurst, and the continuum theory suggested by T. E. Faber. We have also calculated the three order parameters ($\langle P_2 \rangle$, τ, σ) describing the smectic A phase following McMillan's model. Possible causes of the discrepancy are discussed.

Introduction

In order to test the validity of theories of nematic liquid crystals it is necessary to determine the temperature dependence of the orientational order parameter, $\langle P_2 \rangle$. We had already determined by X-ray diffraction the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of the two compounds studied in the present work [1, 2]. These compounds have different central rigid parts. We now have studied the optical birefringence of these two compounds in order to learn about the effect of rigidity on their liquid crystalline properties. To calculate the polarizabilities, we use Vuks's isotropic internal field model [6] and Neugebauer's anisotropic model [7].

We report the refractive indices (n_o, n_e), densities (ϱ), polarizabilities (α_o, α_e) and orientational order parameters ($\langle P_2 \rangle$) as functions of temperature. Our experimental $\langle P_2 \rangle$ values are compared with the mean field theory given by Maier and Saupe (MS) [8], the modified mean field theory by Humphries, James and Luckhurst (HJL) [9], and for one compound with the continuum theory suggested by Faber [10]. In the smectic A phase of the latter compound we have also compared our experimental $\langle P_2 \rangle$ values with McMillan's theory [11].

The names, structural formulae and transition temperatures of the two compounds are as follows:

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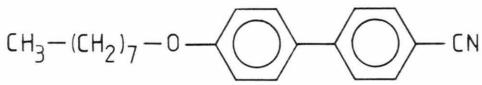
(i) 4′-Octyloxy-4-cyanobiphenyl (8OCB in short).



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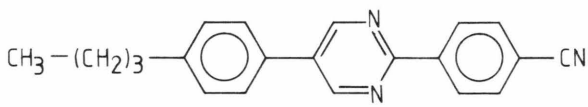
Transition temperatures [1]:

Solid $\underset{35\,^\circ C}{\overset{54.5\,^\circ C}{\rightleftharpoons}}$ Smectic A $\overset{67\,^\circ C}{\rightleftharpoons}$ Nematic $\overset{79.5\,^\circ C}{\rightleftharpoons}$ Isotropic.

(ii) 5-(4-n-Butylphenyl-2-(4-cyanophenyl)-pyrimidine (BPCPP in short).



Transition temperatures [2, 3]:

Solid I $\xrightarrow{73.5\,^\circ C}$ Nematic $\overset{244.7\,^\circ C}{\rightleftharpoons}$ Isotropic.

$\sim 64\,^\circ C \nwarrow$ $\swarrow 87\,^\circ C$

Solid II

The two compounds were donated by M/s. Hoffmann-La Roche and Co., Basel, Switzerland and used without further purification.

Experimental

The refractive indices (n_o, n_e) for ordinary and extra-ordinary rays were measured within ± 0.001 with the thin prism technique. A magnetic field of 0.6 Tesla was applied to the samples. The densities of the two

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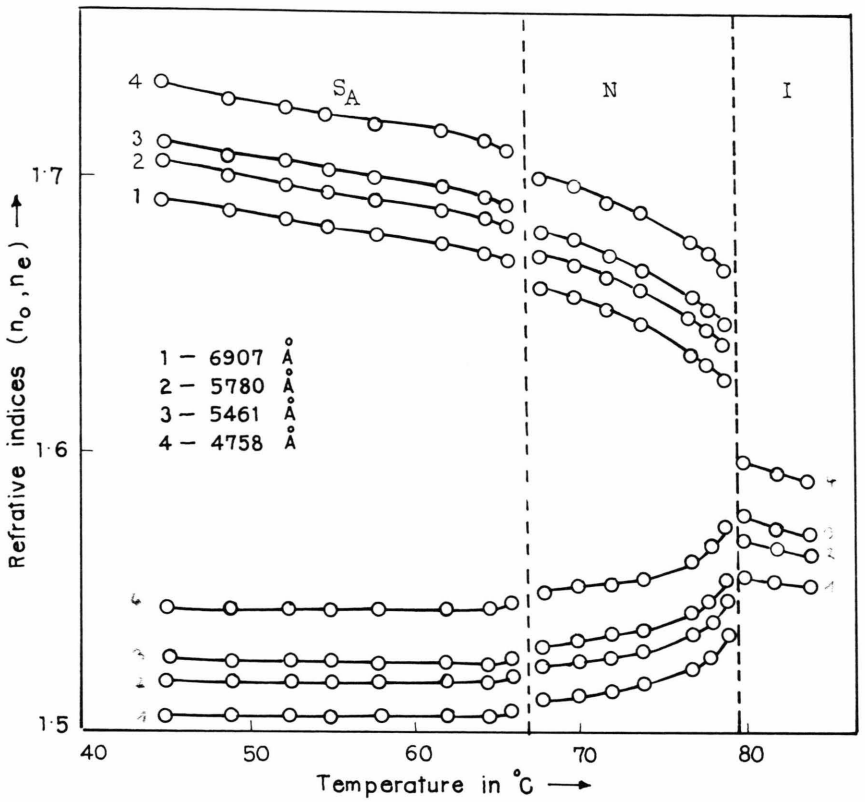

Fig. 1. Temperature dependence of refractive indices of 8OCB. S_A smectic A, N nematic, I isotropic. Upper curves n_e, lower curves n_o. The wavelengths of the light are given.

compounds at different temperatures were determined with an uncertainty of ± 0.1 percent. For details of the experimental procedure we refer to our previous papers [4, 5].

For BPCPP we failed to measure the refractive indices above 200 °C because we did not possess an adhesive to prepare a prism which sustains more than 200 °C. To get the values of n_0 and n_e above 200 °C we adopted the following procedure: We used our n_o data of 5OCB [12], because the structures of 5OCB and BPCPP are similar, i.e. the central part is rigid; one terminal group is CN and the other terminal group is flexible and of about the same length. Also, both compounds are nematic in a wide temperature range. We have assumed that the ordinary refractive index (n_o) is the same function of (T/T_C) for the two compounds. T_C being the clearing temperature. Thus we have estimated the values of n_0 for BPCPP above 200 °C. Then the mean refractive index (n) data for this compound have been extrapolated up to T_C. Using the relation, $n^2 = (n_e^2 + 2n_o^2)/3$, we have got the values of n_e above 200 °C.

Results and Discussions

The variation of refractive indices (n_o, n_e) of both 8OCB and BPCPP with temperature are shown in Figs. 1 and 2, respectively. Figure 1 shows the transition from smectic A to nematic phase in 8OCB. To have a clear picture of the phase transitions of 8OCB we have plotted the optical birefringence Δn $(= n_o - n_e)$ and density (ϱ) versus temperature in Figure 3. Our experimental values of n_o, n_e for 8OCB slightly differ from those reported by Karat and Madhusudana [13]. Figure 3 shows that in smectic A-nematic transition in 8OCB there is a change in volume, implying that the transition is of first order. However, though there are theoretical supports [11, 14] for this conclusion, this apparent first order transi-

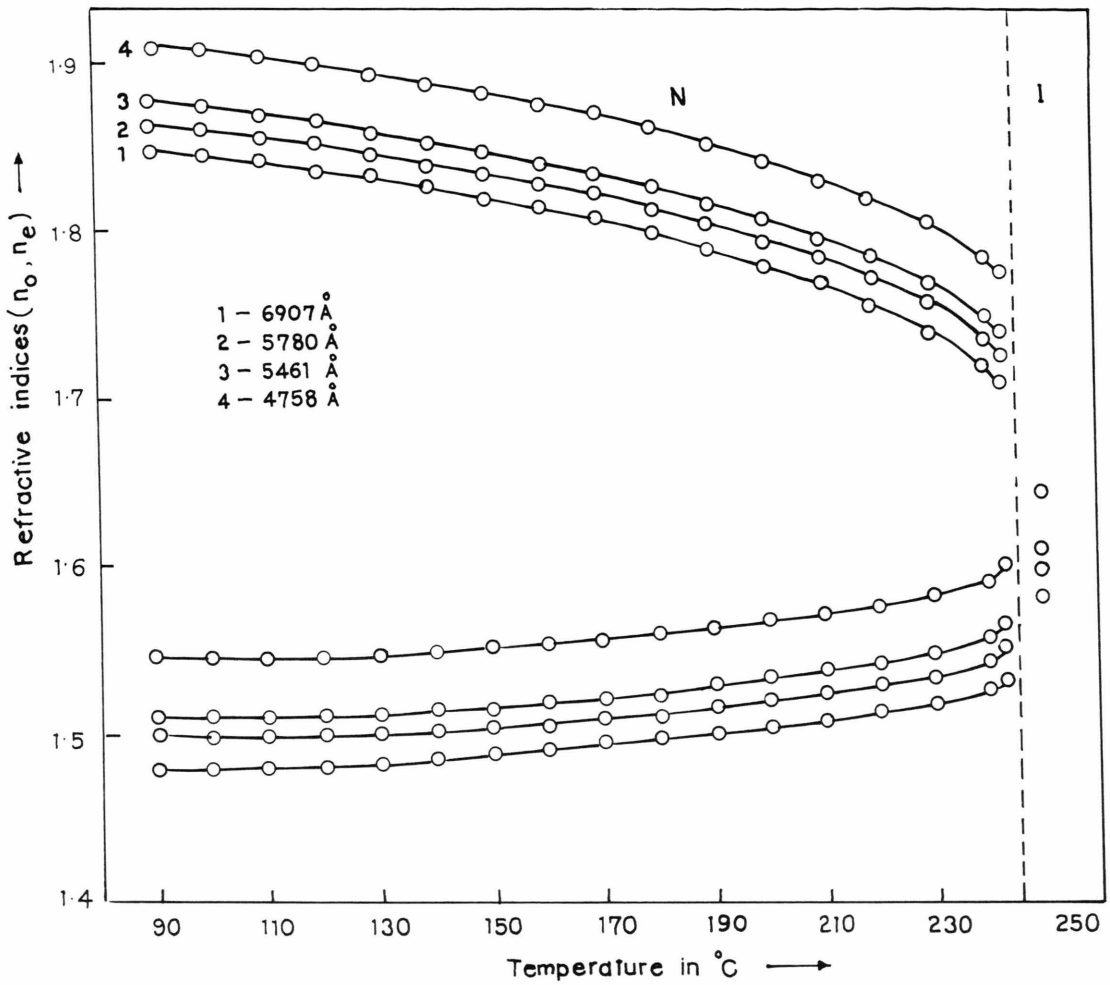

Fig. 2. Temperature dependence of refractive indices of BPCPP, N nematic, I isotropic.

tion is most probably due to the presence of trace impurities in the experimental samples [15].

Table 1 contains our density and polarizability data of both 8OCB and BPCPP for Vuks' as well as Neugebauer's approaches. Although we have calculated α_o and α_e for four different wavelengths, we have given their values corresponding to $\lambda = 5780$ Å only.

The orientational order parameter $\langle P_2 \rangle$ has been calculated using the relation [16], $\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$. $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities along and perpendicular to the long axis, respectively. Although Vuks' and Neugebauer's models give different absolute polarizability values, the variation of the orientational order parameter is in reasonable agreement with these two models. Extrapolated values of $(\alpha_{\parallel} - \alpha_{\perp})$ using Haller's [17] procedure are taken in all these calculations.

Estimation of polarizabilities of a molecule was carried out using the bond additive rule of tabulated bond polarizability data [18, 19]. When calculations are made using the principle of bond polarizabilities taking the molecules to be non-conjugated, it is found that for 8OCB the experimental molecular polarizability values are in good agreement with the calculated values. But for BPCPP the calculated values (taking pyrimidine C–N bond polarizabilities to be the mean of the single and the double CN bond) are too low as compared with the values from refractive index data. So we have calculated the electronic polarizabilities of the two molecules with this rule assuming

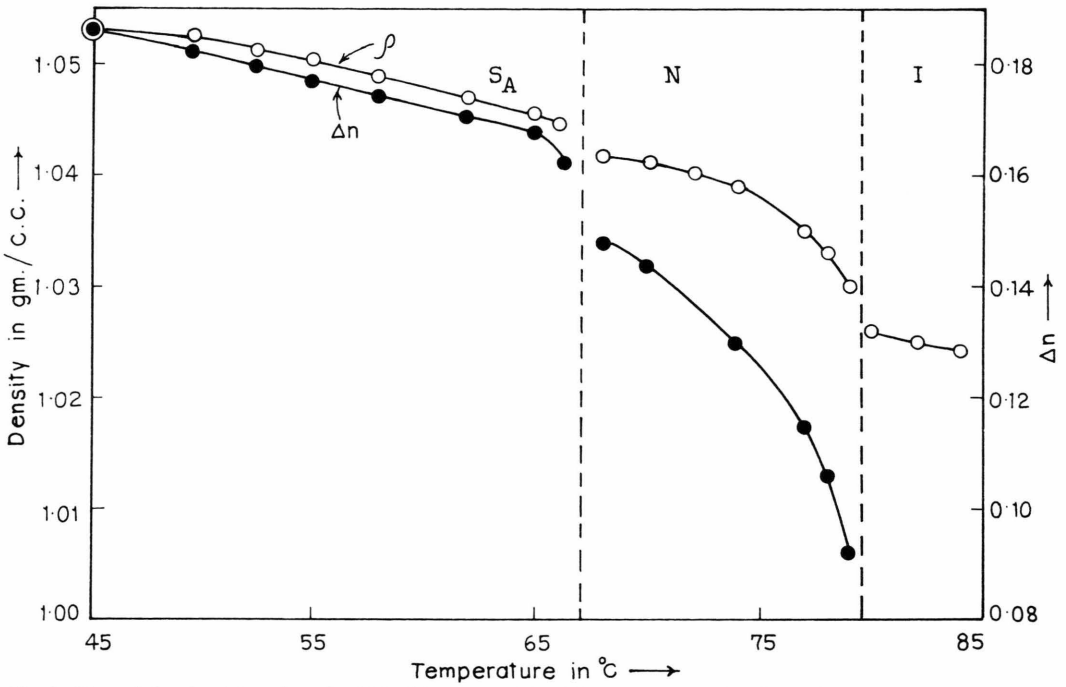

Fig. 3. Plot of density (ϱ) and optical birefringence (Δn) with temperature for 8OCB.

conjugated regions in the two compounds as $-OC_6H_4C_6H_4C(N)$ and $-C_6H_4C_4N_2H_2C_6H_4C(N)$, respectively. For the bonds in conjugated regions, we used the values of double bond polarizabilities. The enhancement of the bond polarizabilities due to the conjugated nature of the molecular structure has been described in detail by Subramhanyam et al. [19]. In the second case the calculated polarizabilities agree better with respect to our experimental values, but for 8OCB the calculated values are somewhat higher than the experimental values. Table 2 shows the experimental and calculated mean polarizabilities, α $[=(\alpha_e+2\alpha_o)/3]$ and $(\alpha_{\|}-\alpha_{\perp})$ for the two compounds. From this table it is clear that the introduction of one pyrimidine (BPCPP case) in the backbone of the biphenyl molecule (8OCB case) changes the mobility of π-electrons so that in case of BPCPP the bond polarizabilities of the conjugated region increase. By comparing the $(\alpha_{\|}-\alpha_{\perp})$ values of 8OCB and BPCPP we may say that BPCPP is more anisotropic than expected just because of the presence of one pyrimidine group in the rigid part of the molecules.

The variation of our experimental $\langle P_2\rangle$ values with temperature for 8OCP and BPCPP are shown in Figs. 4 and 5, respectively. We compared our experimental data with the simple mean field theory given by Maier and Saupe (MS) [8] and the modified mean field theory by Humphries et al. (HJL) [9]. Although it is known that the MS theory does not hold good for smectic A, we have shown it in Figure 4. The continuum theory of disorder in nematics formulated by Faber [10] has also been tested with our experimental $\langle P_2\rangle$ values. Values of the elastic constants of 8OCB are available [13]. These values were later recalculated by Madhusudana and Pratibha [20] and Lister et al. [21]. No such data are available for BPCPP. So we could not compare them with Faber's theory. The compound 8OCB possesses a smectic A phase in a wide temperature range. The $\langle P_2\rangle$ values of this compound in smectic A phase are higher than MS values showing the agreement with our previous $\langle P_2\rangle$ values obtained from X-ray diffraction [1]. Figure 4 also indicates that the smectic A-nematic phase change in 8OCB is of weakly first order since the $\langle P_2\rangle$ values at the smectic A-nematic transition is discontinuous. However, this apparent first order phase transition may be due to the presence of trace impurities in the liquid crystal as shown by Johnson et al. [22]. Using high resolution calorimetry, they found a small latent heat and a two phase region near the nematic-smectic

Table 1. ■ Density (ϱ), polarizability (α) orientational order parameter ($\langle P_2 \rangle$) of the two compounds for $\lambda = 5780$ Å.

Temp. (°C)	ϱ g/cm^3	Vuks' model			Neugebauer's model		
		α_0	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
8OCB							
45	1.0535	33.45	48.82	0.6658	34.42	46.88	0.6631
49	1.0525	33.51	48.56	0.6519	34.46	46.67	0.6497
52.5	1.0510	33.58	48.48	0.6420	34.51	46.61	0.6402
55	1.0502	33.64	48.30	0.6320	34.55	46.47	0.6302
58	1.0490	33.69	48.12	0.6251	34.60	46.32	0.6238
62	1.0470	33.79	47.91	0.6117	34.67	46.15	0.6106
65	1.0455	33.87	47.75	0.6056	34.73	46.03	0.6042
66	1.0445	34.05	47.53	0.5840	34.85	45.85	0.5831
68	1.0415	34.49	46.83	0.5346	35.26	45.29	0.5339
70	1.0410	34.65	46.65	0.5199	35.40	45.16	0.5196
72	1.0401	34.86	46.28	0.4913	35.57	44.86	0.4910
74	1.0391	35.06	45.90	0.4697	35.73	44.56	0.4693
77	1.0352	35.66	45.28	0.4165	36.26	44.08	0.4164
78	1.0331	36.03	44.90	0.3844	36.58	43.80	0.3841
79	1.0302	36.71	44.42	0.3342	37.46	43.46	0.3333
80 (Iso.)	1.0251	38.84		—	38.86		—
BPCPP							
90	0.8880	37.43	74.16	0.7782	39.87	69.28	0.7772
100	0.8851	37.56	74.32	0.7790	40.00	69.44	0.7777
110	0.8810	37.77	74.28	0.7735	40.19	69.44	0.7730
120	0.8772	38.07	74.12	0.7638	40.46	69.35	0.7635
130	0.8731	38.37	73.96	0.7540	40.73	69.25	0.7540
140	0.8680	38.82	73.67	0.7383	41.12	69.06	0.7384
150	0.8641	39.20	73.47	0.7261	41.47	68.94	0.7260
160	0.8590	39.72	73.23	0.7100	41.94	68.80	0.7098
170	0.8540	40.25	73.00	0.6936	42.42	68.66	0.6934
180	0.8492	40.81	72.56	0.6729	42.91	68.36	0.6726
190	0.8430	41.52	71.99	0.6456	43.54	67.96	0.6453
200	0.8371	42.24	71.41	0.6180	44.17	67.55	0.6179
210	0.8299	43.04	70.82	0.5886	44.87	67.14	0.5885
220	0.8220	44.00	70.17	0.5544	45.72	66.71	0.5547
230	0.8141	45.09	69.19	0.5106	46.68	66.01	0.5108
240	0.8012	46.65	67.99	0.4521	48.05	65.19	0.4530
242	0.7970	47.31	67.41	0.4258	48.63	64.77	0.4265
250 (Iso.)	0.7849	53.96		—	53.96		—

α_0 and α_e are in 10^{-24} cm^3 units.

Table 2. Comparison of experimental and calculated polarizability values.

Compounds	$\alpha \times 10^{24}$ cm^3		$(\alpha_{\parallel} - \alpha_{\perp}) \times 10^{24}$ cm^3		
	Calculated from bond pol. values	Experimental (Iso. liquid)	Calculated from bond pol. values	Experimental	
				Vuks' model	Neugebauer's model
8OCB	38.05[a] 44.05[b]	38.80	22.40[a] 23.48[b]	23.10	18.90
BPCPP	38.25[a] 47.32[b]	54.30	28.18[a] 37.01[b]	47.20	37.84

[a] Assuming average of single and double bond polarizabilities for the bonds of the conjugated region.
[b] Assuming double bond polarizabilities for the bonds of the conjugated region.

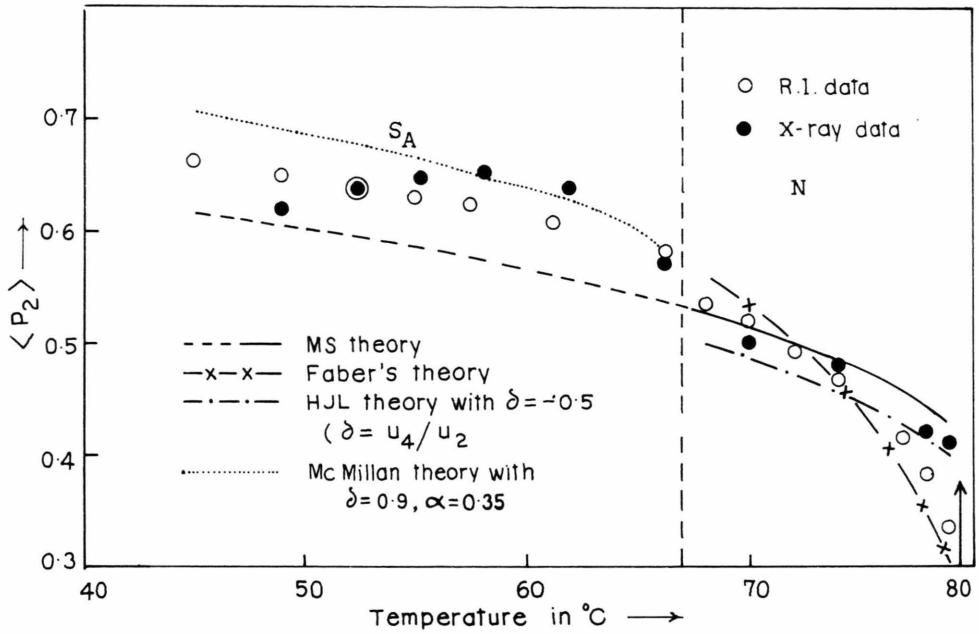

Fig. 4. Variation of order parameter, $\langle P_2 \rangle$ with temperature of 8OCB.

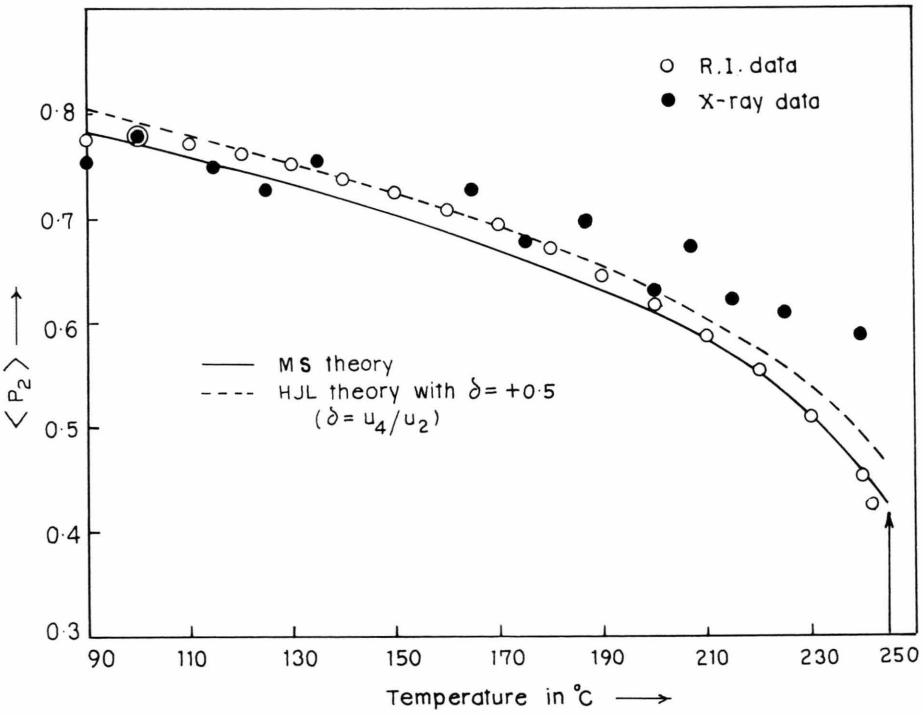

Fig. 5. Variation of order parameter, $\langle P_2 \rangle$ with temperature of BPCPP.

A transition in 8OCB containing trace impurities. Since we have used the commercially available 8OCB without further purification, some trace impurities may be present in our samples and this transition for very pure 8OCB may indeed be of second as observed by others [13]. Anisomov et al. [15, 23] have discussed in detail such impurity induced weakly first order transitions, specially for the smectic A-nematic phase change in 8OCB.

For 8OCB we have also calculated the orientational order parameter ($\langle P_2 \rangle$), translational order parameter (τ) and mixed order parameter (σ) following McMillan's model [11] for different δ and α values. For $\delta = 0.9$ and $\alpha = 0.35$ the model calculations agree with our experimental results quite well. The calculated $\langle P_2 \rangle$ values are shown in Figure 4. From this calculation we have found that for these particular values of δ and α the $S_A - N$ transition is of first order, which supports our experimental observation.

Due to some uncertainties in measuring twist elastic constants, as already mentioned [20], we can not judge conclusively the validity of Faber's theory for this case. Our previous experience on the other nematogens by X-ray diffraction studies suggests [24] that Faber's continuum theory is closer to the experimental observations than the simple mean field theory. The HJL theory does not provide better agreement for 8OCB but for BPCPP the modified mean field theory fits reasonably well with our experimental results with $\delta = +0.5$. In Fig. 5 we have also compared our present $\langle P_2 \rangle$ values with those obtained by us from X-ray diffraction technique [2].

A close observation of the values of $\langle P_2 \rangle$ for 8OCB and BPCPP in the Figs. 4 and 5 will reveal that the variation of $\langle P_2 \rangle$ with temperature fits better with the MS theory for BPCPP than in case of 8OCB in nematic phase. In our opinion, in BPCPP in addition to two phenyl rings one pyrimidine group is present in the rigid part and its terminal flexible alkyl chain part is shorter than in 8OCB. Since thermal fluctuations of the alkyl chain distort the potential of the mean field, hence 8OCB deviates more from this theory. In mean field theory, the molecules are assumed to be rigid. Thus in BPCPP this assumption is more realistic than in 8OCB. The $\langle P_2 \rangle$ values in the smectic A phase of 8OCB are also not very well reproduced by McMillan's theory (Figure 4). This is not surprising since both MS and McMillan's theory are essentially mean field theories which neglect fluctuations of the director. Moreover, molecular flexibilities are also not taken into account in any of these theories.

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