

Optical birefringence and order parameter of three nematogens

M MITRA, S PAUL and R PAUL

Department of Physics, North Bengal University, Siliguri 734 430, India

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Abstract. Results of the measurement of refractive indices and densities of three nematic liquid crystals at different temperatures are reported. The molecular polarizabilities have been calculated from refractive indices using both the Vuks' and the Neugebauer's relations. The orientational order parameters are determined from the polarizability values. The variation of order parameter with temperature for these compounds shows a reasonably good agreement with Maier and Saupe theory except near the clearing points where the experimental values are less than those obtained from the theory. The possible reasons for this have been discussed.

Keywords. Nematogens; optical birefringence; order parameters; density.

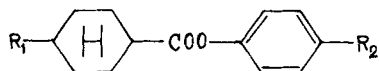
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1. Introduction

It is well-known that most nematic liquid crystals are optically uniaxial and strongly birefringent. Their refractive indices for ordinary and extraordinary rays (n_o , n_e) are very sensitive to temperature. All anisotropic properties such as refractive indices, magnetic and electric susceptibilities, elastic constants, etc are related to the order parameter in a more or less complicated way (De Gennes 1971; Chandrasekhar 1976; Saupe and Maier 1961; Saupe 1968; Stephen and Straley 1974). By studying the birefringence we can estimate the orientational ordering in the liquid crystals at different temperatures. Because of the anisotropy of the molecular arrangements in the liquid crystalline phase the well-known Lorentz-Lorentz formula is generally replaced by Vuks' formula (Vuks 1966), Neugebauer's relations (Neugebauer 1954) or Saupe and Maier anisotropic model (Saupe and Maier 1961). Successful applications of these three methods to liquid crystals have already been reported earlier (Chandrasekhar and Madhusudana 1969; Sarna *et al* 1979; Van Hecke *et al* 1978; O'shea and Kuster 1981; Poggi *et al* 1975; Chang 1975; Subramhanyam *et al* 1974; Sen *et al* 1983; Madhusudana *et al* 1971; Saupe and Maier 1961). Another approach has also been used for liquid crystalline materials (Derzhanski and Petrov 1971; De Jeu and Bordewijk 1978). In this paper we report the refractive indices (n_o , n_e), molecular polarizabilities (α_o , α_e), densities and orientational order parameters of three nematic liquid crystal samples. The orientational order parameter values thus calculated have been compared with the values obtained from the Maier and Saupe (MS) theory (Maier and Saupe 1959, 1960).

All the three samples were kindly donated by M/s. F Hoffmann-La-Roche and Co., Basel, Switzerland in pure form and therefore were not further purified. The names, structural formulae and transition temperatures (as mentioned in the catalogue) are given below:

- (I) *p*-methoxyphenyl trans-4-pentyl cyclohexane carboxylate (MPPCC).
 (II) *p*-propoxyphenyl trans-4-pentyl cyclohexane carboxylate (PPPCC).
 (III) *p*-cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC).



- I. $R_1 = C_5H_{11}$, $R_2 = OCH_3$
 II. $R_1 = C_5H_{11}$, $R_2 = OC_3H_7$
 III. $R_1 = C_5H_{11}$, $R_2 = CN$

2. Experimental

2.1 Texture study

The phase transitions of the pure samples were studied by observing the textures under crossed polarizers with a polarizing microscope equipped with a hot stage (Metler FP-80). The transition temperatures of the compounds as observed by us agree well with the literature values during heating but during cooling we got supercooled nematic phase in all the three compounds. From X-ray diffraction studies (Mitra *et al* 1987) and diamagnetic susceptibility anisotropy measurement (Mitra and Paul 1987) the presence of supercooled nematic phases was confirmed. The transition temperatures reported by Beens and de Jeu were slightly different from our findings (Beens and de Jeu 1985). The transition temperatures of the compounds as obtained by us are given below:

- I. Solid $\xrightleftharpoons[\sim 11.5^\circ C]{40.7^\circ C}$ Nematic $\xrightleftharpoons{71.1^\circ C}$ Isotropic
 II. Solid $\xrightleftharpoons[37^\circ C]{43.3^\circ C}$ Nematic $\xrightleftharpoons{71.1^\circ C}$ Isotropic
 III. Solid $\xrightleftharpoons[\sim 11^\circ C]{47^\circ C}$ Nematic $\xrightleftharpoons{78.7^\circ C}$ Isotropic

2.2 Optical studies

Refractive indices were measured using thin prisms with a refracting angle $< 2^\circ$. The prisms were made of optically flat glass plates, the inside surfaces of which were rubbed for aligning the liquid crystalline samples.

The liquid crystal samples were allowed to flow in the prism by melting a few crystals at the top. The samples were then cooled very slowly in the presence of magnetic field (6 kG) applied in the direction of rubbing. The combination of rubbing and flow together with the magnetic field produced a homogeneous nematic specimen with the optic axis parallel to the edge of the prism. The experimental details of this procedure were given by Zeminder *et al* (1980). The prisms were put inside a brass thermostat

heated electrically and controlled by a temperature controller to $\pm 0.5^\circ\text{C}$. A precision spectrometer and a nicol prism were used to measure the refractive indices (n_o, n_e) (within ± 0.001) for four different wavelengths corresponding to a mercury source. The densities were determined (within $\pm 0.1\%$) by putting weighed samples inside a glass capillary tube which was placed in a water bath heated using a temperature controller. Sufficient time was allowed for attaining the desired temperature. The length of the column was measured by a travelling microscope. The densities were calculated after correcting for the expansion of the glass capillary.

3. Results and discussions

The Vuks' formulae (Vuks 1966) relating the molecular polarizabilities (α_o, α_e) and refractive indices (n_o, n_e) are taken to be

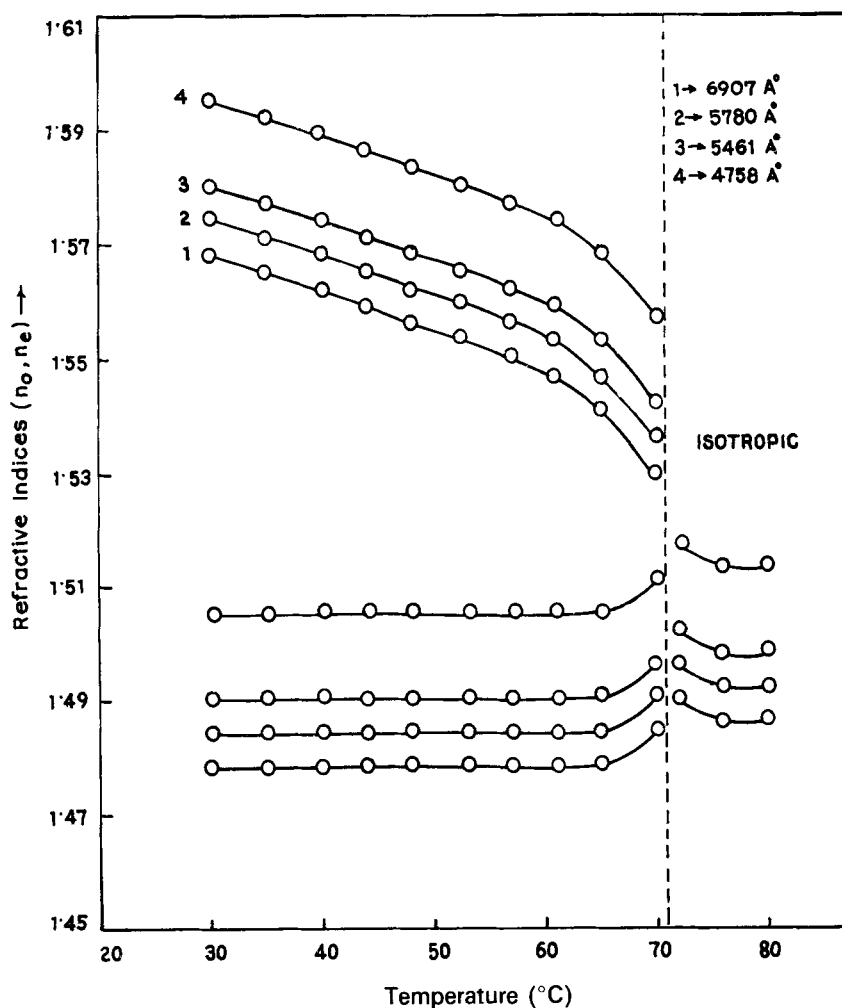


Figure 1. Variation of refractive indices with temperature of MPPCC.

$$(n_e^2 - 1)/(n^2 + 2) = 4\pi N\alpha_o/3 \tag{1a}$$

and

$$(n_e^2 - 1)/(n^2 + 2) = 4\pi N\alpha_e/3. \tag{1b}$$

We have also calculated the polarizability values (α_o, α_e) by using Neugebauer's method (Neugebauer 1954). The relevant equations for calculating the polarizabilities (α_o, α_e) are as follows

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

and

$$\alpha_e + 2\alpha_o = \frac{9}{4\pi N} \left[\frac{n^2 - 1}{n^2 + 2} \right]. \tag{2b}$$

Here $n^2 = (2n_o^2 + n_e^2)/3$. n is the mean refractive index and N is the number of molecules per c.c. Figures 1-3 show the temperature variation of refractive indices (n_o, n_e) of the three compounds respectively. In table 1 we have shown the polarizability values

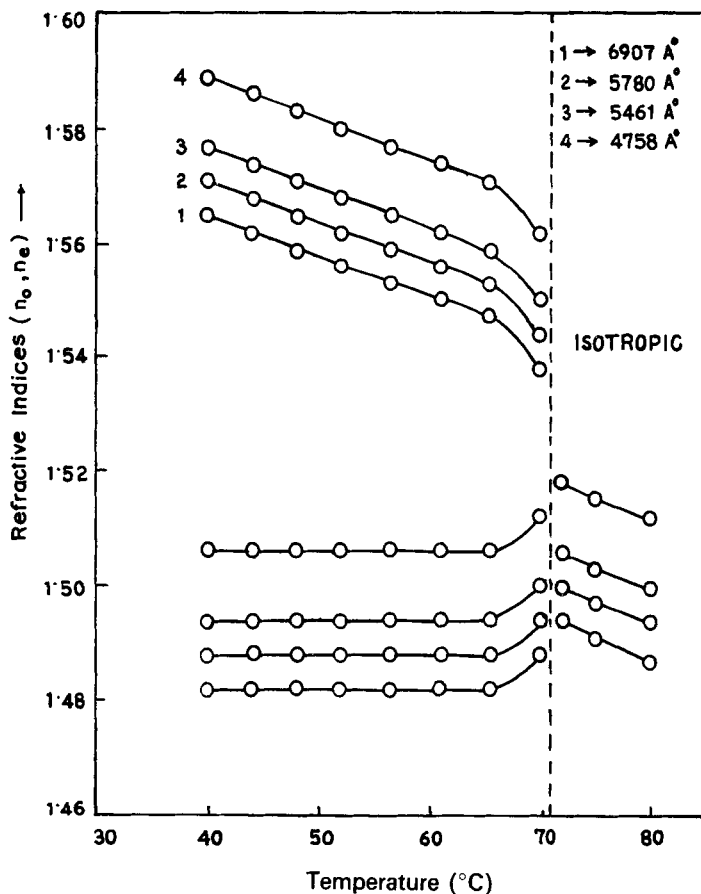


Figure 2. Variation of refractive indices with temperature of PPPCC.

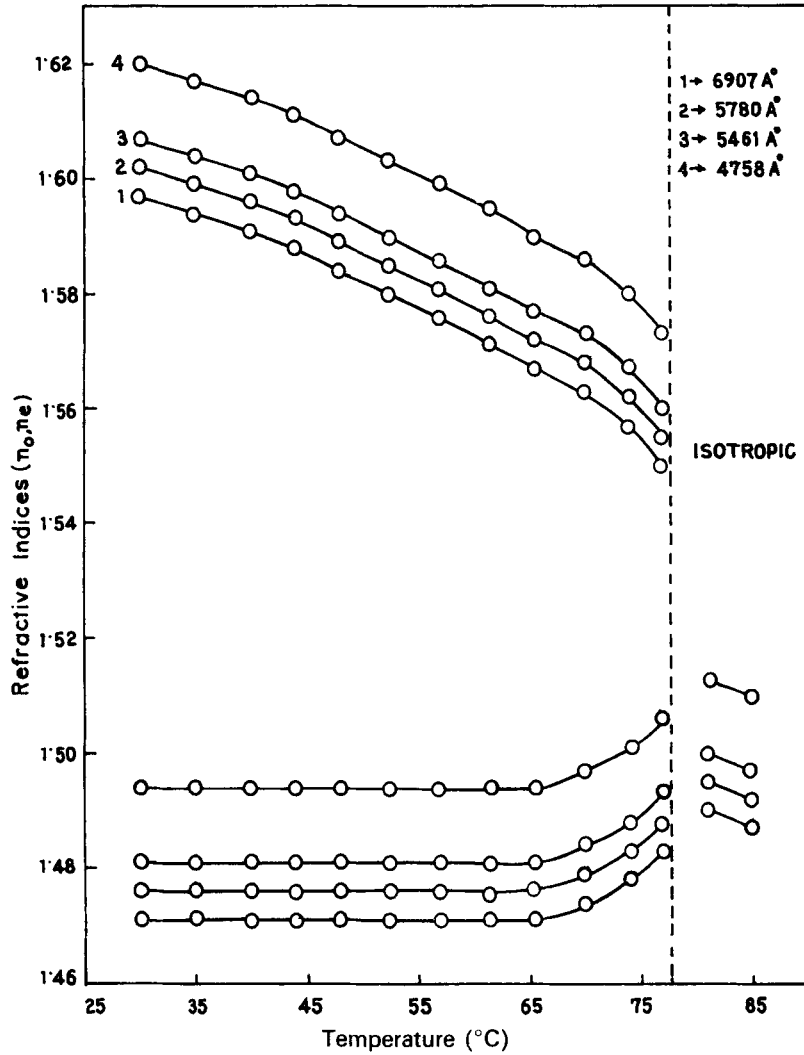


Figure 3. Variation of refractive indices with temperature of CPPCC.

calculated by these two methods. Density values in nematic and isotropic phases are also included in table 1.

The orientational order parameter $\langle P_2 \rangle$ is given by

$$\langle P_2 \rangle = 1/2(3 \langle \cos^2 \theta \rangle - 1)$$

where θ is the angle between the macroscopic optic axis and the major axis of the rod-like molecule. The relation between the order parameter $\langle P_2 \rangle$ and the principal polarizabilities is given by (De Gennes 1971)

$$\alpha_e = \alpha + \frac{2}{3}\alpha_a \langle P_2 \rangle \quad (3a)$$

$$\alpha_o = \alpha - \frac{1}{3}\alpha_a \langle P_2 \rangle \quad (3b)$$

Table 1. Density, polarizability (α) and order parameter $\langle P_2 \rangle$ for $\lambda = 5780 \text{ \AA}$.

Sample	Temp. (°C)	Density (gm/cm ³)	Vuks' method			Neugebauer's method		
			α_o	α_e	$\langle P_2 \rangle$	α_o	α_e	$\langle P_2 \rangle$
I	30	1.068	31.61	38.84	0.6603	30.21	35.89	0.6590
	40	1.060	31.89	38.69	0.6206	30.56	35.93	0.6230
	48	1.050	32.24	38.61	0.5815	30.99	36.04	0.5859
	57	1.040	32.60	38.53	0.5416	31.40	36.13	0.5488
	61	1.035	32.78	38.49	0.5215	31.62	36.18	0.5291
	65	1.025	33.15	38.41	0.4805	32.07	36.29	0.4896
	70	1.001	34.44	38.37	0.3586	33.61	36.80	0.3701
72(Iso)		0.998						
II	40	1.0361	35.89	43.40	0.6180	34.42	40.34	0.6182
	48	1.0337	36.03	43.00	0.5744	34.65	40.18	0.5774
	56.5	1.0285	36.26	42.72	0.5320	34.96	40.11	0.5367
	65.5	1.0195	36.63	42.60	0.4911	35.41	40.18	0.4982
	70	1.0092	37.53	42.16	0.3810	36.56	40.30	0.3898
72(Iso)		1.0023						
III	29	1.0725	30.25	40.20	0.6792	28.46	36.10	0.6750
	40	1.0650	30.51	40.05	0.6511	28.77	36.12	0.6494
	48	1.0569	30.79	39.84	0.6174	29.12	36.13	0.6193
	57	1.0496	31.07	39.53	0.5776	29.48	36.07	0.5822
	65.5	1.0420	31.36	39.15	0.5313	29.87	35.98	0.5398
	74	1.0280	32.32	38.81	0.4424	31.04	36.18	0.4541
	77	1.0102	33.28	38.87	0.3813	32.15	36.61	0.3940
80(Iso)		1.0025						

α_o and α_e are in 10^{-24} cm^3 .

where $\alpha = (2\alpha_o + \alpha_e)/3$ is the mean polarizability and $\alpha_a = (\alpha_{||} - \alpha_{\perp})$ is the molecular polarizability anisotropy. Therefore,

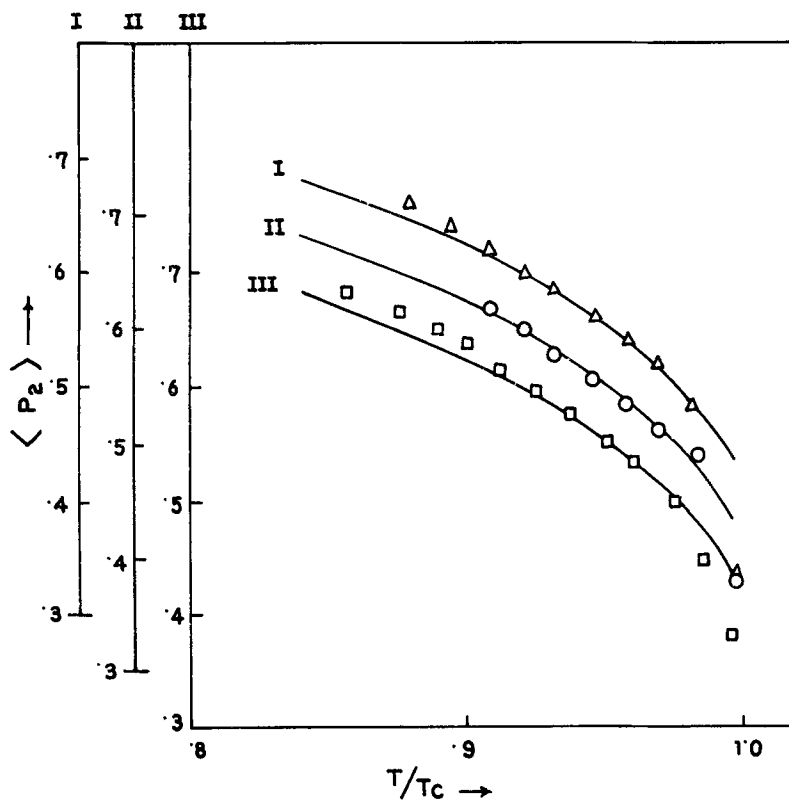
$$\langle P_2 \rangle = (\alpha_e - \alpha_o) / (\alpha_{||} - \alpha_{\perp}). \quad (4)$$

Due to the strong absorption in the solid phase, we could not measure α_a directly. Following Haller *et al* (1973) we plotted $\log(\alpha_e - \alpha_o)$ vs $\log(T_c - T)$ giving a straight line which is extrapolated to $\log T_c$. The limiting value of $(\alpha_e - \alpha_o)$ is assumed to correspond to $(\alpha_{||} - \alpha_{\perp})$. We have tested these extrapolated values of α_a for the three compounds by calculating α_a using the additive rule of the bond polarizability. We used the bond polarizability values from the literatures (Le Fevre and Le Fevre 1955; Le Fevre 1965). The mean polarizability values (α) have also been calculated from additive rule of the bond polarizability. Table 2 contains α_a and α values of these three compounds calculated by different methods.

Table 2 clearly indicates that the α_a values obtained from bond polarizability technique using the data obtained from Vuks formula are very close to the values obtained by bond polarizability calculations, whereas the α_a values calculated from Neugebauer's relations are significantly different. Although the Haller's plot is not fully

Table 2. α and $(\alpha_{\parallel} - \alpha_{\perp})$ of three compounds.

Compounds	$\alpha \times 10^{24} \text{ cm}^3$		$(\alpha_{\parallel} - \alpha_{\perp}) \times 10^{24} \text{ cm}^3$		
	Calculated from bond polarizability	Vuks' or Neugebauer's approach (isotropic liquid)	Calculated from bond polarizability	Haller's process (Vuks' data)	Haller's process (Neugebauer data)
I	33.50	35.65	12.65	11.05	8.65
II	37.08	38.91	12.75	12.15	9.62
III	33.98	34.74	15.75	14.75	11.50

**Figure 4.** Orientational order parameter with reduced temperature of the three samples. Continuous curves correspond to Maier-Saue theoretical values.

justifiable in all cases and the additive rule of the bond polarizability to estimate the molecular polarizability anisotropy (α_a) may be more realistic, but we have not used the bond polarizability values in any further calculations in this paper since the difference between these two sets of α_a values, one obtained from bond polarizability and the other from extrapolation procedure from Vuk's data, is marginal. In case of $\langle P_2 \rangle$

values calculated from Neugebauer's approach we have used the extrapolated values of α_a (table 1).

The order parameter values calculated using Vuks' formula and Neugebauer's relations agree well for all the three compounds in their respective nematic phases. This may be due to the fact that although α_e and α_o vary considerably in the two approaches, the variation of $(\alpha_e - \alpha_o)$ with temperature is more or less the same in the two cases (Sarna *et al* 1979; Subramanyam *et al* 1974). Figure 4 shows the variation of $\langle P_2 \rangle$ values with reduced temperature for the three compounds. The continuous curves are obtained from Maier and Saupe mean field theory (Maier and Saupe 1959, 1960).

From figure 4 it is seen that the experimental order parameter values agree well with Maier and Saupe theoretical values except near the nematic-isotropic transition temperature where the experimental $\langle P_2 \rangle$ values are significantly lower than the theoretical values. This trend has also been observed in $\langle P_2 \rangle$ values obtained from diamagnetic anisotropy measurements done by us for these compounds (Mitra and Paul 1987). Some other workers have also found such behaviour for other compounds near nematic-isotropic transition temperatures (Chang 1975; Sen *et al* 1983; Madhusudana *et al* 1971; Dunmur *et al* 1978). This may be due to the fluctuations of the director, which is more pronounced near the clearing point. Moreover, there may be lowering effect of the orientational order parameter with temperature due to the enhanced vibrations of the aliphatic chain part of the molecules. However, our X-ray diffraction measurements (Mitra *et al* 1987) on these compounds show good agreement of $\langle P_2 \rangle$ values with the Maier-Saupe theoretical values. This may be due to the fact that order parameter values obtained from X-ray data involve different types of approximations and averaging than those obtained from the refractive index and the magnetic susceptibility anisotropy measurements.

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