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S. Biswas^a; S. Haldar^a; P. K. Mandal^a; W. Haase^b

^a Physics Department, North Bengal University, Siliguri 734430, India ^b Institute of Physical Chemistry, Darmstadt University of Technology, Germany

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X-ray diffraction and optical birefringence studies on four nematogenic difluorobenzene derivatives

S. BISWAS†, S. HALDAR†, P.K. MANDAL*† and W. HAASE‡

†Physics Department, North Bengal University, Siliguri 734430, India

‡Institute of Physical Chemistry, Darmstadt University of Technology, D-64287, Germany

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The results of optical microscopy, DSC, X-ray diffraction and optical birefringence studies on four nematogenic difluorobenzene derivatives are presented. The thermal stability of the compounds increases substantially as greater flexibility is introduced into the core structure. Average intermolecular distances, obtained from X-ray data, are found to increase when a comparatively rigid planar phenyl ring is substituted by a flexible non-planar cyclohexyl ring in the core structure. From the values of apparent molecular lengths in the nematic phase, a short range antiferroelectric type of association is found to exist between neighbouring molecules. Density values suggest that the molecular packing is less efficient with increasing flexibility either in chain- or in core-structure. All the refractive indices exhibit normal dispersive behaviour, and a positive optical anisotropy is observed in all the compounds which decreases quickly with temperature. Temperature dependences of orientational order parameters, determined from both X-ray and optical birefringence studies, are presented. Variations of different physical properties with order parameters are discussed.

1. Introduction

Four difluorobenzene derivatives have been studied by optical microscopy, DSC, X-ray diffraction and optical birefringence techniques. These materials have a wide range nematic phase, high chemical stability, large dielectric anisotropy, low optical anisotropy and very good voltage-holding ratio. Mixtures of these compounds are found to exhibit mesomorphism at ambient temperatures and have high bulk resistivity and low current consumption. All these features are important for liquid crystal displays (LCDs) with large information content, as in portable colour TVs and computer terminals. These materials are, therefore, expected to be useful in active matrix displays (AMDs) such as in TFT (thin film transistor) and MIM (metal–insulator–metal) systems [1–4].

In order to investigate the relationship between molecular structures and temperature dependence of density, optical birefringence, order parameters and several other physical and molecular properties, the difluorobenzene compounds shown in section 3 have been investigated in detail. The crystal and molecular structures of compound **1** have also been determined from single crystal X-ray diffraction data and will be reported separately.

2. Experimental

Phase behaviours of the compounds were studied by polarizing optical microscopy (POM). X-ray diffraction (XRD) photographs of magnetically oriented samples were taken using a home-built high temperature camera [5]. The diffraction photographs were scanned by a HP2200C scanner in 24 bit RGB colour format. Optical densities of the pixels were calculated from the colour values and subsequently converted to X-ray intensities with the help of a calibration strip prepared by exposing the film for several known time intervals. Intensity distribution data were then used to determine average intermolecular distance (D), apparent molecular length (l) in the nematic phase, and orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with an accuracy of ± 0.02 , ± 0.1 and ± 0.02 , respectively; detailed procedures have been described previously [6–8].

Densities of the compounds were measured as a function of temperature using a dilatometer. Ordinary and extraordinary refractive indices were measured for three different wavelengths using the thin prism technique [9]. From the measured refractive indices and density values, the principal polarizabilities were calculated following the methods of Neugebauer [10] and Vuks [11] and used to find the orientational order parameter (S) given by $S = (\alpha_e - \alpha_o) / (\alpha_{||} - \alpha_{\perp})$. The value

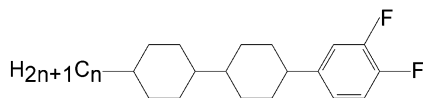
*Corresponding author. Email: mandal_pradip@yahoo.com

of $(\alpha_{\parallel} - \alpha_{\perp})$ was calculated by Haller's extrapolation method [12].

3. Results and discussion

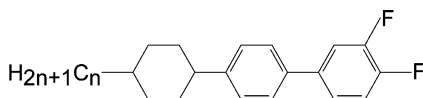
Transition temperatures (in °C), as obtained from POM are given below; supercooling temperatures are shown in parenthesis:

4-alkyl-4'-(3,4-difluorophenyl)bicyclohexane



1 3CCP-FF $n=3$ Cr 46.0 (38.5) N 123.8 I
2 5CCP-FF $n=5$ Cr 47.0 (26.8) N 125.2 I

3,4-difluoro-4'-(4-alkylcyclohexyl)biphenyl



3 3CPP-FF $n=3$ Cr 68.5 (46.4) N 97.9 I
4 5CPP-FF $n=5$ Cr 56.0 (38.7) N 105.8 I

All four compounds exhibit a nematic phase showing a considerable supercooling effect which was not reported in previous communications [1–4]. In some cases a small difference in transition temperature is observed between texture and DSC studies. Transition temperatures from X-ray and refractive index studies also vary slightly, indicating that sample geometry and thermal history have an effect on transition temperatures. Such a small variation has been reported before [13]. Changes in enthalpy (ΔH) and entropy (ΔS) values at transitions are shown in table I. The thermal stability of the nematic phase is 85.3, 98.4, 51.5 and 67.1 K in compounds 1–4, respectively as obtained from texture study. The stability is thus found to increase substantially as greater flexibility is introduced into the core structure.

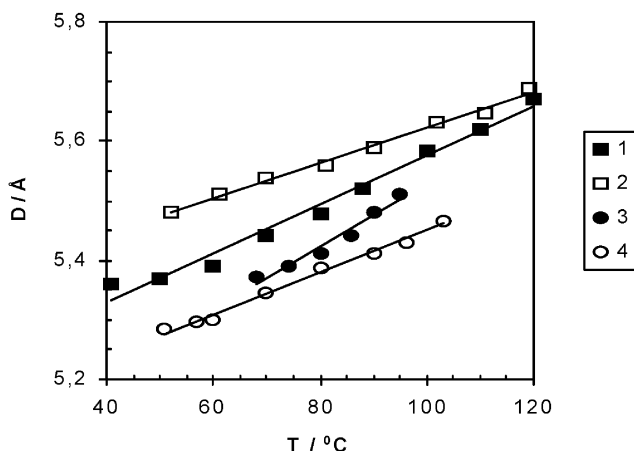


Figure 1. Variation of D with temperature for compounds 1–4. Lines are a guide to the eye only.

XRD photographs show that the mesophases are ordinary nematic in all cases. The average intermolecular distance D , calculated from the outer diffraction peaks, is found to increase from 5.36 to 5.67 Å with temperature in compound 1, from 5.48 to 5.69 Å in 2, from 5.37 to 5.51 Å in 3 and from 5.28 to 5.47 Å in 4. Thus D values are found to increase when a comparatively rigid planar phenyl ring is substituted by a flexible non-planar cyclohexyl ring in the core structure ($3 \Rightarrow 1$ or $4 \Rightarrow 2$). However, no such systematic variation with chain length is observed. Moreover, these D values are considerably higher than in two cyanobiphenyls [5CB and 7CB] (4.9–5.0 Å) [14] and in several alkylcyclohexyl isothiocyanatobenzenes [n CHBTs] (5.06–5.12 Å) [15]. Even three-ring benzoates such as 4-pentylphenyl 2chloro-4-(4-pentylbenzyloxy)benzoate and 4-octylphenyl 2chloro-4-(4-hexylbenzyloxy)benzoate having a lateral chloro spacer group in the central phenyl ring have lower D values (5.08–5.09 Å) [16]. In all cases, D values increase linearly with temperature as shown in figure 1, indicating a decrease in the molecular packing.

Table I. Table of significant data. Values in columns (6–13) are at 80 °C. Values in columns 8 and 9 are at 6907 Å.

Compounds	N range/°C	ΔH_{Cr-N} , ΔH_{N-I} /kJ mol ⁻¹	ΔS_{Cr-N} , ΔS_{N-I} /J mol ⁻¹ K ⁻¹	L_{calc} /Å	l /Å	D /Å	n_e	n_o	$\langle P_2 \rangle$ (RI)	$\langle P_2 \rangle$ (XRD)	ρ /g cm ⁻³	$\Delta\alpha \times 10^{24}$
1	85.3	12.85	40.35	17.64	22.61	5.48	1.578	1.512	0.70	0.73	1.00	4.93
		0.38	0.96									
2	98.4	16.76	52.39	19.38	23.28	5.55	1.581	1.484	0.72	0.77	0.98	8.01
		0.37	0.93									
3	51.5	14.05	41.34	17.25	21.90	5.41	1.598	1.465	0.63	0.62	1.05	9.08
		0.21	0.57									
4	67.1	12.19	37.20	19.29	23.04	5.39	1.619	1.483	0.71	0.67	1.01	10.57
		0.45	1.19									

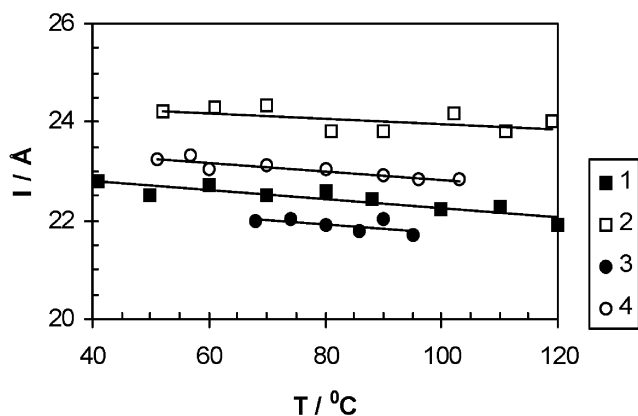


Figure 2. Variation of l with temperature for compounds 1–4. Lines are a guide to the eye only.

Some important physical parameters are given in table I.

Effective lengths of the molecules (l) in the LC phase are found to be considerably higher than the calculated lengths of the molecules (L). By optimizing the geometry of the molecules using the software Hyperchem V6.03 [17] L values were calculated for all, and are found to be in good agreement with the model lengths of the molecules in all-*trans* conformation. A plot of l as a function of temperature is shown in figure 2; l values are found to increase with the chain length in both systems ($1 \Rightarrow 2$ and $3 \Rightarrow 4$), and also when the phenyl group is replaced by the cyclohexyl group. The ratio l/L is found to vary between 1.18 and 1.29 in all the compounds suggesting the presence of short range antiferroelectric-type associations between neighboring molecules. Overlap of the dimerized molecules slightly decreases (l/L ratio increases) when a phenyl group is replaced by a cyclohexyl group as a consequence of increased steric hindrance. The formation of this type of dimer is also found in cyanobiphenyls, where the observed ratio is higher (~ 1.4) [14]. The effect of decreased overlapping has also been observed when an isothiocyanato group is replaced by a cyano group [15]. For example, in nCHBTs this ratio varies between 1.04 and 1.16. Thus the effect of the difluorophenyl terminal group on l/L is between that of $-\text{CN}$ and $-\text{NCS}$ groups. From the dielectric study, the molecular dipole moment (μ) of **1** is found to be 2.64 D, inclined at an angle of 29.8° with the molecular axis [18]. For this compound we find the value of μ to be 3.21 D, calculated using the semi-empirical PM3 force field in Hyperchem V6.03 [17]; previously reported values are 3.32 D [2] and 3.2 D [19]. The reported value in 8CB is 5.0 D [20] and in 6CHBT it is 3.5 D [21, 22] and the dipoles are axial. Thus it is seen that the polar molecules give rise to antiferroelectric-type associations between

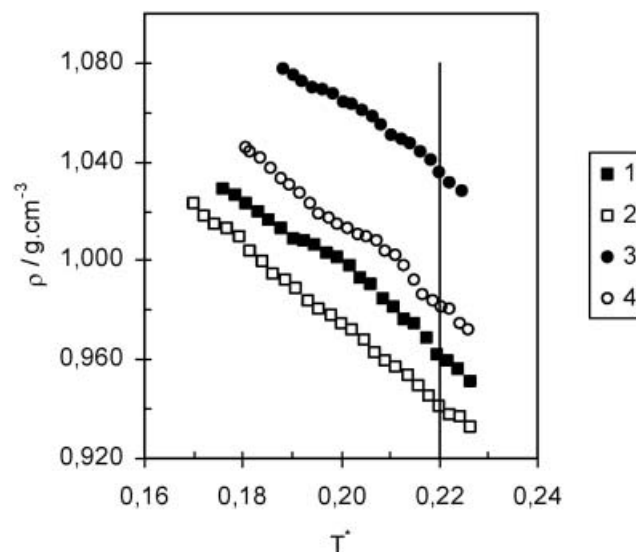


Figure 3. Variation of density with reduced temperature for compounds 1–4.

neighbouring molecules. No such association is observed in non-polar systems from either X-ray [23–25] or dielectric studies [26–28].

With increasing temperature, the apparent molecular lengths are found to decrease slightly. This may be due to the change of conformation or a change in the molecular overlap. Decrease in dimer concentration with T may also be responsible for this. The presence of both monomers and dimers has been observed in 5CB [4, 29, 30] and 6CHBT [21, 22] solutions in a non-polar solvent.

Variation of density with reduced temperature ($T^* = 0.22019T/T_{NI}$) for all the compounds is shown in figure 3. The density is found to decrease linearly with temperature. It is evident that as the chain length increases ($1 \Rightarrow 2$ or $3 \Rightarrow 4$) the density decreases although the effect is dominant in the second group of compounds. Also when more flexibility is introduced into the core structure of the molecules, replacing a phenyl ring by a cyclohexyl ring ($3 \Rightarrow 1$ or $4 \Rightarrow 2$), reduction in density is observed. Thus molecular packing is less efficient, as expected, with increasing flexibility either in chain or in core structure. If densities are fitted linearly with temperatures by the least squares method, one gets as fitted coefficients, $\rho_0 = 1.065, 1.045, 1.111, 1.078 \text{ g cm}^{-3}$; $\rho_1 = -8.0 \times 10^{-4}, -9.0 \times 10^{-4}, -7.0 \times 10^{-4}, -9.0 \times 10^{-4} \text{ g cm}^{-3} \text{ K}^{-1}$ in the compounds 1–4, respectively. Thus at $T^* = 0.19$ the estimated volume expansion coefficients are found to be $7.39 \times 10^{-4}, 9.17 \times 10^{-4}, 6.49 \times 10^{-4}$ and $8.75 \times 10^{-4} \text{ K}^{-1}$, respectively. Thus the coefficients are greater for greater chain length and for increased flexibility.

Temperature variations of the refractive indices (n_o , n_e and $\bar{n}=(2n_o+n_e)/3$), measured at wavelengths 5461, 5780 and 6907 Å, are shown in figure 4 for compound 1. Other compounds show similar variations. Extraordinary refractive indices are found to decrease quite fast with temperature, whereas for the average refractive indices the rate of decrease is intermediate. Ordinary refractive indices do not vary appreciably with T . In all cases a pretransition effect is observed very near to T_{NI} ; n_{iso} is found to be less than \bar{n} within the phase except in compound 1 where it is greater. All the refractive indices exhibit normal dispersive behaviour, i.e. the parameters decrease with increasing wavelength. This type of behaviour was reported earlier in many systems such as n CBs [31], Schiff's bases [24, 32, 33], benzoyloxybenzoates [34] and isothiocyanatobenzenes [15]. The average refractive index (\bar{n}) is found to be almost the same in 1 and 4 and greater than the values in 2 and 3, which also have close values (figure 5). The rate of decrease of \bar{n} with T is similar in all compounds.

A positive optical anisotropy (Δn) is observed in all the compounds; it decreases quite quickly with temperature as shown in figure 6. The rate of decrease rises moving from 1 to 3; in 4 the rate is slightly less. Δn values are found to increase as on moving from 1 \Rightarrow 4 except at low T where compounds 3 and 4 possess almost the same value. Maximum values of Δn are found to be 0.085, 0.128, 0.168 and 0.169, respectively, in compounds 1 to 4. When extrapolated to 20°C these become 0.091, 0.126, 0.173 and 0.172, respectively. Klasen *et al.* [19] theoretically estimated the Δn values as 0.097 in 1 and 0.176 in 3, which are in good agreement with our experimental values. Δn values for these compounds are considerably larger than those observed in alkenyl/alkenyloxy bicyclohexane compounds [35, 36], except in 1 where they are comparable. Low optical anisotropy is required for developing fast and high

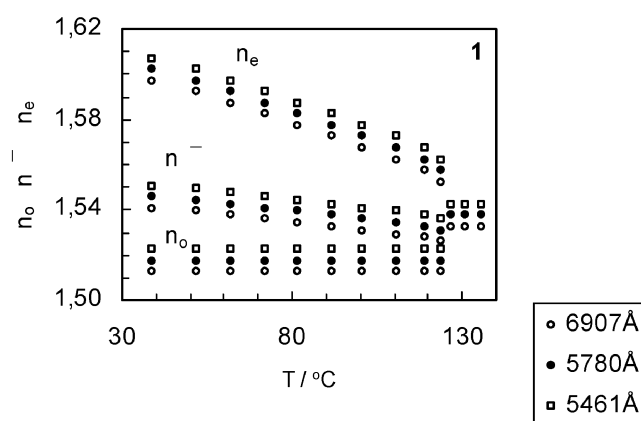


Figure 4. Temperature variation of n_e , n_o and \bar{n} of compound 1 for three wavelengths.

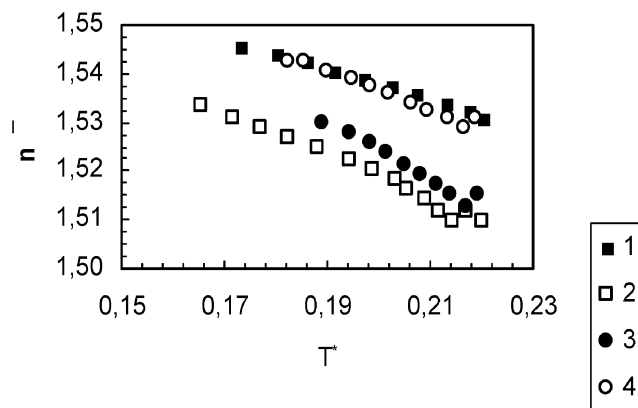


Figure 5. Variation of average refractive index (\bar{n}) of compounds 1–4 with reduced temperature for 5780 Å.

information content LCDs [37], compound 1 will therefore be an ideal candidate in this respect. As mentioned earlier, this compound also possesses maximum thermal stability (85.3°C). The introduction of another fluoride group in the 5-position of the terminal phenyl ring in 1–4 will result in the reduction of Δn to 0.073, 0.078, 0.137 and 0.134, as obtained by extrapolation of solution data [2]. Measurements on these compounds are in progress. However, mesophase thermal stability of trifluoro compounds is much less (29, 13.9, monotropic and 27.6 K, respectively) compared with the difluoro derivatives [2].

Using the measured refractive indices and density values it is possible to calculate the principal molecular polarizabilities (α_e , α_o), parallel and perpendicular to the

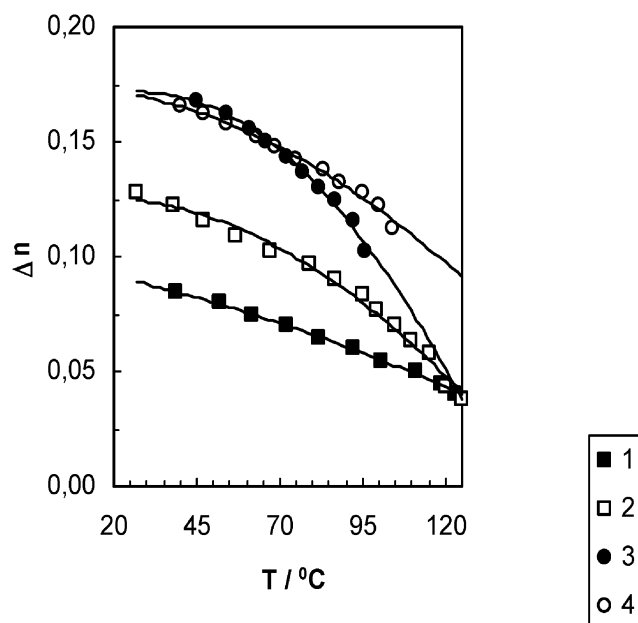


Figure 6. Temperature variation of Δn for compounds 1–4.

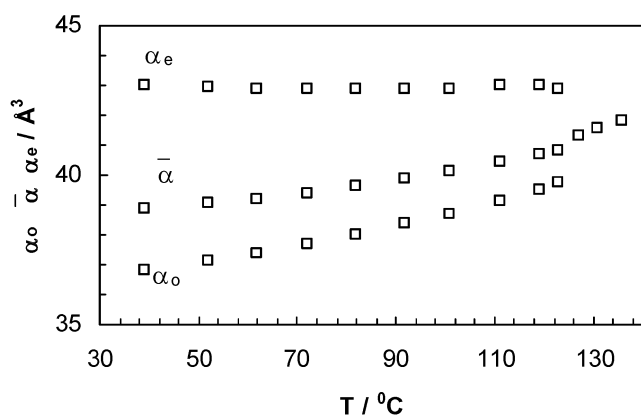


Figure 7. Variation of α_e , α_o and $\bar{\alpha}$ with temperature for **1**.

molecular long axis, following the methods of Vuks' [11] and Neugebauer's [10], which were developed, respectively, on the assumption of isotropic and anisotropic internal fields. The polarizabilities are calculated for all three wavelengths and since the values are found to be almost same, their average is finally considered for further discussions. Temperature variation of the polarizabilities calculated using Neugebauer's method is shown in figure 7 for compound **1** as a representative example. The rate of change of polarizabilities with T is similar in compounds **1**, **2** and is found to be more than in **3**, **4**; the latter compounds also, however, exhibit a similar temperature dependence. As the number of C atoms in the chain increases, $\bar{\alpha}$ increases from 38.90 to 40.79 Å³ in **1**, to 41.49 to 43.83 Å³ in **2**. With the introduction of the more rigid phenyl ring in the core, $\bar{\alpha}$ values decrease to 35.38–35.89 Å³ in **3**. These values vary between 40.83 and 42.16 Å³ in **4**, and less than values in the corresponding cyclohexyl compound **2**. No significant temperature variation in $\bar{\alpha}$ is observed in any case, as shown in figure 8.

It is observed that $\Delta\alpha$ increases systematically in

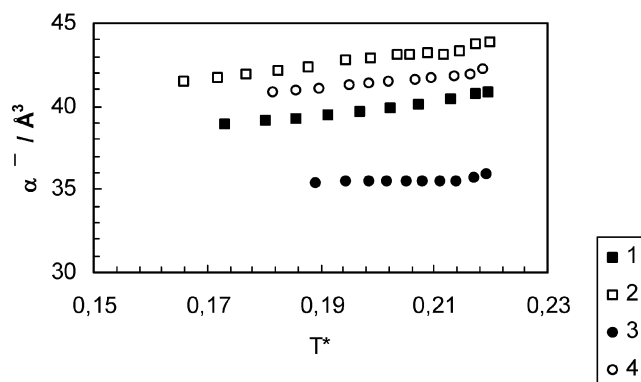


Figure 8. Variation of $\bar{\alpha}$ with reduced temperature for compounds **1–4**.

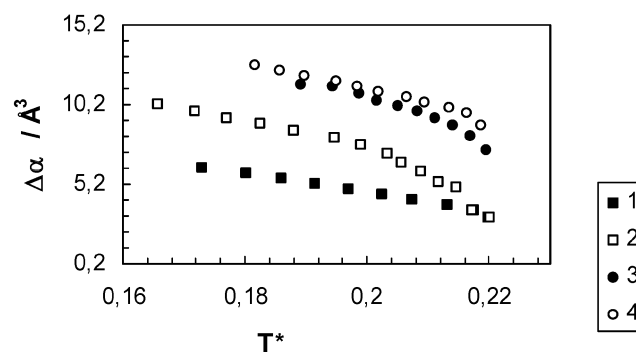


Figure 9. Variation of $\Delta\alpha$ with reduced T for compounds **1–4**.

compounds **1**⇒**4** although the increment from **3**⇒**4** is small (figure 9). Thus the contributions of increased chain length and enhanced core rigidity to $\Delta\alpha$ are additive. With temperature, $\Delta\alpha$ decreases quite quickly, unlike $\bar{\alpha}$ which increases with T . When $\Delta\alpha/\bar{\alpha}$ is plotted against reduced temperature (figure 10), its behaviour is found to be similar to that of $\Delta\alpha$, but **4** shows a slightly lower value than **3**.

In the nematic phase molecules have no positional correlation but they do have long range orientational ordering. The extent of ordering is usually qualified by orientational order parameters (OOPs); it is uniaxial and is expressed by a traceless symmetric tensor of rank two. Many physical properties, such as optical birefringence, dielectric anisotropy, threshold voltage for switching, etc., which are important device parameters, depend upon the OOPs. Although by determining the orientational distribution functions from the azimuthal intensity distribution of the XRD photographs one can, in principle, determine different order OOPs, we have determined the second and fourth order OOPs- $\langle P_2 \rangle$ and $\langle P_4 \rangle$. Variation of these OOPs with temperature is shown in figure 11. OOPs calculated following Maier–Saupe (MS) mean field theory [38] are also shown in this figure for comparison. In compounds **1** and **2**, both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are found to be quite high and

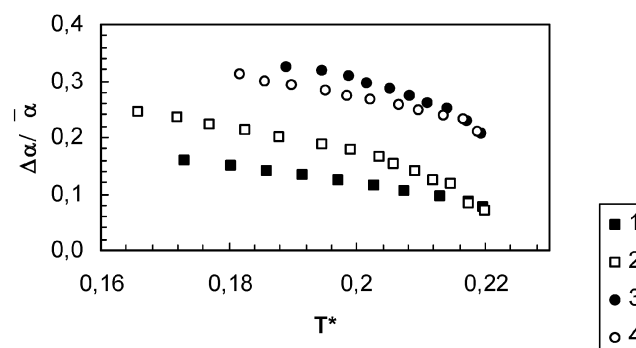


Figure 10. Variation of $\Delta\alpha/\bar{\alpha}$ with reduced T for compounds **1–4**.

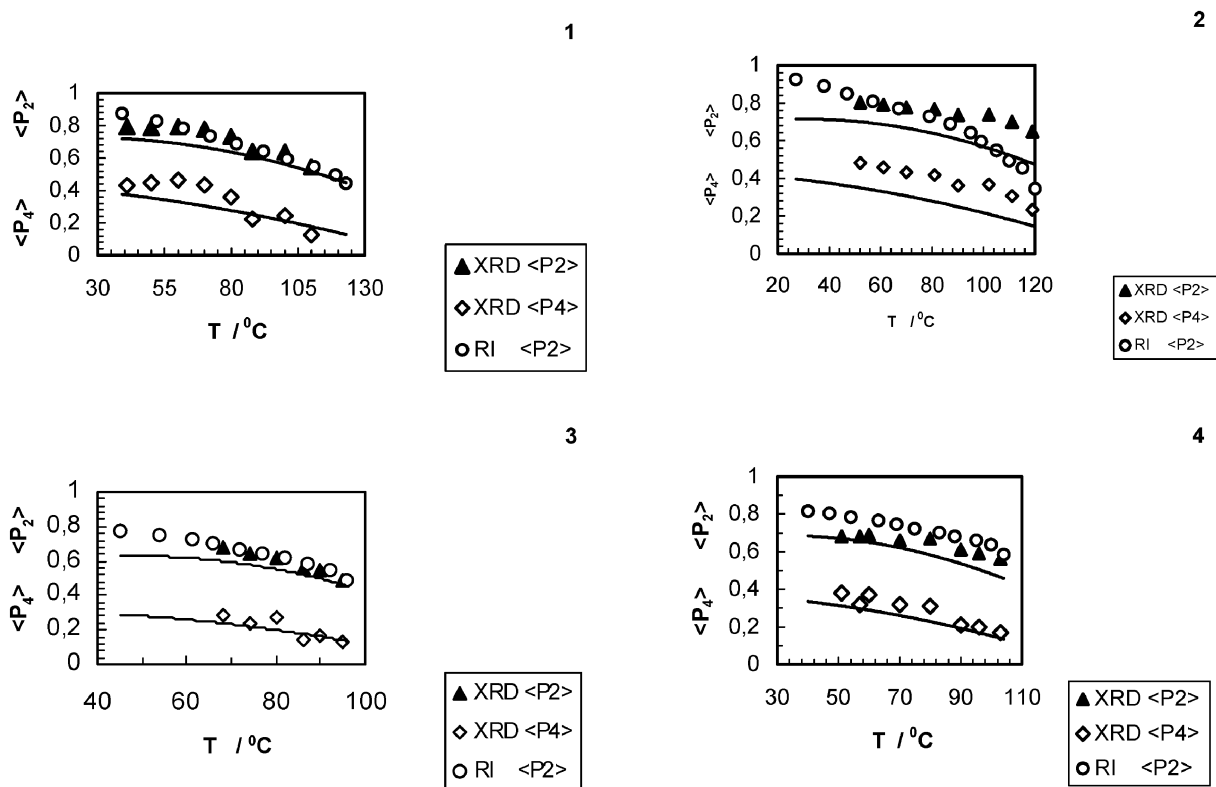


Figure 11. Temperature variation of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ of compounds **1–4** for 5780 Å. Continuous line corresponds to Maier-Saupe theoretical value.

considerably larger than that predicted by MS mean field theory. In **3** and **4** the values are large but nearer to the MS values. Magnuson *et al.* [39] measured the orientational order parameters of the difluorophenyl ring in **1** (not of the entire molecule) by C_{13} NMR and found that the S_{ZZ} order parameter is about 0.68 at around 50°C, compared with our $\langle P_2 \rangle$ value of 0.83 for the entire molecule. The orientational behaviour of the nematic molecules may be divided into two parts, a long range and a short range order. The MS model reflects only long range ordering in the liquid crystalline phase, a short range ordering also exists due to interaction with neighbouring molecules. This short range ordering persists even in the isotropic phase and may be the reason for higher $\langle P_2 \rangle$ values than predicted from MS theory [7, 40].

Orientalional order parameters $\langle P_2 \rangle$ have also been determined from the polarizability values using the relation $\langle P_2 \rangle = (\alpha_e - \alpha_o) / (\alpha_{||} - \alpha_{\perp})$, where the denominator is the polarizability anisotropy of the medium in the perfectly ordered state. Following Haller *et al.* [12], the value of this parameter was determined by extrapolating the least squares fitted $\log(\alpha_e - \alpha_o)$ vs. $\log(T_C - T)$ straight line to $\log(T_C)$. These order parameters are also shown in figure 11 for comparison. $\langle P_2 \rangle$ values

are found to be larger than the mean field values in all the systems. In **1** and **3** the $\langle P_2 \rangle$ values obtained from both techniques agree fairly well, although in the other two compounds the agreement is not good. A difference in $\langle P_2 \rangle$ values obtained from the two different techniques has also been reported previously [41–43]. This may be due to different averaging procedures involved in the two methods. Moreover there may be error in the estimation of $\langle P_2 \rangle$ using polarizability values of the crystalline state obtained by Haller's extrapolation method.

In Figure 12, the order parameter $\langle P_2 \rangle$, obtained from refractive index data, is plotted as a function of reduced temperature for all the compounds, to see the effect of molecular structure on $\langle P_2 \rangle$. In the low T region it is almost same for all. In the high T region, $\langle P_2 \rangle$ increases with increasing rigidity (**1** \Rightarrow **3**) and (**2** \Rightarrow **4**); with chain length it increases in systems **3**, **4** but decreases in **1, 2**.

H. Ishikawa *et al.* [44] observed that the splay elastic constant (k_{11}) of **1** is proportional to the square of the order parameter (S) as expected from the theoretical consideration proposed by Kimura *et al.* [45]. The dielectric anisotropy ($\Delta\epsilon$) parameter was also found to be proportional to the square of the order parameter,

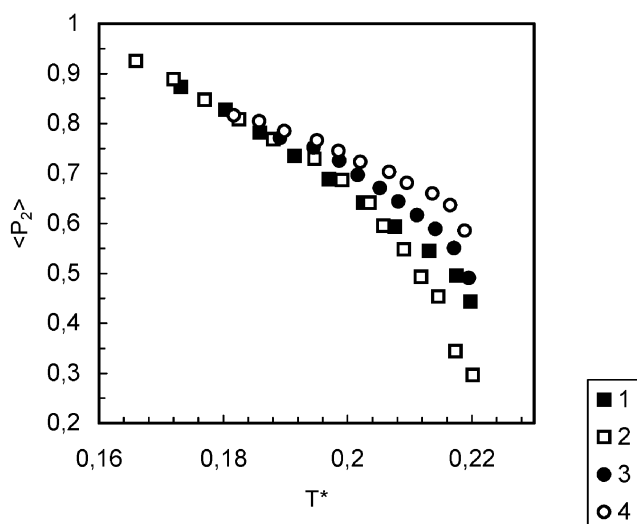


Figure 12. Variation of order parameter $\langle P_2 \rangle$, obtained from refractive indices, with reduced temperature for compounds 1-4.

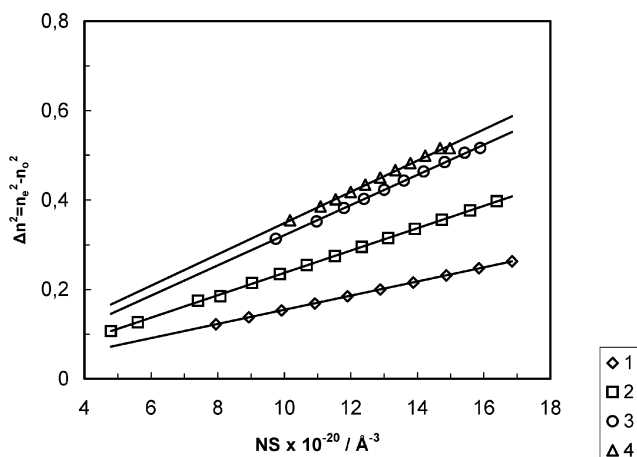


Figure 13. Variation of Δn^2 with NS for compounds 1-4.

although according to Maier and Meier theory [46] a linear dependence is expected. Since in the optical frequency region $\Delta\varepsilon = n_e^2 - n_o^2$, it can be shown [47] that $n_e^2 - n_o^2 (= \Delta n^2) \sim NS$, where N is the number density. From figure 13 it is observed that all the compounds show perfect linear dependence. Moreover, the value of Δn^2 increases systematically as one moves from 1 to 3; the increment in 4 is small.

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