

# CHAPTER VIII

## Mesomorphic and Structural Properties of Some Liquid Crystals possessing a Bicyclohexane Core

### 8.1. Introduction:

Liquid crystal material research have contributed significantly both to the development of liquid crystal display (LCD) technology [1-3] and also at the same time to the better understanding of the phase behaviour of soft condensed matter systems. Quantitative knowledge of orientational ordering is necessary so that improved materials may be devised for applications. Study of pure compounds is an important prerequisite in the preparation of mixtures, better tuned to meet the specific demands of the electro-optical display devices [4, 5]. Prerequisites for the attainment of the goals are experimental techniques to investigate and correlate the relevant material and electro-optical properties with molecular structural elements. Research can then be made to establish molecular design criteria to find new and applicable materials. Thus, attempts are being continuously made to study the material properties for a better insight into the basic understanding of liquid crystalline behaviour, and also that newer and more acceptable class of materials suitable for display devices emerges.

The compounds studied in this work are of extraordinary interest since they contain bicyclohexane core, uncommon to most liquid crystalline compounds. They belong to a new class of liquid crystals, expected to show low optical anisotropy ( $\Delta n < 0.1$ ), low rotational viscosity, low magnetic and

dielectric anisotropy ( $\Delta\chi \approx 0$ ,  $\Delta\epsilon \approx 0$ ) [6] and low visco-elastic ratios [7] leading to faster response times in field effect liquid crystal displays. Moreover, the bicyclohexane compounds are frequently used in multicomponent mixtures to adjust the birefringence and hence the study of the physical properties of these compounds is of utmost importance.

In this work, the results of refractive indices, density and dielectric permittivity measurements on seven alkenyl bicyclohexane compounds [8-10] of which five compounds show only nematic phase while other two compounds possesses a smectic B phase which is the precursor of nematic phase, has been presented. Optical Transmission (OT) method [11] has also been employed to obtain a high resolution (accuracy $\sim 10^{-5}$ ) measurement of the temperature dependences of the optical birefringence,  $\Delta n$ , which provides a macroscopic measure of the anisotropy of the liquid crystalline phase, and can also, be considered as a measure of the orientational ordering of the same. The optical birefringence data obtained from optical transmission method have been compared with the same as obtained from thin prism technique. The high resolution OT technique provides a quite sufficient number of data points for  $\Delta n$  near the phase transitions, thus making it possible to characterize the transitional anomaly quite precisely. The effect of molecular structure on the birefringence of these compounds has also been discussed.

The high resolution optical birefringence ( $\Delta n$ ) data have directly been used for analyzing the temperature behavior of Orientational (nematic) Order Parameter. Moreover, the ordinary and extraordinary refractive indices as well as the density data have also been used to determine the orientational order parameter ( $\langle P_2 \rangle$ ) using the standard Vuks isotropic model [12]. The  $\langle P_2 \rangle$  values determined from the thin prism refractive index data have been compared with those measured from optical transmission method. These values have also been compared with the theoretical values of Maier-Saupe [13] for

the compound having only nematic phase and McMillan's theory [14] for compounds having both Smectic B and nematic phases.

Furthermore, in the field of liquid crystals the nematic-isotropic (N-I) phase transition is quite interesting due to its several surprising features. In a mean field theory Landau and de Gennes [14] gave a simple description of the dynamical behaviour of the N-I phase transition by expressing the free energy density in powers of the nematic order parameter  $S(T)$ . It has been observed that the mean field theory [15] can satisfactorily explain the behaviour of the mesophase over most of the temperature ranges, but very close to transition it fails to describe the critical region. However, along with few disagreements, most of them, reveals a tricritical nature [16-18] for the N-I phase transition which again can be explained in the context of Landau-de Gennes theory with the free energy density expanded up to sixth order in powers of the nematic order parameter  $\langle P_2 \rangle$ . In literature one can obtain numerous examples regarding the study on the critical behavior of  $\langle P_2 \rangle$  extracted from the birefringence and refractive index studies [19-29]. However, as for the dependence of most of the methods on visual inspection, the availability of high resolution birefringence data with less uncertainty is quite scarce, particularly in the neighborhood of the phase transitions. It has been predicted that the critical exponent  $\beta$ , describing the limiting behavior of nematic order parameter at the N-I transition, should take on any one of the available theoretical values, quantitatively 0.5 (for a critical point) or 0.25 (for a tricritical point) or 0.325 (for Ising system). But the fit to the experimental  $\langle P_2 \rangle$  data to the well known Haller's approximation [18] frequently yields relatively lower values of  $\beta$  with  $\beta \leq 0.2$ . Indeed this model is quite unsuited as for its incompatibility with the weakly first order character of the N-I phase transition [30, 31]. Later, the introduction of a four parameter analytical model [21] in concurrence with the weakly first order character of the N-I transition helps to overcome this difficulty, providing theoretically consistent values of  $\beta$ .

However, estimation of precise  $\beta$  value with the aid of such a model requires a quite high resolution and accuracy of the corresponding experimental data, especially near the transition.

Nevertheless, in the literature one can find numerous studies on the critical behavior of the Orientational (nematic) Order Parameter ( $\langle P_2 \rangle$ ) obtained from refractive index or birefringence measurements directly [25, 32-36]. Moreover, by analyzing the temperature behavior of Orientational (nematic) Order Parameter both from optical birefringence  $\Delta n$  directly and also from density and individual refractive indices, the validity of the measurement of the temperature behavior of Orientational (nematic) Order Parameter obtained from optical birefringence  $\Delta n$  have been tested.

Additionally, the dielectric permittivities parallel and perpendicular to the molecular long axis ( $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$ ) and dielectric anisotropy ( $\Delta\epsilon$ ) throughout their mesomorphic range of the seven pure liquid crystalline compounds has also been measured. The structure property relationship of these compounds has also been discussed.

## 8.2. Physical properties of bicyclohexane compounds:

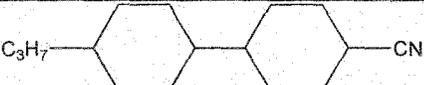
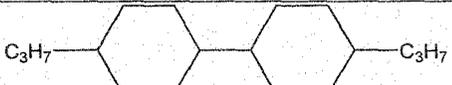
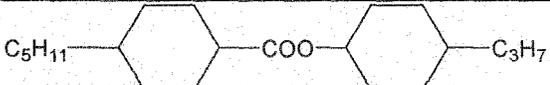
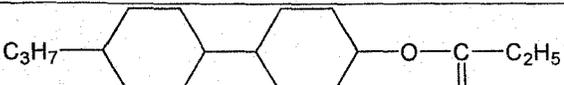
A number of new non-polar bicyclohexane liquid crystal classes have been introduced which exhibit pronounced nematic mesophases. Their optical and dielectric properties, as well as density have been presented. The classes differ from each other with respect to the systematic changes made in the position of the alkenyl double bond in their side chains and/or with respect to their polar or non-polar substituents. The bicyclohexane compounds are of three types either non-polar (i) alkenyl-alkoxy, (ii) alkyl-alkenyloxy or (iii) alkenyl-alkenyl bicyclohexanes which exhibit (except for compounds **b** and **f**, which shows smectic B phase) purely nematic mesophases. Like their polar counterparts their diamagnetic anisotropy  $\Delta\chi$  is virtually zero. Therefore, and because of their simultaneously very small dielectric anisotropy ( $\Delta\epsilon \sim 0$ ), the

pure, non-polar bicyclohexanes can be aligned neither in usual magnetic nor in electric fields and surface alignment techniques are usually employed to align them.

### 8.2.1. Materials:

The compounds were procured from AWAT Co. Ltd., Warsaw, Poland and were used without further purification. The chemical structure and transition temperatures of the compounds are shown in Table 8.1.

**Table 8.1.** Chemical structure and transition temperatures of compounds a-g.

Compound No.	Structure	$T_m$ (°C)	$T_{SmB-N}$ (°C)	$T_{NI}$ (°C)
a		80	--	86.4
b		56.5	53.4	84
c		68.7	--	80.8
d		--	--	53
e		55.4	--	88.5
f		34.8	--	68.8
g		84.7	81.2	158

So far, there are only a few liquid crystal classes described in the literature which exhibit a low birefringence and whose rigid core consists of two cyclohexane rings. All of these possess saturated side chains [14-17]. The non-polar representatives among them, that is, the directly linked [37], as well as the ester [38] and the ethane [39] linked, bicyclohexanes exhibit pronounced smectic B phases which strongly diminish their applicability in nematic mixtures. Moreover, the large viscosities of the esters do not render them applicable for LCD's with faster response times. For these reasons as well as for the experimental difficulties which result from the very low diamagnetic and dielectric anisotropy of the bicyclohexane cores, there are few experimental results available in the literature.

### 8.2.2. Texture Studies:

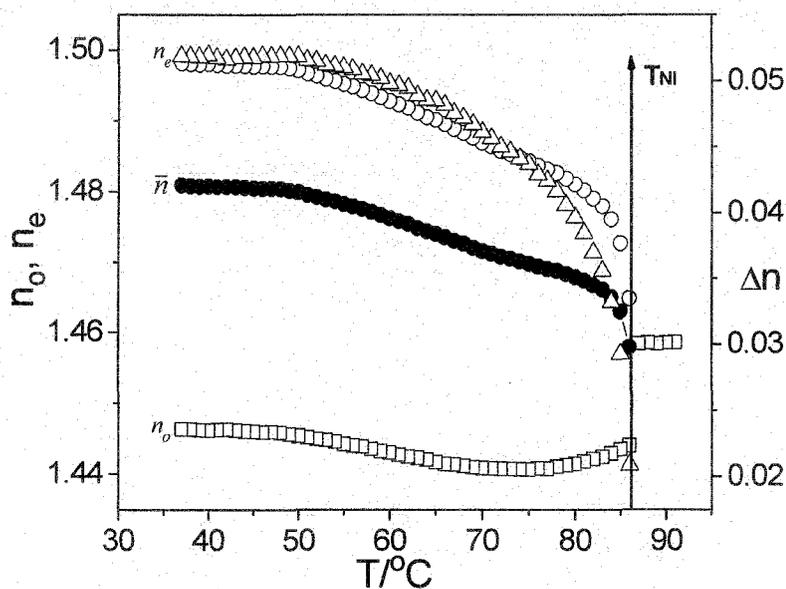
The transition temperatures and textures [40] were observed using polarizing microscope (Motic BA300) equipped with Mettler Toledo FP900 Hot Stage. Typical thread-like textures characteristic of the nematic phase were observed upon heating for all the compounds. Upon cooling, compounds **b** and **g** exhibited Smectic B phase with mosaic texture, while compounds **a** and **c-f** showed only nematic phase. All the compounds show large super cooling.

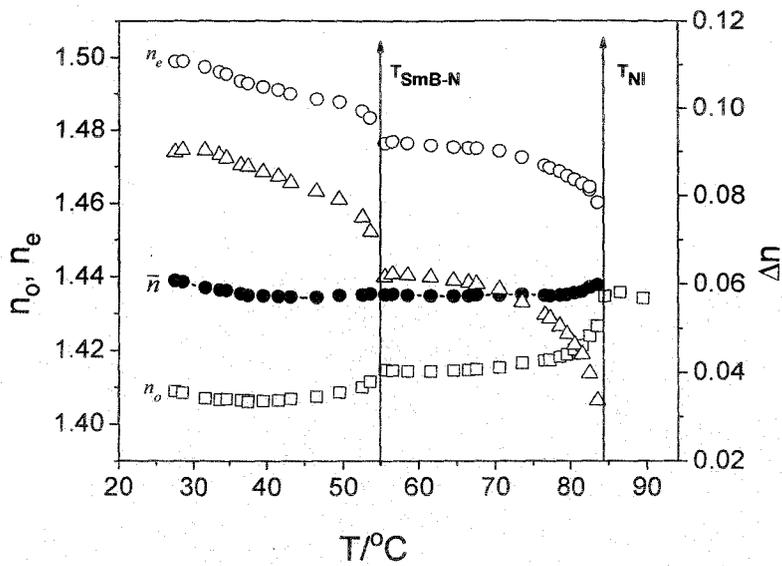
### 8.2.3. Refractive index measurements:

The temperature dependence of the principal refractive indices  $n_o$  and  $n_e$ , the mean value  $\bar{n} = \frac{n_e + 2n_o}{3}$  and the refractive index in the isotropic phase ( $n_{iso}$ ) at a wavelength of  $\lambda = 632.8$  nm for the seven compounds were measured by thin prism technique [25] and are shown in Figures 8.1(a)-8.1(g).

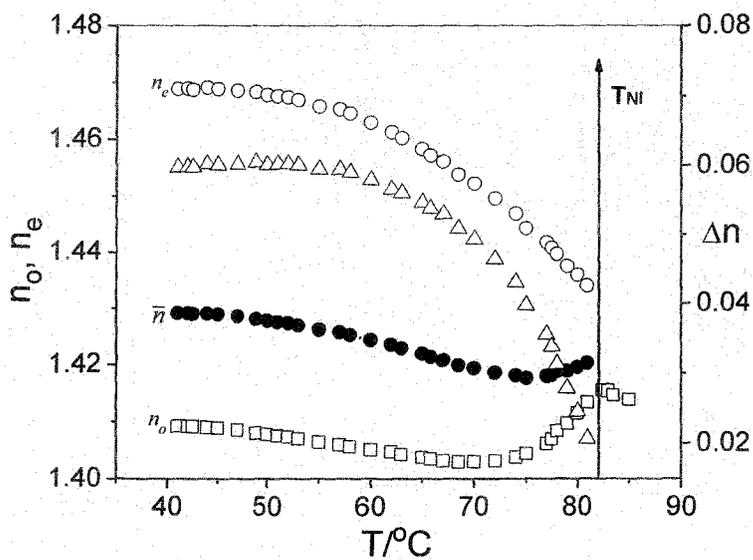
For all the compounds, the values of the extraordinary refractive index decreases with increase in temperature, while the values of the ordinary refractive index remains almost constant in the lower temperature region but

increases with increase in temperature near the N-I phase transition. On cooling from isotropic to nematic phase, a pronounced change in the refractive index values is observed. There is an abrupt increase in the birefringence in going from the nematic to the smectic B phase of compounds **b** and **f**. The birefringence values of all the compounds are very low and are less than 0.1 even in the smectic B phase [41]. This is not surprising because all the bicyclohexane compounds have low polarizability anisotropy due to their nonlinear structure and absence of conjugated  $\pi$ -bond in the molecules. In this context it may be mentioned that this low optical anisotropy are required to develop fast and high information-content liquid crystal displays [42].



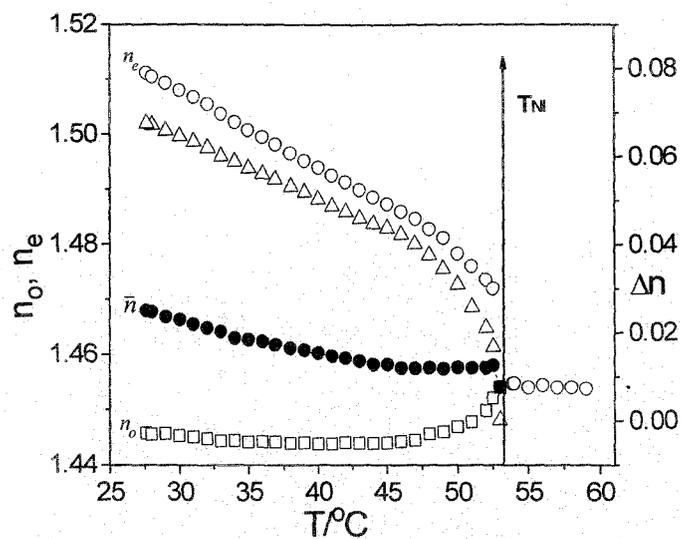


(b)

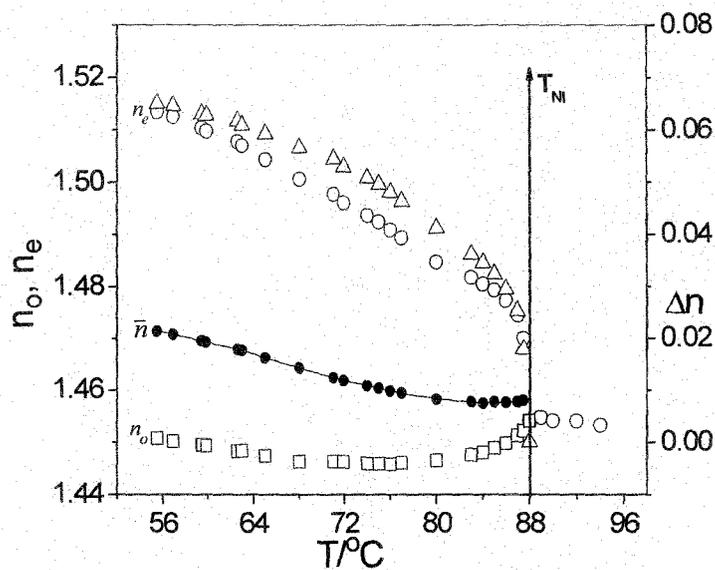


(c)

**Figure 8.1.** 'contd. Experimental values of refractive indices  $n_o$  and  $n_e$ , mean value ( $\bar{n}$ ) and birefringence ( $\Delta n$ ) as a function of temperature for (b) compound **b** and (c) compound **c**.  $T_{\text{NI}}$  = nematic - isotropic phase transition temperature and  $T_{\text{SmB-N}}$  = smectic-nematic phase transition temperature.

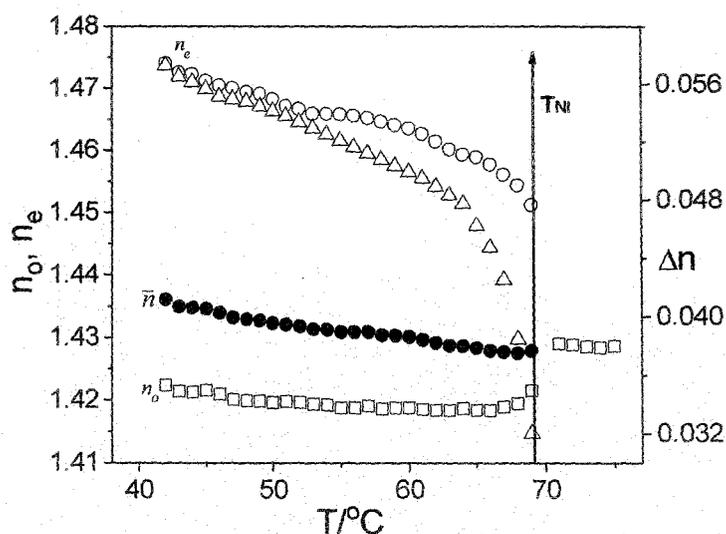


(d)

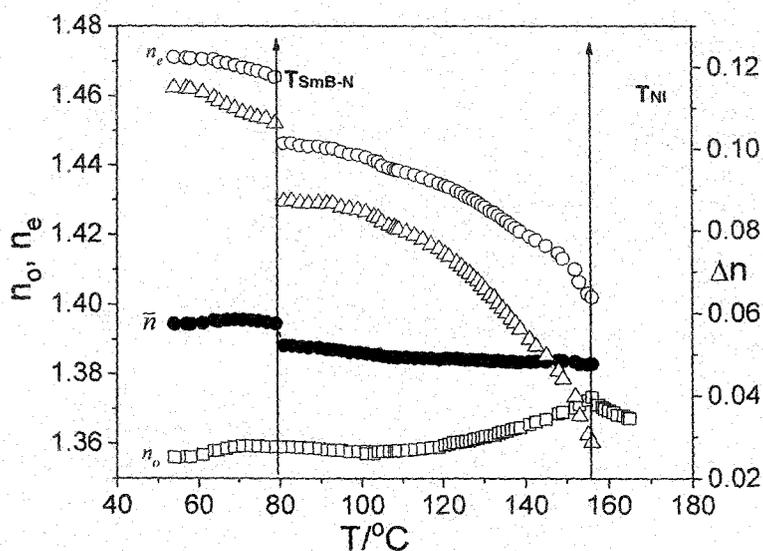


(e)

**Figure 8.1.** 'contd. Experimental values of refractive indices  $n_o$  and  $n_e$ , mean value ( $\bar{n}$ ) and birefringence ( $\Delta n$ ) as a function of temperature for (d) compound **d** and (e) compound **e**.  $T_{NI}$  = nematic - isotropic phase transition temperature.



(f)



(g)

**Figure 8.1.** 'contd. Experimental values of refractive indices  $n_o$  and  $n_e$ , mean value ( $\bar{n}$ ) and birefringence ( $\Delta n$ ) as a function of temperature for (f) compound f and (g) compound g.  $T_{NI}$  = nematic - isotropic phase transition temperature and  $T_{SmB-N}$  = smectic-nematic phase transition temperature.

These materials find use in vertically aligned mode mixtures to fine tune the birefringence of the finished product to meet the specifications prescribed by the existing cell gap.

#### 8.2.4. Optical birefringence measurements:

The optical birefringence ( $\Delta n$ ) of the compounds have also been measured for wavelength  $\lambda = 632.8$  nm using high resolution temperature scanning technique. These values have been compared with those obtained from thin prism technique and is shown in Figure. 8.2. It is observed that the  $\Delta n$  values obtained from thin prism technique are slightly lower than the values obtained from Optical Transmission (OT) method. The possible reason for this discrepancy in the two sets of measurements is due to the fact that in case of thin prism, the sample thickness is much higher (40–80 times) than the  $5.0 \mu\text{m}$  cell which is used in the transmission method. Therefore, the surface anchoring is much better for the thin cells in comparison to the bulk samples in thin prism [25] which causes relatively higher values of the birefringence in the transmission method. The birefringence data covers the nematic as well as smectic B phase of the compounds. There is an abrupt increase in the birefringence values in going from nematic to smectic B phase of compounds **b** and **f**. A comparison of the birefringence of the different compounds is given below:

$$\Delta n \quad \mathbf{g} > \mathbf{b} > \mathbf{d} > \mathbf{e} \sim \mathbf{a} > \mathbf{c} > \mathbf{f}$$

Compound **g** with unsaturated phenyl ring and polar terminal atom shows the highest value of the optical birefringence among all the investigated compounds due to elongation of the  $\pi$  electron conjugation through the entire rigid core of the molecules. Presence of highly polar CN terminal in compound **b** also leads to higher values of the  $\Delta n$ . The optical anisotropy strongly depends on the length of the total alkyl chain (i.e.  $R+R'$ ). The experimental temperature dependence of  $\Delta n$  in the nematic phase has been fitted to the form

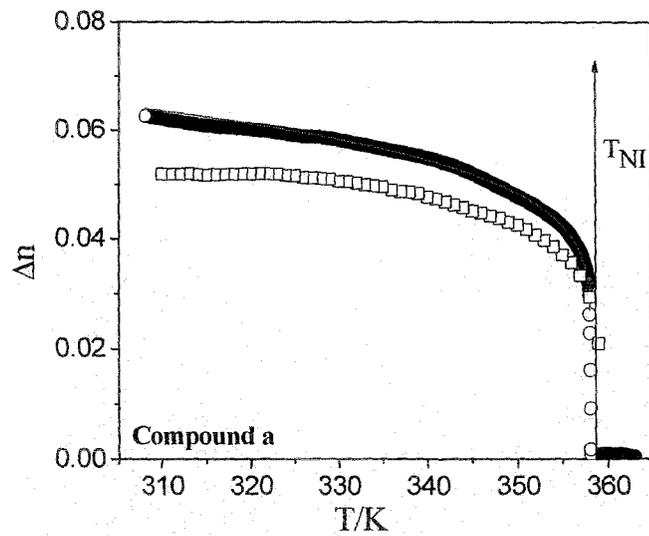
$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T^*}\right)^\beta \quad (8.1)$$

where,  $T$  is the absolute temperature and  $T^*$  is slightly greater than the clearing temperature  $T_{NI}$ .  $\Delta n_0$ , the birefringence at  $T=0K$  and  $\beta$  are fitting parameters by Haller's extrapolation method [19]. This procedure is equivalent to the extrapolation of  $\Delta n$  to the temperature of absolute zero. The values of the fitting parameters are shown in Table 8.2.

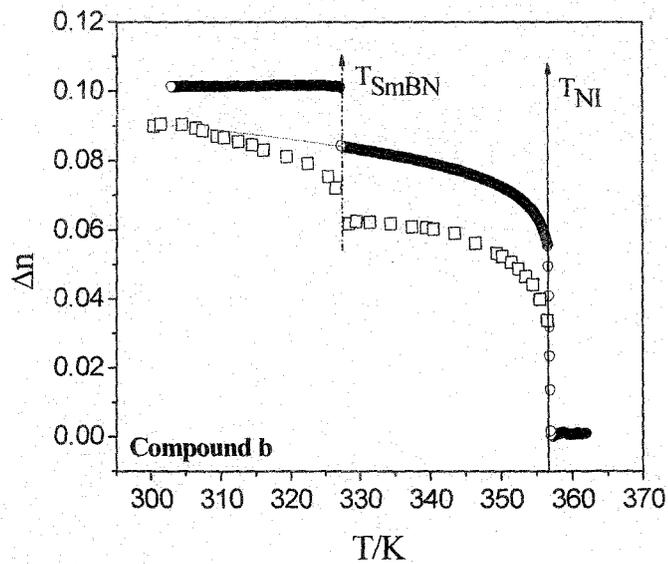
**Table 8.2.** Values of adjustable parameters  $\Delta n_0$ ,  $T^*$  and  $\beta$ .

Compound Name	$\Delta n_0$	$T^*$ in K	$\beta$
<b>a</b>	0.090±0.001	359.0±0.1	0.170±0.001
<b>b</b>	0.108±0.001	357.1±0.1	0.102±0.001
<b>c</b>	0.100±0.010	360.6±0.7	0.197±0.047
<b>d</b>	0.113±0.020	328.5±0.5	0.152±0.002
<b>e</b>	0.090±0.001	361.9±0.1	0.188±0.001
<b>f</b>	0.083±0.001	341.9±0.1	0.180±0.003
<b>g</b>	0.136±0.001	433.2±0.2	0.230±0.003

The order parameter is a very crucial quantity in the field of liquid crystals, manifesting the exact description of a phase transition. Indeed, any anisotropic physical quantity pertaining to a nematic mesogenic medium can be a measure of the orientational ordering of the same and hence can be employed to quantify the critical characteristics near a transition. In that sense, the optical birefringence ( $\Delta n$ ) is also very useful from the view point of both practical applications as well as in assessing theoretical approaches for its approximately proportioned relation with the nematic order parameter  $\langle P_2 \rangle$ .

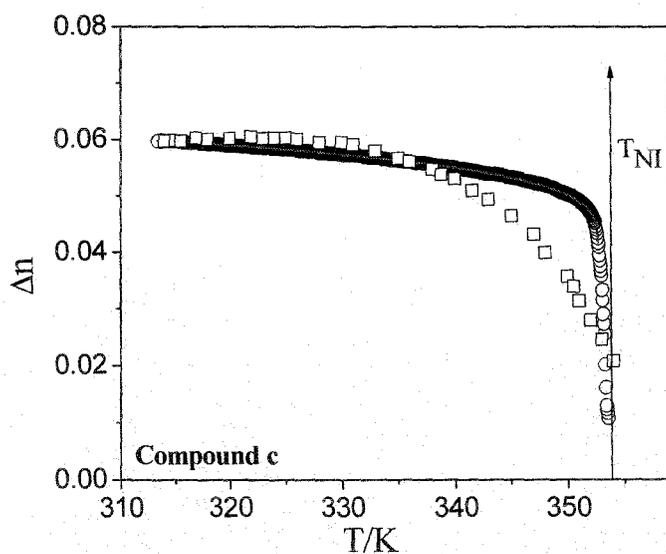


(a)

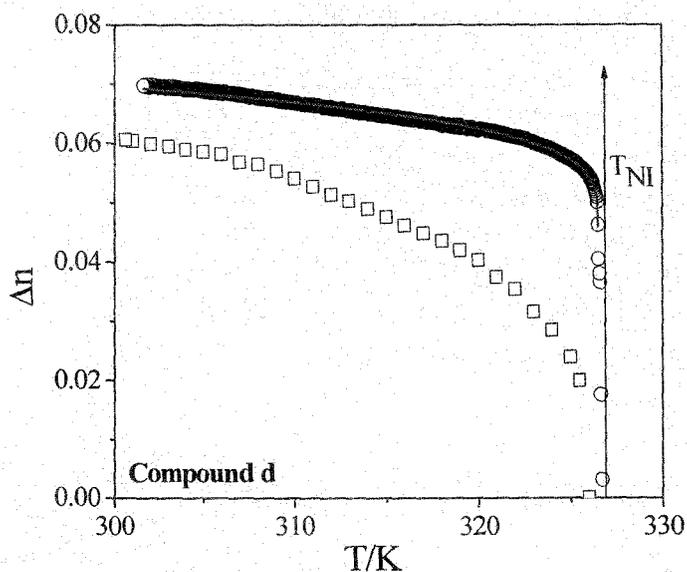


(b)

**Figure 8.2.** Birefringence ( $\Delta n$ ) as a function of temperature for (a) compound a and (b) compound b. Solid arrow denotes nematic-isotropic transition ( $T_{NI}$ ) and dashed arrow represents nematic-smectic B transition ( $T_{SmBN}$ ) temperatures respectively.  $\circ$  - represent the birefringence data from O.T. method and  $\square$  - represent the birefringence data from thin prism method and the solid lines are fit to Equation (8.2).

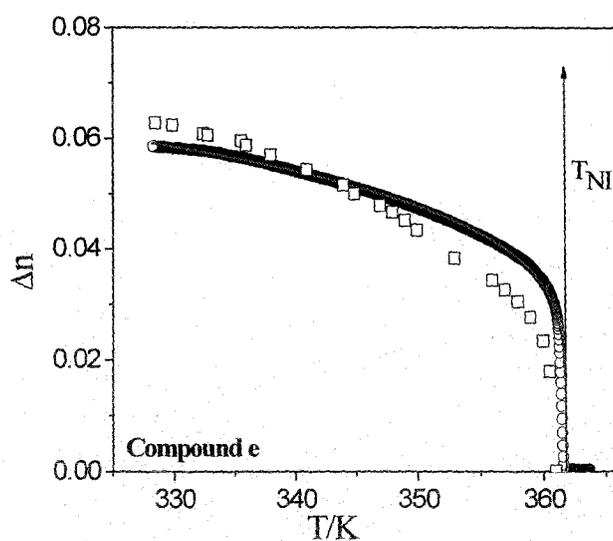


(c)

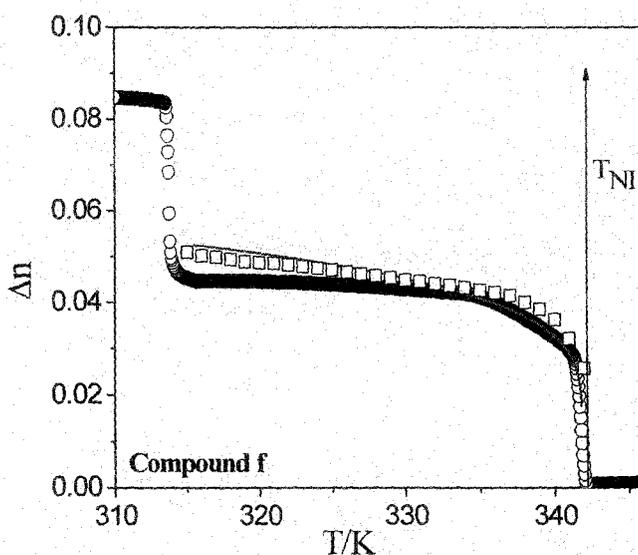


(d)

**Figure 8.2.** Birefringence ( $\Delta n$ ) as a function of temperature for (c) compound c and (d) compound d. Solid arrow denotes nematic-isotropic transition ( $T_{NI}$ ). o - represent the birefringence data from O.T. method and  $\square$  - represent the birefringence data from thin prism method and the solid lines are fit to Equation (8.2).

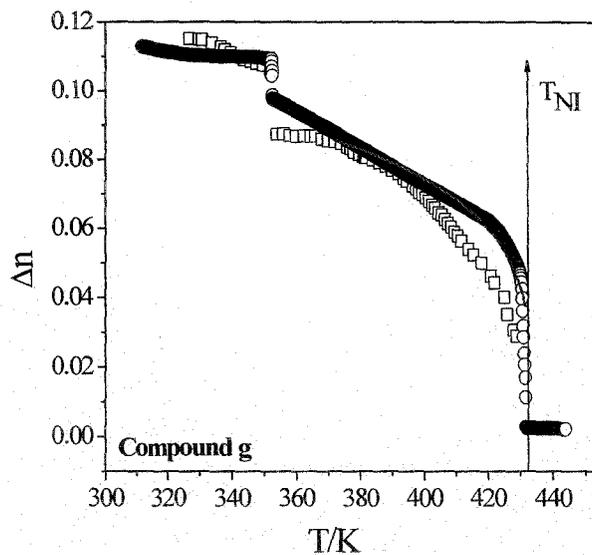


(e)



(f)

**Figure 8.2.** Birefringence ( $\Delta n$ ) as a function of temperature for (e) compound e and (f) compound f. Solid arrow denotes nematic-isotropic transition ( $T_{NI}$ ). o - represent the birefringence data from O.T. method and  $\square$  - represent the birefringence data from thin prism method and the solid lines are fit to Equation (8.2).



(g)

**Figure 8.2.** Birefringence ( $\Delta n$ ) as a function of temperature for (g) compound **g**. Solid arrow denotes nematic-isotropic transition ( $T_{NI}$ ) and dashed arrow represents nematic-smectic B transition ( $T_{SmBN}$ ) temperatures respectively. o - represent the birefringence data from O.T. method and  $\square$  - represent the birefringence data from thin prism method and the solid lines are fit to Equation (8.2).

It is expected that the critical exponent  $\beta$ , characterizing the temperature dependence of the order parameter, should indicate the membership of one of the possible universality classes of phase transitions in liquid crystals. The critical exponents  $\beta$  obtained from Haller's extrapolation lies within the range 0.10 to 0.19 which are less compare to the predicted theoretical value. This is due to the fact that Haller's extrapolation does not always account for the weakly first order nature of nematic-isotropic phase transition and hence results systematically lower value of  $\beta$  which do not fit with any of the theoretical predictions. According to the mean field prediction for a critical or tricritical point  $\beta$  values are equal to 0.5 or 0.25 respectively while for 3D Ising system  $\beta$  yields to be 0.325. Recently, a four parameter power-law expression [21, 25, 30, 31], consistent with the mean-field theory for critical as well as tricritical

behavior of weakly first-order transition has been introduced and expressed in the form

$$D = A[B + (1 - B)(1 - \frac{T}{T^*})^\beta] \quad (8.2)$$

where, D is the physical parameter under consideration (birefringence in this case), A and B are constants,  $\beta$  is the critical exponent and  $T^*$  is slightly greater than the clearing temperature. The solid lines in Figures 8.2(a)-8.2(g) represent the four parameter fit to birefringence ( $\Delta n$ ) data for all the compounds studied. The fitting were done by considering the nematic phase only and the curves were extrapolated to the smectic phase.

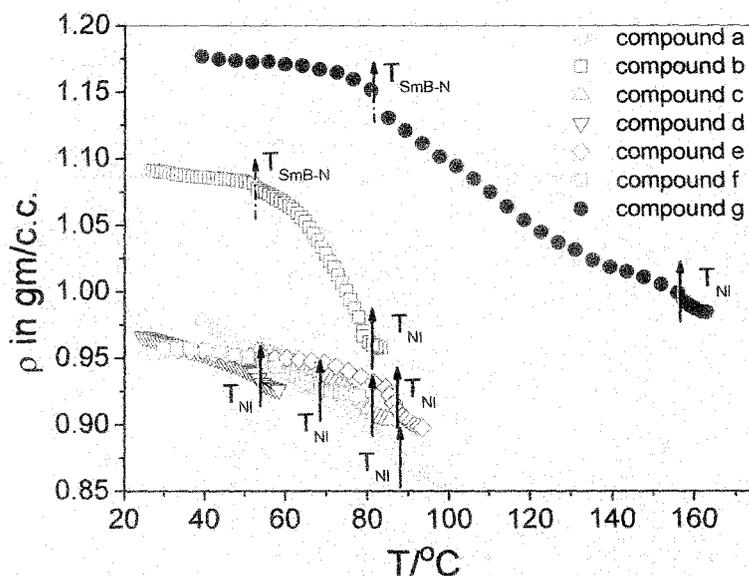
**Table 8.3.** Values of the four adjustable parameters A, B,  $T^*$  and  $\beta$ .

Comp. Name	A	B	$T^*$ in K	$\beta$
<b>a</b>	0.091±0.0003	0.213±0.003	358.1±0.01	0.240±0.002
<b>b</b>	0.117±0.0015	0.392±0.033	356.7±0.4	0.247±0.029
<b>c</b>	0.074±0.0016	0.531±0.043	352.6±0.6	0.244±0.055
<b>d</b>	0.091±0.0011	0.498±0.027	326.5±0.3	0.249±0.031
<b>e</b>	0.099±0.0015	0.097±0.041	361.7±0.3	0.248±0.022
<b>f</b>	0.089±0.0531	0.125±0.002	341.8±1.1	0.245±0.011
<b>g</b>	0.138±0.011	0.107±0.030	431.3±0.1	0.249±0.038

Table 8.3 lists the different parameters obtained by fitting the experimental data to Equation (8.2). It is found that the order parameter critical exponent  $\beta$  has the values in between 0.240 to 0.249. These values of the  $\beta$  are very close to the predicted value 0.25 according to the tricritical hypothesis ( $\beta_{TCH} = 0.25$ ) which strongly supports the tricritical nature of the nematic-isotropic (N-I) phase transition.

### 8.2.5. Density measurement and determination of orientational order parameter:

The temperature variation of the density [41-43] values for pure compounds **a-g** is shown in Figure 8.3. There is a discontinuity in the density values at the nematic – smectic B phase transition of compounds **b** and **g**. The rest compounds however show normal temperature dependence.



**Figure 8.3.** Density as a function of temperature for compounds **a-g**. Key to symbol:  $\circ$  Compound a,  $\square$  Compound b,  $\Delta$  Compound c,  $\nabla$  Compound d,  $\diamond$  Compound e,  $\bullet$  Compound f and  $+$  Compound g. Solid arrow denotes nematic-isotropic transition ( $T_{NI}$ ) and dashed arrow represents nematic-smectic B transition ( $T_{SmBN}$ ) temperatures respectively.

Using the density and refractive index data ( $n_e$ ,  $n_o$ ), the principal molecular polarizabilities ( $\alpha_e$ ,  $\alpha_o$ ) has been calculated using Vuks method [12]. Thus the orientational order parameter  $\langle P_2 \rangle$  can be determined from the relation:

$$\langle P_2 \rangle = \frac{\Delta\alpha}{\Delta\alpha_0} \quad (8.3)$$

where  $\Delta\alpha$  is the polarizability anisotropy and  $\Delta\alpha_0$  is the same in the perfectly ordered state or at  $T=0\text{K}$ . The  $\Delta\alpha_0$  values were determined from the Haller's extrapolation technique [18] using the following equation:

$$\Delta\alpha = \Delta\alpha_0 \left(1 - \frac{T}{T^*}\right)^\beta \quad (8.4)$$

where  $T^*$  and  $\beta$  are two adjustable parameters,  $T^*$  is the virtual phase transition temperature which is higher than the clearing temperature  $T_{NI}$ ; and the critical exponent  $\beta$  depends on the molecular structure and its value is close to 0.2.

### 8.2.6. Determination of order parameter from the high resolution birefringence measurement:

In this work a simple procedure has been adopted to calculate the Orientational Order Parameter ( $\langle P_2 \rangle$ ) for the seven compounds under study. The optical birefringence,  $\Delta n$ , obtained from the optical transmission (OT) method was utilized to determine the temperature variation of the orientational order parameter  $\langle P_2 \rangle$  [11] in the liquid crystalline phases of these compounds. According to de Gennes [15], the anisotropy of any physical quantity can be a measure of the order parameter. Moreover, de Jeu [44] have showed that birefringence ( $\Delta n$ ) can be used for this purpose. Kuczynski *et. al.* [45] have also proposed a simple method to obtain the order parameter from birefringence ( $\Delta n$ ) data which can be applied to nematogens as well as some smectogens. The temperature dependent birefringence is related to the order parameter as:

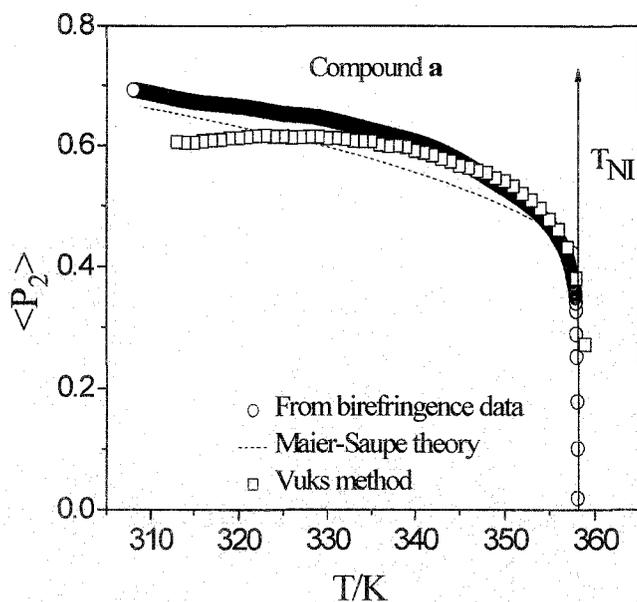
$$\langle P_2 \rangle = \frac{\Delta n}{\Delta n_0} \quad (8.5)$$

where  $\Delta n_0$  is the same as mentioned earlier. The order parameters determined in this way for all the compounds are shown in Figure 8.4(a) – 8.4(g). It may be mentioned that for compounds **b** and **g** equation 8.1 have been fitted by taking the values of  $\Delta n$  in the higher temperature nematic phase only.

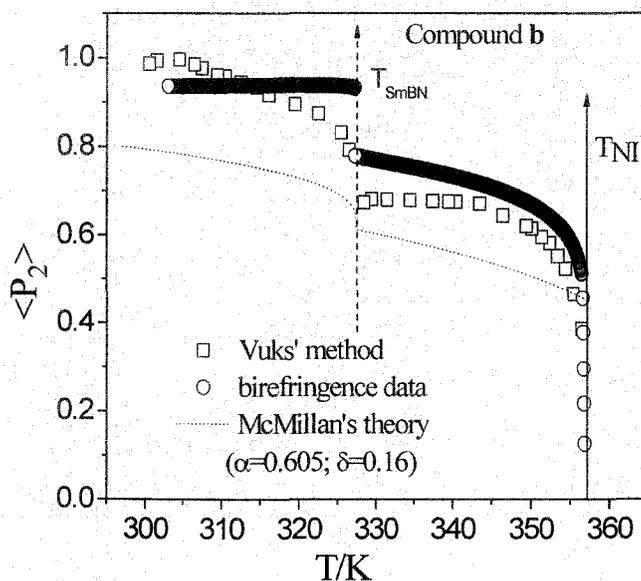
The temperature dependence of Orientational Order Parameter (OOP) obtained from the above mentioned method for all the compounds studied were compared with the orientational order parameter in the liquid crystalline phases obtained from the Equation (8.5) and are shown in Figure 8.4.

From Figure 8.4 it is observed that the temperature variation of the orientational order parameter determined from Vuks method and direct extrapolation method are close to each other and the agreement with the Maier-Saupe [13] values is reasonably good. The two sets of experimental data from two different methods marginally differ. Thus the direct extrapolation technique can be used to determine the order parameter of all the compounds from the birefringence data obtained from thin prism technique. It may also be mentioned that Kuczynski *et al.* [45] have also shown that the order parameter determined directly from birefringence measurements are consistent with the  $\langle P_2 \rangle$  values calculated from the polarizability data. The values of adjustable parameters  $\Delta\alpha_0$ ,  $T^*$  and  $\beta$  are shown in Table 8.4.

The values of Orientational Order parameter (OOP),  $\langle P_2 \rangle$ , are found to be relatively high in the smectic B phase for both of these compounds (compounds **b** and **g**), showing the phase to be much more orientationally ordered than the neighbouring nematic phase. Compounds **b** and **g** exhibits Smectic B phase along with nematic phase. The experimental data have been fitted with those calculated from McMillan's theory for Smectic A [14] phase for compounds **b** and compound **g** using the potential parameters  $\delta$  fixed (0.16) and  $\alpha$  as adjustable constant, due to lack of other alternatives. The best fitted theoretical curves were obtained for  $\alpha$  equal to 0.605 and 0.505 for compound **b** and compound **g** respectively. However, the agreement between the experimental and theoretical values seems to be fair for compound **g** and very poor for compound **b**.

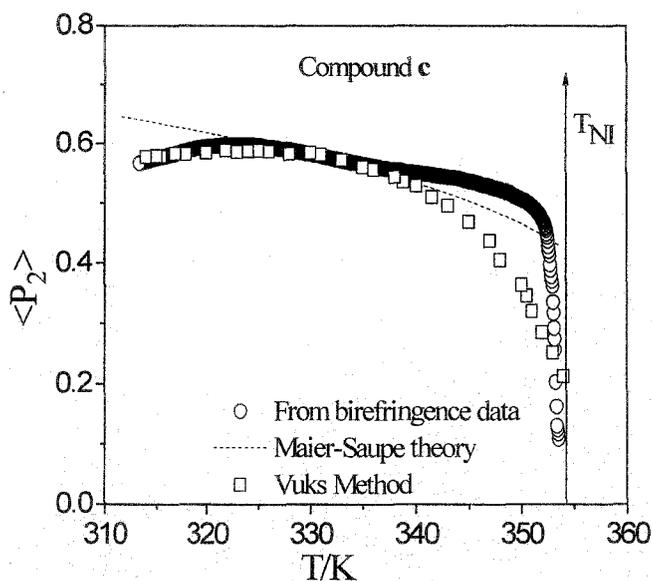


(a)

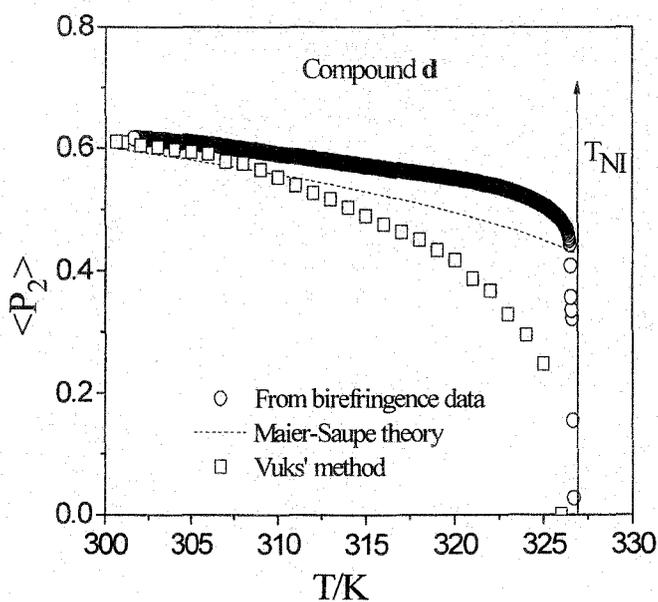


(b)

**Figure 8.4.** Temperature variation of  $\langle P_2 \rangle$  for (a) Compound a and (b) Compound b. Solid arrow indicates nematic–isotropic phase transition temperature ( $T_{NI}$ ). The dashed lines represent  $\langle P_2 \rangle$  values from Maier-Saupe theory and McMillan's theory (only for Compound b).

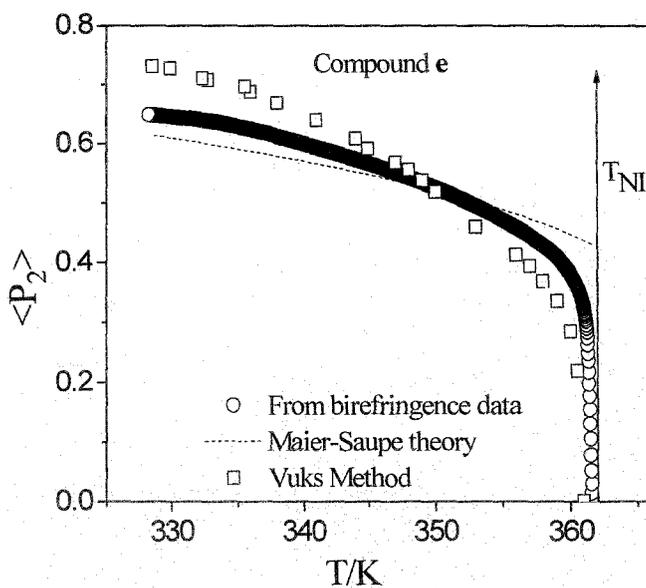


(c)

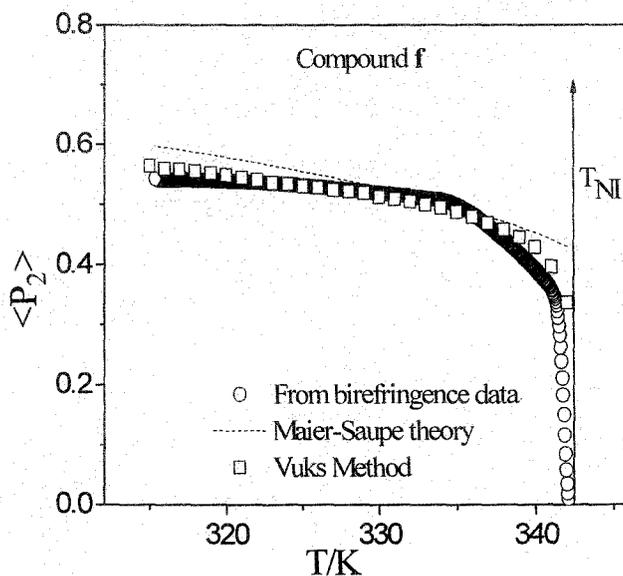


(d)

**Figure 8.4.** 'contd. Temperature variation of  $\langle P_2 \rangle$  for (c) Compound c and (d) Compound d. Solid arrow indicates nematic-isotropic phase transition temperature ( $T_{NI}$ ). The dashed lines represent  $\langle P_2 \rangle$  values from Maier-Saupe theory.

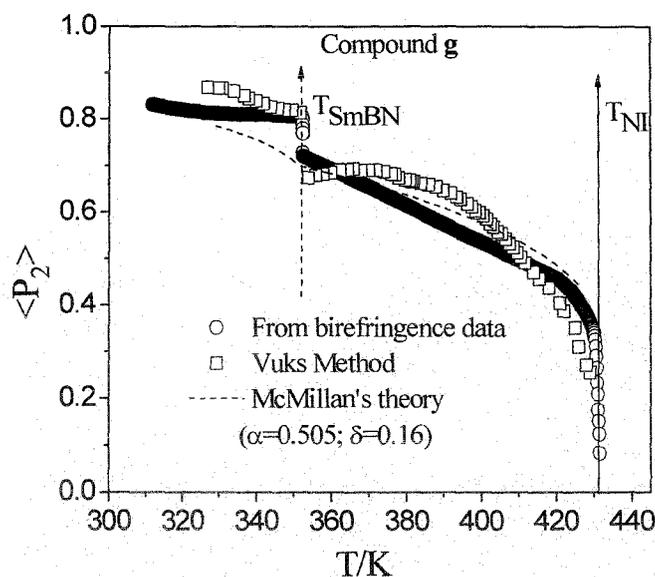


(e)



(f)

**Figure 8.4.** 'contd. Temperature variation of  $\langle P_2 \rangle$  for (e) Compound e and (f) Compound f. Solid arrow indicates nematic–isotropic phase transition temperature ( $T_{NI}$ ). The dashed lines represent  $\langle P_2 \rangle$  values from Maier-Saupe theory.



(g)

**Figure 8.4.** 'contd. Temperature variation of  $\langle P_2 \rangle$  for (g) Compound g. Solid arrow indicates nematic-isotropic phase transition temperature ( $T_{NI}$ ). The dashed lines represent  $\langle P_2 \rangle$  values from Maier-Saupe theory and McMillan's theory.

**Table 8.4.** Values of adjustable parameters  $\Delta\alpha_0$ ,  $T^*$  and  $\beta$

Comp. Name	$\Delta\alpha_0 \times 10^{24}$	$T^*$ in K	$\beta$
<b>a</b>	$3.85 \pm 0.15$	$359.1 \pm 0.1$	$0.166 \pm 0.009$
<b>b</b>	$3.37 \pm 0.12$	$356.6 \pm 0.4$	$0.104 \pm 0.003$
<b>c</b>	$4.96 \pm 0.27$	$354.2 \pm 0.6$	$0.218 \pm 0.021$
<b>d</b>	$5.85 \pm 0.07$	$325.4 \pm 0.2$	$0.212 \pm 0.003$
<b>e</b>	$4.22 \pm 0.05$	$360.7 \pm 0.01$	$0.204 \pm 0.003$
<b>f</b>	$4.90 \pm 0.95$	$344.6 \pm 0.7$	$0.206 \pm 0.07$
<b>g</b>	$6.61 \pm 0.23$	$429.2 \pm 0.5$	$0.200 \pm 0.013$

### 8.2.7. Dielectric permittivity measurements:

The static permittivities [46, 47]  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  along and perpendicular to the molecular long axis and the mean value  $\bar{\epsilon} = \frac{\epsilon_{\parallel} + 2\epsilon_{\perp}}{3}$ , are shown in Figure 8.5(a)-8.5(g). The dielectric anisotropy  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$  of all the seven compounds are also presented in Figure 8.5(a)-8.5(g). The differences observed in their (compounds **a-g**) measured dielectric parameters are due to the difference in terminal alkyl chains. The dielectric anisotropy of compound **g** is high in comparison to other compounds mainly due to the strong dipole moment of C-F bonds of the phenyl ring (Figure 8.5(g)). A tiny difference in the anisotropy value for different molecules is possible as dielectric permittivities are influenced by the molecular rotation and again molecular rotation changes due to the dissimilarity in flexibility of the side chains [48].

All the compounds exhibit a low positive dielectric anisotropy ( $\Delta\epsilon > 0$ ) due to the presence of non planar cyclohexane ring. The values of  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$  and  $\Delta\epsilon$  change in the following way:

$$\epsilon_{\parallel} \quad \mathbf{f > a > b > d \sim e > c > g}$$

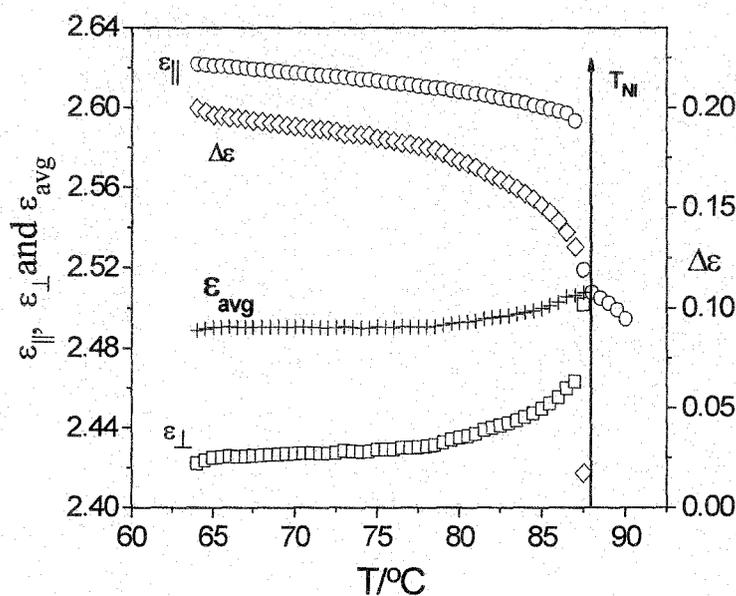
$$\epsilon_{\perp} \quad \mathbf{f > a > b > d \sim e > c > g}$$

$$\Delta\epsilon \quad \mathbf{g > a > c > b > d \sim e > f}$$

Generally presence of a polar group in the terminal position introduces additional dipole moment that increases the dipole moment along the long molecular axis. Therefore, compound **e** and compound **f** with polar ester linkage adjacent to the terminal hydrocarbon has much higher  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  than other compounds. It is observed that by decreasing the length of the terminal hydrocarbon  $\text{CH}_3$  to  $\text{C}_2\text{H}_5$  in compound **e** the  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  values decrease.

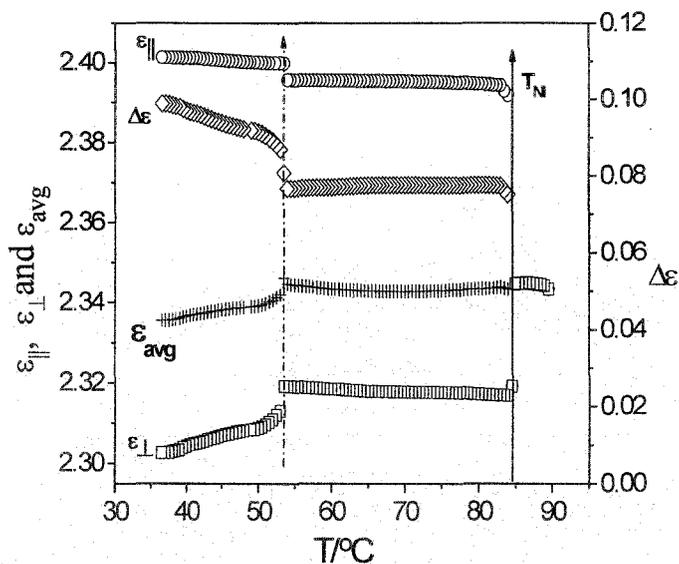
Generally presence of a polar group in the terminal position introduces additional dipole moment that increases the dipole moment along the long

molecular axis. Therefore, compound **e** and **f** with polar ester linkage adjacent to the terminal hydrocarbon has much higher  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  than other compounds. It is observed that by decreasing the length of the terminal hydrocarbon  $\text{CH}_3$  to  $\text{C}_2\text{H}_5$  in compound **e** the  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  values decrease. The change in position of ester linkage in compound **d** further reduces the dielectric parameters values. Presence of another highly polar CN terminal in compound **b** and ethylene double bond (conjugated  $\pi$  bonds) in compounds **a** leads to  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  values close to the ester compounds **d**, **e** and **f**.

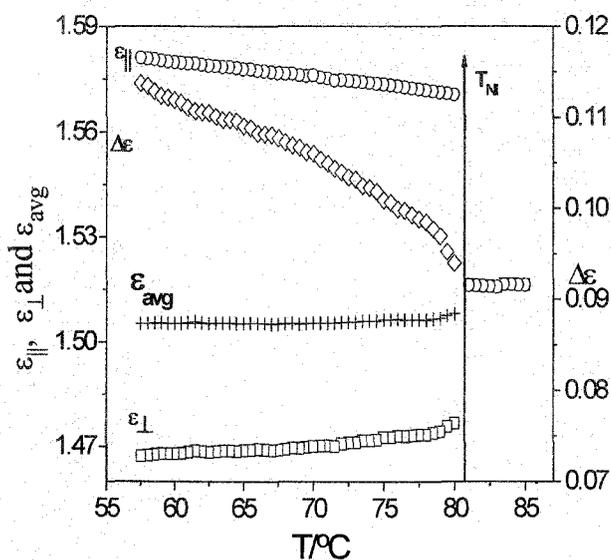


(a)

**Figure 8.5.** Variation of dielectric permittivities ( $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ ), dielectric anisotropy ( $\Delta\epsilon$ ) and average value of dielectric permittivity ( $\epsilon_{\text{avg}}$ ) with temperature for (a) compounds **a**. Key to symbols: o  $\epsilon_{\parallel}$ ,  $\square$   $\epsilon_{\perp}$ ,  $\diamond$   $\Delta\epsilon$  and +  $\epsilon_{\text{avg}}$ .

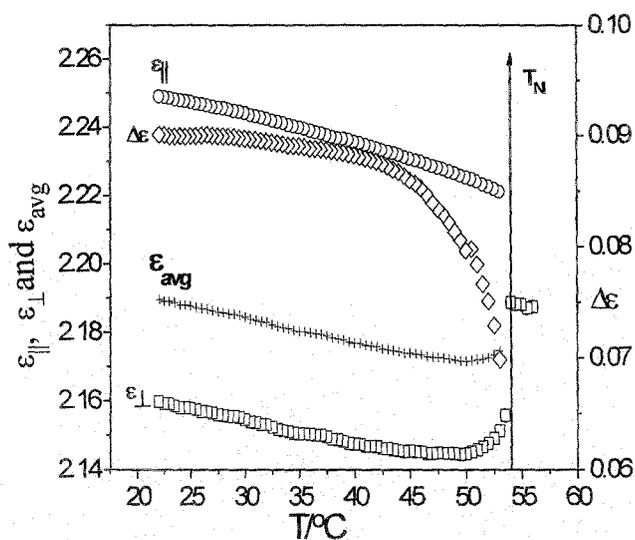


(b)

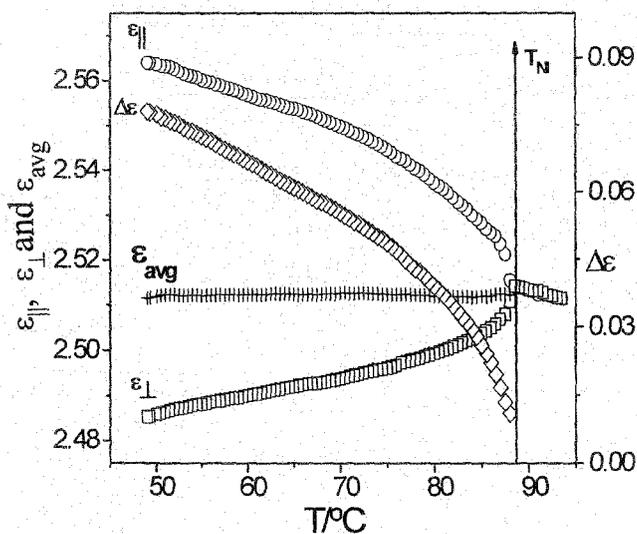


(c)

**Figure 8.5.** Variation of dielectric permittivities ( $\epsilon_{||}$  and  $\epsilon_{\perp}$ ), dielectric anisotropy ( $\Delta\epsilon$ ) and average value of dielectric permittivity ( $\epsilon_{\text{avg}}$ ) with temperature for (b) compounds **b** and (c) compound **c**. Key to symbols:  $\circ$   $\epsilon_{||}$ ,  $\square$   $\epsilon_{\perp}$ ,  $\diamond$   $\Delta\epsilon$  and  $+$   $\epsilon_{\text{avg}}$ .

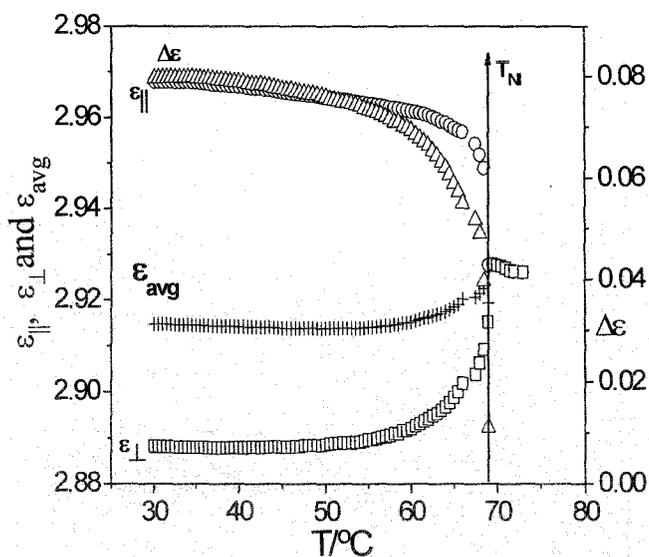


(d)

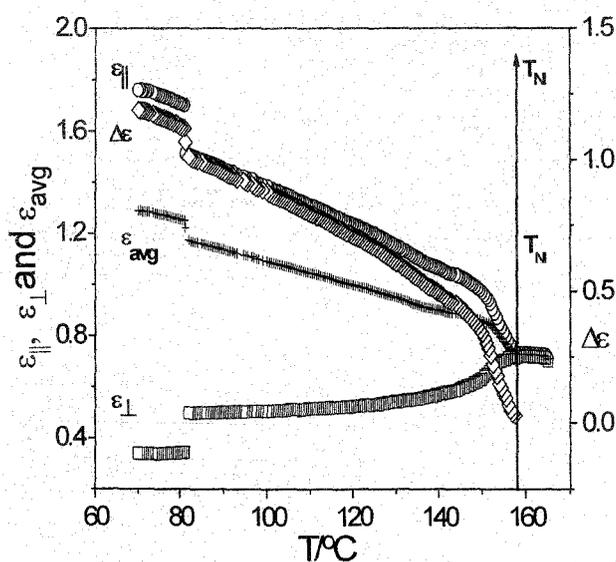


(e)

**Figure 8.5.** 'contd. Variation of dielectric permittivities ( $\epsilon_{||}$  and  $\epsilon_{\perp}$ ), dielectric anisotropy ( $\Delta\epsilon$ ) and average value of dielectric permittivity ( $\epsilon_{\text{avg}}$ ) with temperature for (d) compounds **d** and (e) compound **e**. Key to symbols:  $\circ$   $\epsilon_{||}$ ,  $\square$   $\epsilon_{\perp}$ ,  $\diamond$   $\Delta\epsilon$  and  $+$   $\epsilon_{\text{avg}}$ .



(f)



(g)

**Figure 8.5.** 'contd. Variation of dielectric permittivities ( $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$ ), dielectric anisotropy ( $\Delta\epsilon$ ) and average value of dielectric permittivity ( $\epsilon_{\text{avg}}$ ) with temperature for (f) compounds f and (g) compound g. Key to symbols:  $\circ$   $\epsilon_{\parallel}$ ,  $\square$   $\epsilon_{\perp}$ ,  $\diamond$   $\Delta\epsilon$  and  $+$   $\epsilon_{\text{avg}}$ .

### 8.3. Summary and Conclusions:

Liquid crystals formed by non-polar molecules are of great interest from both application as well as fundamental point of view. Mesomorphic properties of various liquid crystalline materials which have same bicyclohexane core and terminal groups have been investigated. These non-polar compounds (compound a-g) show several characteristics (high purities, low birefringence and low electrical conductivity) that make them useful as components of liquid crystal mixtures for display applications. Moreover, they allow studies of electrostatic and electrodynamical phenomena which are present in dielectrics in general, and in liquid crystals in particular, without the effects resulting from the coupling between applied electric fields and molecular dipoles. All of the compounds belong to the non-polar bicyclohexane liquid crystal class that exhibits pronounced nematic mesophases. Only problem with them is that they show a larger viscosity which leads to a greater response time. Thus, these materials are used in a minute amounts in the vertically aligned mode negative dielectric nematic mixtures as discussed in Chapter VI (mixture A-G), mainly to lower the birefringence of the mixtures.

The difference in the terminal molecule or chain markedly affects the physical parameters of the compounds studied. Compound g exhibits a higher birefringence ( $\Delta n$ ) and dielectric anisotropy ( $\Delta\epsilon$ ) in comparison to others as it is the only compound which posses highly negative fluorine atom and benzene ring at the terminal position. The  $\langle P_2 \rangle$ ,  $\Delta n$  and density ( $\rho$ ) values in the nematic phase for compounds a, c-f have a moderate value while for compound b and g these values are slightly higher in Sm B phase.

Measurements of optical birefringence have been conducted by two different probing methods viz. thin prism and optical transmission (OT) methods and the two sets of values are in good agreement with a small deviation of about 5-6%. Interestingly, the high resolution  $\Delta n$  data obtained from temperature scanning measurement of optical birefringence are quite

successful in characterizing the transitional anomaly associated with the nematic-isotropic phase transition. For the investigated compounds, the values of the critical exponent  $\beta$  related to the limiting behavior of the nematic order parameter close to the N-I transitions, are found to be close to 0.25 and thus are in well accordance with the tricritical hypothesis and also excludes the possibility of any higher  $\beta$  values. Moreover, by analyzing the temperature behavior of the orientational order parameter both from optical birefringence  $\Delta n$  directly (OT data) and also from density and individual refractive indices, it has been found that temperature dependent behavior of the order parameter from two different methods marginally differ.

The measurements of dielectric permittivities parallel and perpendicular to the molecular long axis ( $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$ ) and dielectric anisotropy ( $\Delta\epsilon$ ) throughout their mesomorphic range of the seven pure liquid crystalline compounds have been conducted. All the compounds exhibit a low positive dielectric anisotropy ( $\Delta\epsilon > 0$ ) due to the presence of non planar cyclohexane ring. The structure property relationship of the dielectric behaviour of these compounds has also been discussed.

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