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RESEARCH ARTICLE

Mesomorphic and structural properties of some liquid crystals possessing a bicyclohexane core

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Abstract

The physical properties of seven bicyclohexane compounds have been investigated from polarizing optical microscopy, refractive indices, high resolution optical birefringence, density and dielectric permittivity measurements. These materials are characterized by low optical anisotropy and are often introduced as an effective component to reduce the birefringence (Δn) of the commercial mixtures. The refractive indices and density data have been used to determine the orientational order parameter as a function of temperature using the standard Vuks method and the results are compared with the mean field values. Optical Transmission (OT) method has also been employed to obtain a high resolution (better than 10^{-5}) measurement of the temperature dependences of the optical birefringence (Δn), 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. For the investigated compounds, the values of the order parameter critical exponent β related to the limiting behavior of the nematic order parameter in the vicinity of the nematic–isotropic (N-I) transitions, are found to be close to 0.25, thus are in well accordance with the tricritical hypothesis. Additionally, the dielectric permittivities parallel and perpendicular to the molecular long axis throughout their mesomorphic range of the seven pure liquid crystalline compounds has also been measured.

INTRODUCTION

Liquid crystal (LC) 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 also an important prerequisite in the preparation of mixtures, better tuned to meet the specific demands of the electro-optical display devices [4,5]. Several 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 LC compounds with a bicyclohexane core are of extraordinary interest since it belongs to a substantially investigated class of liquid crystalline material and is expected to show low optical anisotropy ($\Delta n<0.1$), low magnetic and dielectric anisotropy ($\Delta\chi \approx 0$, $\Delta\varepsilon \approx 0$) [6] and moderate visco-elastic ratios [7]. Moreover, the biyclohexane compounds are frequently used in multi-component mixtures to adjust the birefringence and hence the study of the physical properties of these compounds is of utmost importance.

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 order parameter critical exponent β, 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 well known Haller's approximation [8] frequently yields relatively lower values of β 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 [9,10]. Later, the introduction of a four parameter analytical model [11] in concurrence with the weakly first order character of the N-I transition helps to overcome this difficulty, providing theoretically consistent values of β. However, estimation of β value with the aid of such a model requires a quite high resolution and accuracy of the corresponding experimental data, especially near the transition.

In this work, the results of refractive indices, density and dielectric permittivity measurements on seven alkenyl bicyclohexane compounds [12-14] 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 [15-18] has also been employed to obtain a high resolution measurement of the temperature dependences of the optical birefringence, Δn, 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 effect of molecular structure on the birefringence of these compounds has also been discussed.

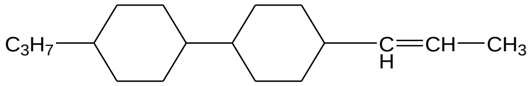
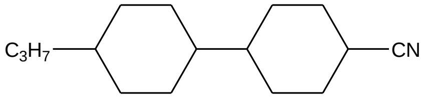
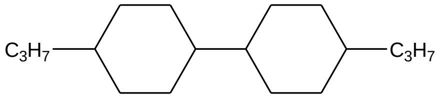
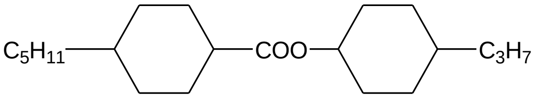
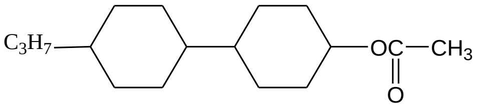
Moreover, the ordinary and extraordinary refractive indices as well as the density data have been used to determine the orientational order parameter ($\langle P_2 \rangle$) using the standard Vuks isotropic model [19]. The $\langle P_2 \rangle$ values determined from the thin prism refractive index data have been compared with those measured from optical transmission method. These values have also been compared with the theoretical values of Maier-Saupe [20] for the compound having only nematic phase and McMillan's theory [21] for compounds having both smectic and nematic phases.

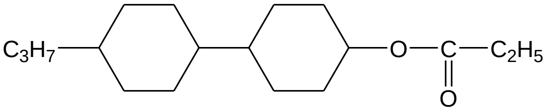
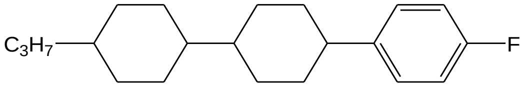
2. Experimental

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 1.

Table 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 [22,23]. The non-polar representatives among them, that is, the directly linked, as well as the ester and the ethane linked, bicyclohexanes exhibit pronounced smectic B phases which strongly diminish their applicability in nematic mixtures. Moreover, the esters are not applicable for LCD's with faster response time due to their larger viscosity values. For these reasons as well as for the experimental difficulties which result from the very low diamagnetic and dielectric anisotropy of the biyclohexane cores, there are few experimental results available in the literature.

2.2 Optical birefringence measurements

2.2.1 Thin prism technique

The refractive indices (n_o, n_e) for a wavelength of λ= 632.8nm were measured within ±0.0006 by thin prism technique [24]. A hollow glass prism (refracting angle <2°) was constructed by placing the rubbed surfaces inside, with the rubbing direction parallel to the refracting edge of the prism. The temperature of the sample filled prism was controlled by a temperature controller (Eurotherm PID 2404) with an accuracy of ±0.1°C. A magnetic field of about 0.8 Tesla was also applied to align the liquid crystalline sample. When a He-Ne laser beam passes through the aligned sample it splits into two rays *i.e.* ordinary and extraordinary rays. From the high resolution photograph of the two images the ordinary (n_o) and extra ordinary refractive indices (n_e) have been calculated using the prism angle.

2.2.2 Optical transmission (OT) method

High resolution optical birefringence (Δn) measurements were performed by measuring the intensity of a laser beam (λ = 632.8nm) transmitted through a planar aligned cell of thickness 5.0μm filled with liquid crystalline (LC) sample and hence probing the related phase retardation. The sample filled cell was placed in a brass made heater and the temperature of which was controlled and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of ±0.1°C. The intensity of the transmitted laser beam was scanned by a photo diode connected with a digital multimeter at a time interval of 3 seconds. The heater temperature was varied at a rate of 0.5°C min^{-1}; this translates into a temperature difference of 0.025°C between two successive readings. The whole experimental set up and method for the birefringence measurement from optical transmission (OT) method have been described in details in our earlier publications [15-18]. In our present method, the precision of measurement of the birefringence values is found to be slightly higher than 10^{-5}.

2.3 Density measurement

The densities of liquid crystals were measured with the help of a dilatometer of the capillary type. A weighed sample of the liquid crystal was introduced inside the capillary tube of the dilatometer, placed in an insulated glass chamber, the temperature of which was controlled by a temperature controller (Eurotherm PID 2404). Sufficient time was allowed for equilibrium at any desired temperature before taking each reading. The length of the liquid crystal column was measured with a travelling microscope. The densities were calculated after correction for the expansion of glass. The accuracy of the measurement of the densities was within 0.1% [25].

2.4 Static dielectric permittivity measurements

The dielectric permittivities $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ along and perpendicular to the molecular long axis respectively were determined, by measuring the capacitance of suitably aligned liquid crystal filled cells, the details of which have been discussed elsewhere [26,27]. For this study homogeneously aligned ITO coated liquid crystal cell of thickness 5μm, procured from AWAT Co. Ltd., Warsaw, Poland, has been used. Agilent E4980A digital LCR-bridge was used to measure the dielectric permittivity with a relative accuracy of 0.05%. The measurements were done with an accuracy of ±0.1°C by using an electrically powered thermostat block and a temperature controller (Eurotherm PID 2404).

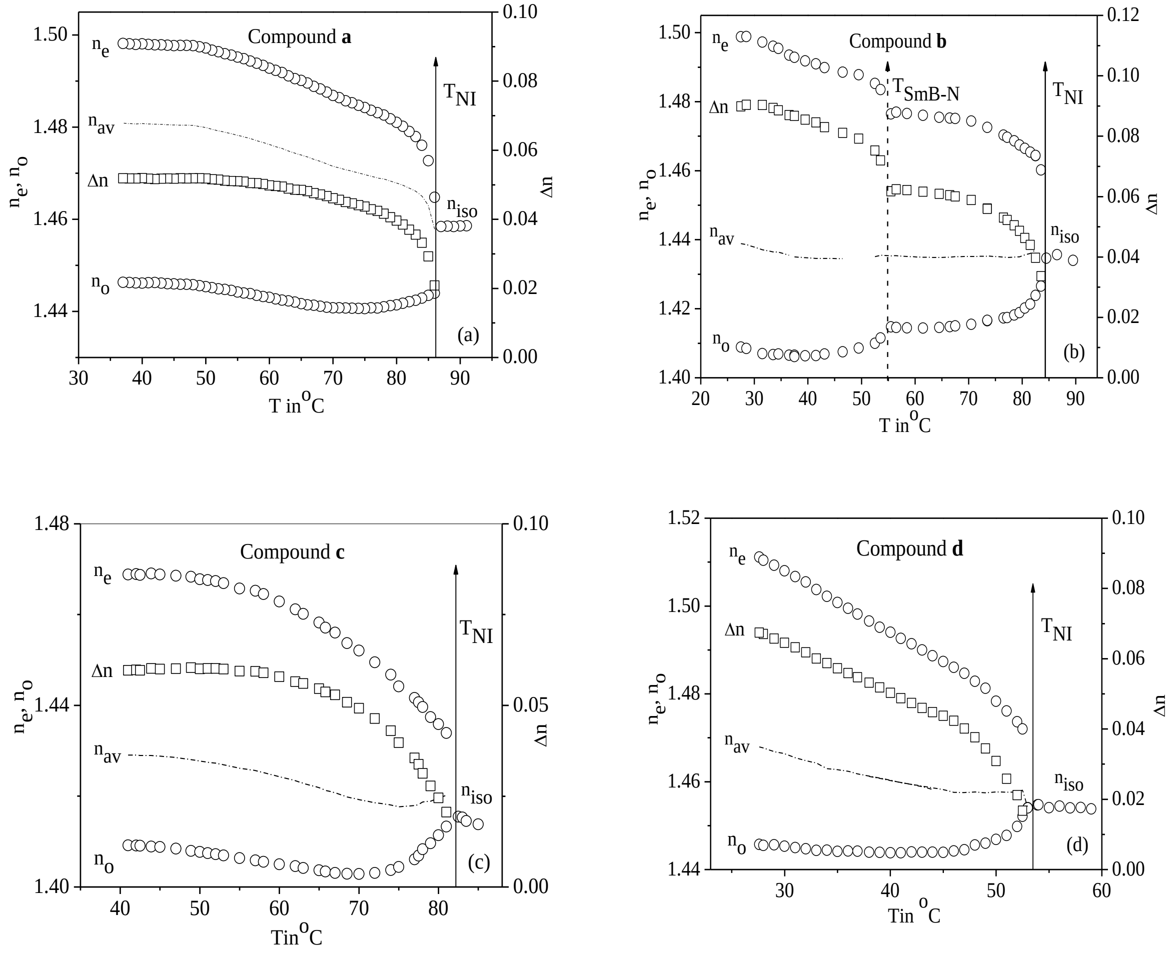
3. Results and discussions

3.1 Texture studies

The transition temperatures and textures [28] 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.

3.2 Refractive index measurements

The temperature dependence of the principal refractive indices n_o and n_e, the average value $n_{av} = \frac{n_e + 2n_o}{3}$ and the refractive index in the isotropic phase (n_{iso}) at a wavelength of λ = 632.8nm for the seven compounds were measured by thin prism technique [24] and are shown in Fig. 1(a)-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. The birefringence (Δn) values of all the compounds are very low and are less than 0.12 even in the smectic B phase [29]. This is not surprising because all the bicyclohexane compounds have low polarizability anisotropy due to their nonlinear structure and absence of conjugated π-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 [25]. These materials are used in vertically aligned mode mixtures to fine tune the birefringence of the finished product and to meet the specifications prescribed by the existing cell gap.



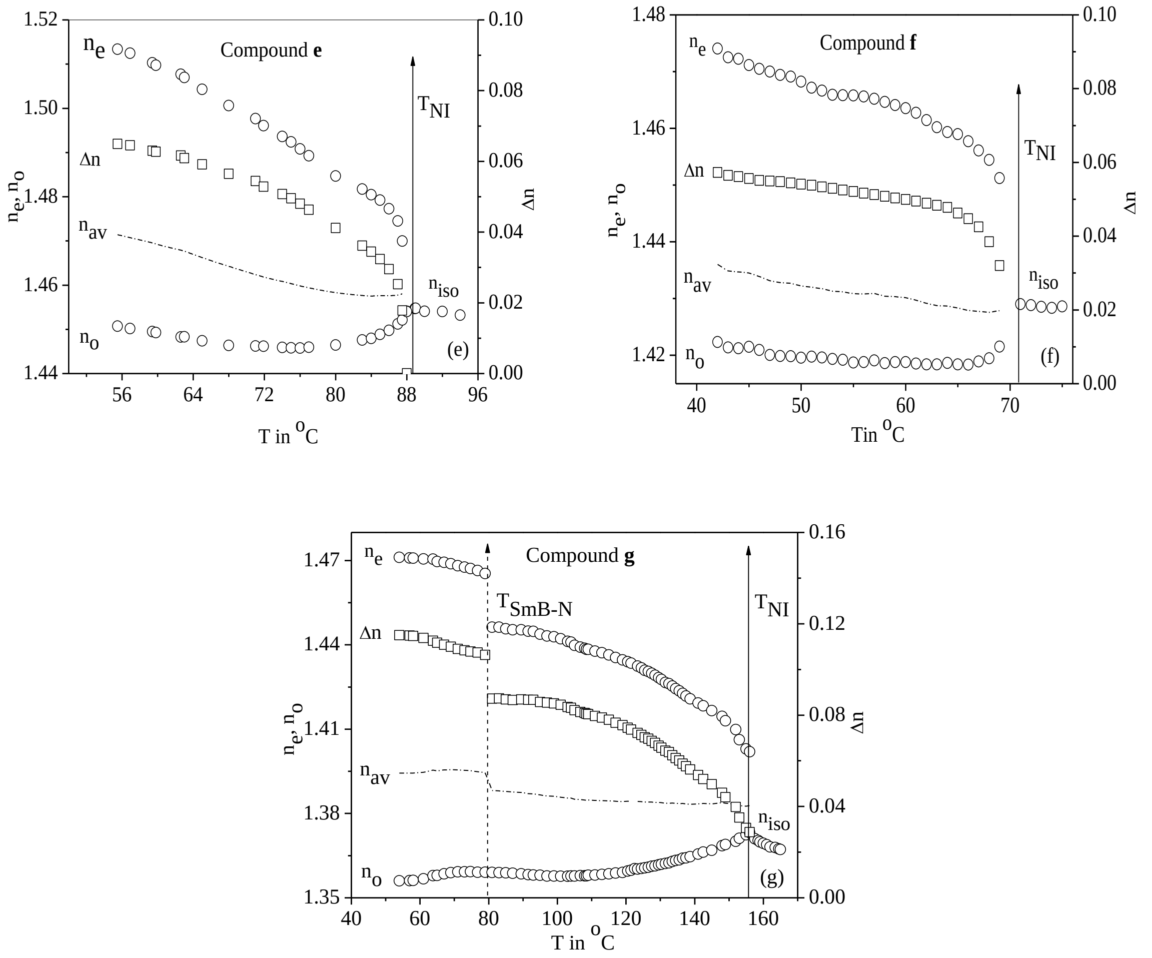


Fig. 1. Experimental values of the refractive indices n_e and n_o as a function of temperature for (a) compound **a**, (b) compound **b**, (c) compound **c**, (d) compound **d**, (e) compound **e**, (f) compound **f** and (g) compound **g**. Solid arrow and dashed arrow denote the nematic-isotropic (T_{NI}) and nematic-smectic B (T_{SmB-N}) phase transition temperatures respectively.

3.3 Optical birefringence measurements

The optical birefringence (Δn) of the compounds have also been measured for wavelength λ= 632.8nm using a high resolution temperature scanning technique. These values have been compared with those obtained from thin prism technique and is shown in Fig. 2. It is observed that the Δn values obtained from the 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 5.0µm 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 [24] 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 **g**. A comparison of the birefringence of the different compounds is given below:

Δn **g>b>d>e~a>c>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 π 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 Δn. The optical anisotropy strongly depends on the length of the total alkyl chain. The experimental temperature dependence of Δn in the nematic phase has been fitted to the form [8]:

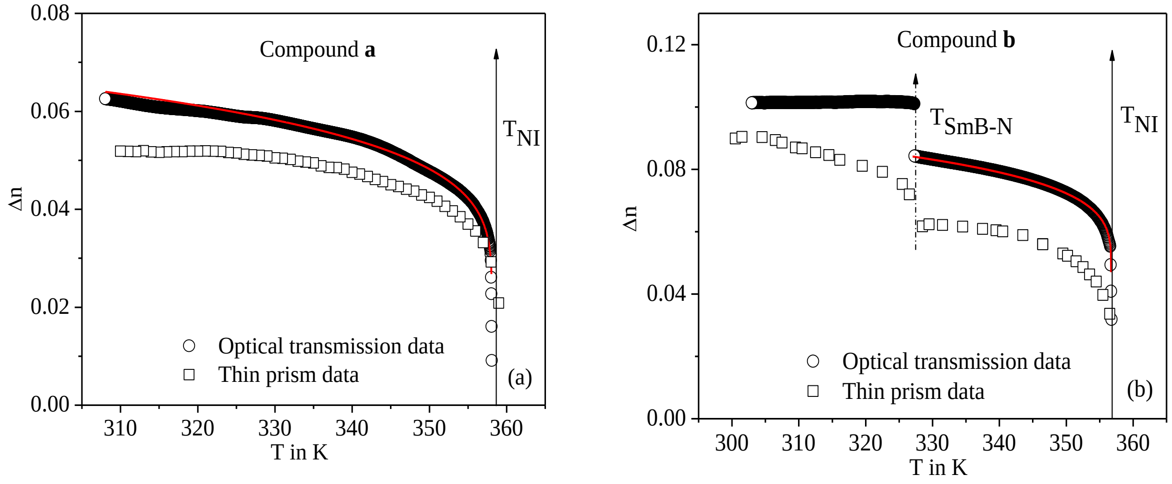
$$\Delta n = \Delta n_0 (1 - \frac{T}{T*})^{\beta} \tag{1}$$

where, Δn_0, the birefringence at T=0K, T* and β are fitting parameters. T is the absolute temperature and T* is slightly greater than the clearing temperature T_{NI}. This procedure is equivalent to the extrapolation of Δn to the temperature of absolute zero. The values of the fitting parameters are shown in Table 2.

Table 2. Values of adjustable parameters Δn_0, T* and β

Comp. Name	**Δn_0**	**T* in K**	**β**
a	0.090±0.001	359.0±0.1	0.170±0.001
b	0.108±0.001	357.1±0.1	0.102±0.001
c	0.100±0.010	360.6±0.7	0.197±0.047
d	0.113±0.020	328.5±0.5	0.152±0.002
e	0.090±0.001	361.9±0.1	0.188±0.001
f	0.083±0.001	341.9±0.1	0.180±0.003
g	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 (Δn) 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 $<P_2>$.



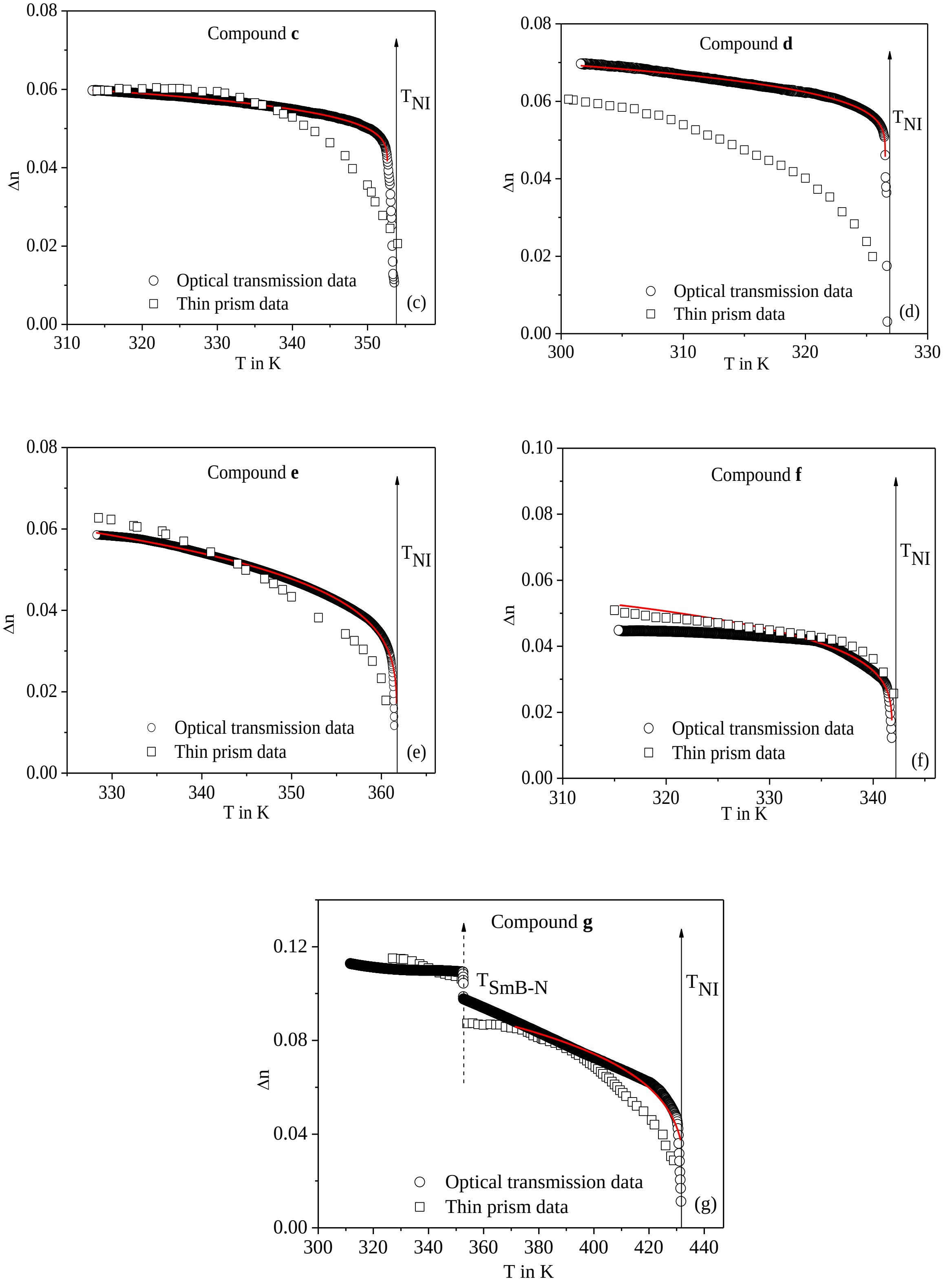


Fig. 2. Birefringence (Δn) as a function of temperature for (a) compound **a**, (b) compound **b**, (c) compound **c**, (d) compound **d**, (e) compound **e** (f) compound **f** and (g) compound **g**. Solid arrow and dashed arrow denote the nematic-isotropic (T_{NI}) and nematic-smectic B (T_{SmB-N}) phase transition temperatures respectively. o - represent the

birefringence data from OT method and □ - represent the birefringence data from thin prism method and the solid lines are fit to Equation (2).

It is expected that the critical exponent β, characterizing the temperature dependence of the order parameter, should indicate the membership of one of the possible university classes of phase transitions in liquid crystals. The critical exponents β obtained from Haller's extrapolation lies within the range 0.102 to 0.230 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 β which do not fit with any of the theoretical predictions. Recently, a four parameter power-law expression, 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 [11]:

$$D = A[B + (1-B)(1-\frac{T}{T^*})^{\beta}] \qquad (2)$$

where, D is the physical parameter under consideration (birefringence in this case), A and B are constants, β is the critical exponent and T* is slightly greater than the clearing temperature. The solid lines in Fig. 2 represent the four parameter fit to birefringence (Δn) data for all the compounds studied. The fitting were performed by considering the data points in the nematic phase only. Table 3 lists the different parameters obtained by fitting the experimental data to Equation (2). It is found that the order parameter critical exponent β has the values in between 0.240 to 0.249. These values of the β are very close to the predicted value 0.25 acoording to the tricritical hypothesis (β_{TCH} = 0.25) which strongly supports the tricritical nature of the nematic-isotropic (N-I) phase transition.

Table 3. Values of the four adjustable parameters A, B, T* and β

Comp. Name	**A**	**B**	**T* in K**	**β**
a	0.091±0.001	0.213±0.003	358.05±0.01	0.240±0.002
b	0.117±0.002	0.392±0.033	356.71±0.36	0.247±0.029
c	0.074±0.002	0.531±0.043	352.63±0.59	0.244±0.055
d	0.091±0.001	0.498±0.027	326.53±0.34	0.249±0.031
e	0.099±0.002	0.097±0.041	361.71±0.28	0.248±0.022
f	0.089±0.053	0.125±0.002	341.82±1.10	0.245±0.011
g	0.138±0.011	0.107±0.030	431.30±0.09	0.249±0.038

3.4 Density measurements and determination of orientational order parameter

The temperature variation of the density [25, 29, 30] values for pure compounds **a**-**g** is shown in Fig. 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.

Using the density and refractive index data (n_e, n_o), the principal molecular polarizabilities (α_e, α_o) has been calculated using Vuks method [19]. Thus the orientational order parameter $<P_2>$ can be determined from the relation

$$< P_2 > = \frac{\Delta\alpha}{\Delta\alpha_0} \qquad (3)$$

where Δα is the polarizability anisotropy and $\Delta\alpha_0$ is the same in the perfectly ordered state or at T= 0K. The $\Delta\alpha_0$ values were determined from the Haller's extrapolation technique [8] using the following equation:

$$\Delta\alpha = \Delta\alpha_0 \left(1 - \frac{T}{T^*}\right)^{\beta} \qquad (4)$$

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

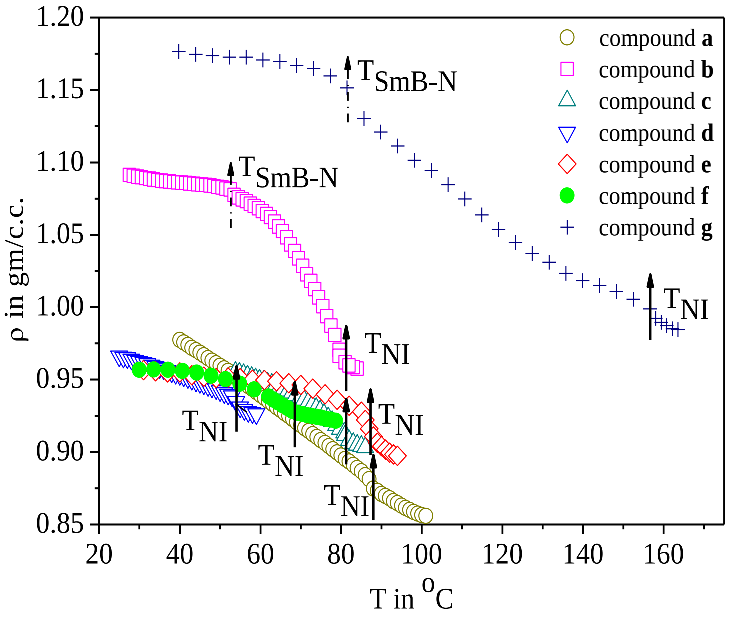


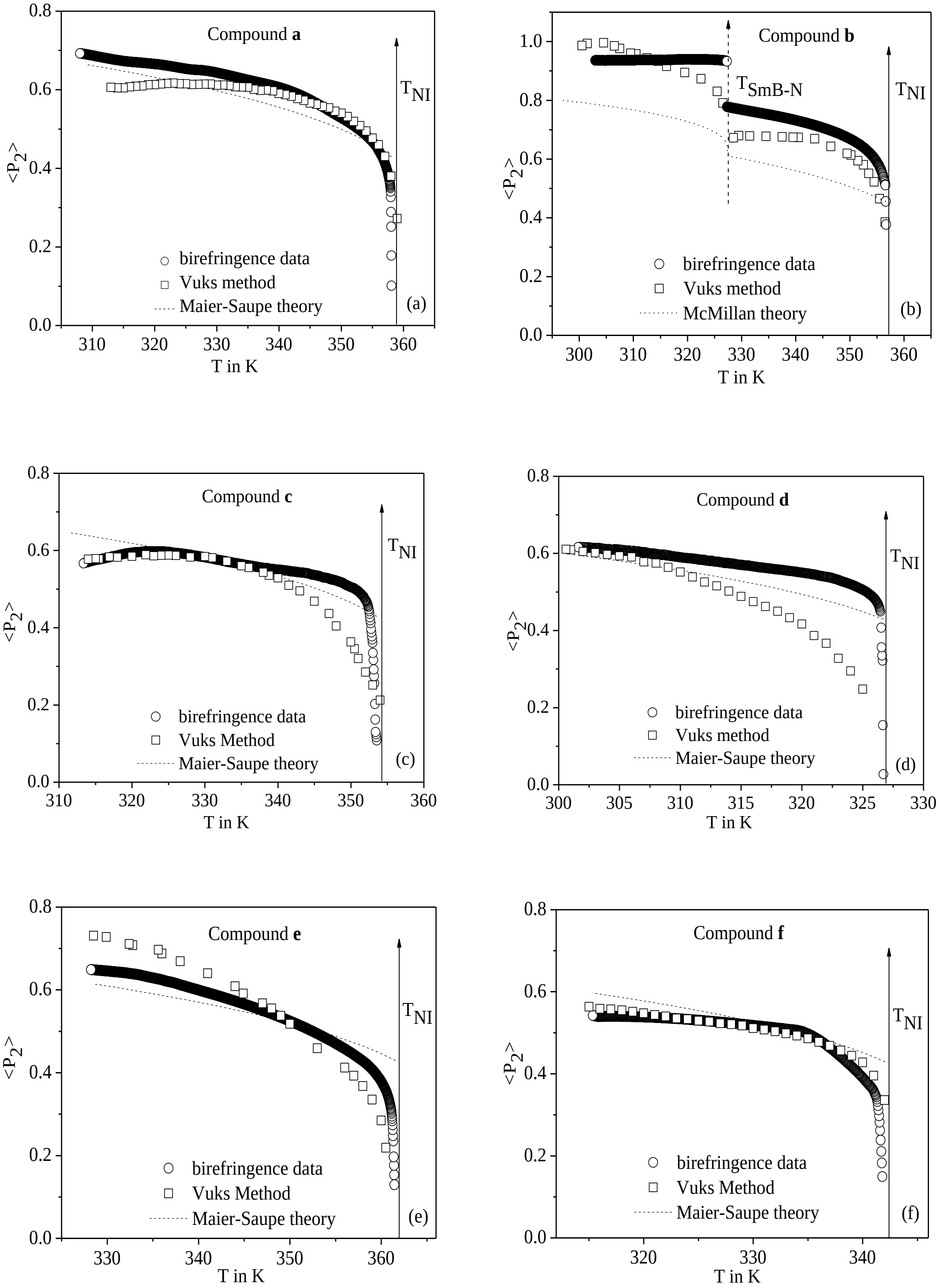
Fig. 3. Density as a function of temperature for compounds **a**-**g**. Key to symbol: o compound **a**, □ compound **b**, Δ compound **c**, ∇ compound **d**, ◊ compound **e**, ● compound **f** and + compound **g**. Solid arrow and dashed arrow denote the nematic-isotropic (T_{NI}) and nematic-smectic B (T_{SmB-N}) phase transition temperatures respectively.

In this work a simple procedure has been adopted to calculate the orientational order parameter ($<P_2>$) for the seven compounds under study. The optical birefringence, Δn, obtained from the optical transmission (OT) method was utilized to determine the temperature variation of the orientational order parameter $<P_2>$ in the liquid crystalline phases of these compounds. According to de Gennes [31], the anisotropy of any physical quantity can be a measure of the order parameter. Moreover, de Jeu [32] have showed that birefringence (Δn) can be used for this purpose. Kuczynski *et al.* [33] have also proposed a simple method to obtain the order parameter from birefringence (Δn) data which can be applied to nematogens as well as some smectogens. The temperature dependent birefringence is related to the order parameter as:

$$< P_2 >= \frac{\Delta n}{\Delta n_0} \tag{5}$$

where Δn_0 is the same as mentioned earlier. The order parameters determined in this way for all the compounds are shown in Fig. 4(a) – 4(g). It may be mentioned that for compounds **b** and **g** Equation (1) have been fitted by taking the values of Δn in the higher temperature nematic phase only.

The temperature dependence of orientational order parameter 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 (5) and are shown in Fig. 4. From Fig. 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 agreements with the Maier-Saupe [20] values and the McMillan theory [21] are reasonably good. The two sets of experimental data from two different methods differ by about 2%. Thus the direct extrapolation technique can be used to determine the order parameter of all the compounds from the optical birefringence data. It may also be mentioned that Kuczynski *et al.* [33] have also shown that the order parameter determined directly from birefringence measurements are consistent with the $<P_2>$ values calculated from the polarizability data. The values of adjustable parameters $\Delta\alpha_0$, T* and β are shown in Table 4.


Compound **a**
T_{NI}
birefringence data
Vuks method
Maier-Saupe theory
(a)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
310
320
330
340
350
360
Compound **b**
$T_{SmB\text{-}N}$
T_{NI}
birefringence data
Vuks method
McMillan theory
(b)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
1.0
300
310
320
330
340
350
360
Compound **c**
T_{NI}
birefringence data
Vuks Method
Maier-Saupe theory
(c)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
310
320
330
340
350
360
Compound **d**
T_{NI}
birefringence data
Vuks method
Maier-Saupe theory
(d)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
300
305
310
315
320
325
330
Compound **e**
T_{NI}
birefringence data
Vuks Method
Maier-Saupe theory
(e)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
330
340
350
360
Compound **f**
T_{NI}
birefringence data
Vuks Method
Maier-Saupe theory
(f)
$<P_2>$
T in K
0.0
0.2
0.4
0.6
0.8
320
330
340

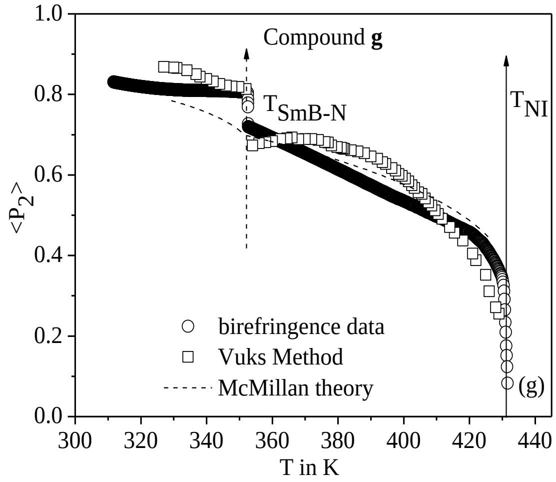


Fig. 4. Temperature variation of $<P_2>$ for (a) compound **a**, (b) compound **b**, (c) compound **c**, (d) compound **d**, (e) compound **e**, (f) compound **f** and (g) compound **g**. Solid arrow and dashed arrow denote the nematic-isotropic (T_{NI}) and nematic-smectic B (T_{SmB-N}) phase transition temperatures respectively. The dashed lines represent $<P_2>$ values from Maier-Saupe theory and McMillan's theory (only for Compound **b** and Compound **g**).

Table 4. Values of adjustable parameters $\Delta\alpha_0$, T* and β

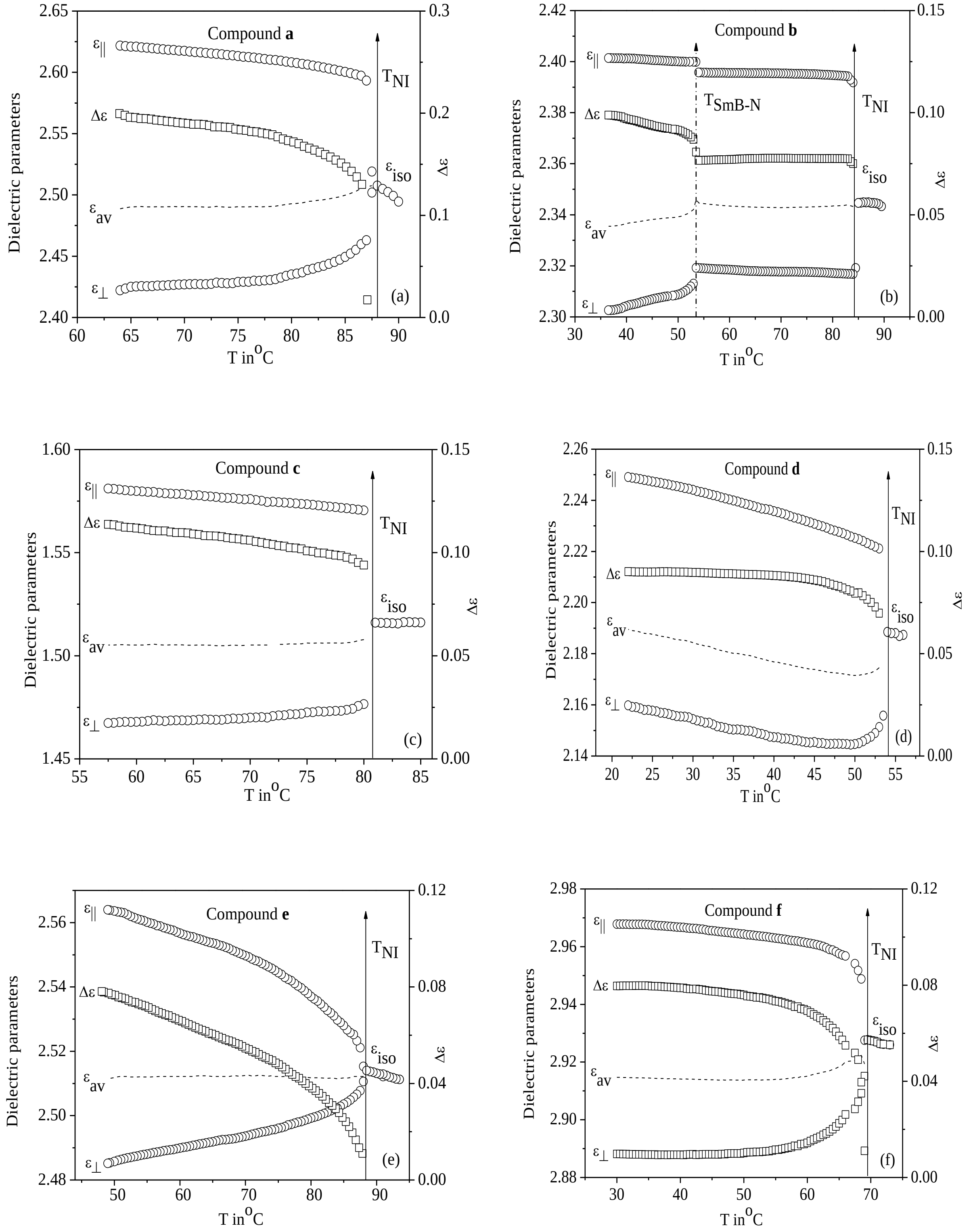
Comp. Name	$\Delta\alpha_0 \times 10^{24}$	**T* in K**	**β**
a	3.85±0.15	359.1±0.1	0.166±0.009
b	3.37±0.12	356.6±0.4	0.104±0.003
c	4.96±0.27	354.2±0.6	0.218±0.021
d	5.85±0.07	325.4±0.2	0.212±0.003
e	4.22±0.05	360.7±0.1	0.204±0.003
f	4.90±0.95	344.6±0.7	0.206±0.070
g	6.61±0.23	429.2±0.5	0.200±0.013

3.5 Dielectric permittivity measurements

The static dielectric permittivities $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ along and perpendicular to the molecular long axis and the average value $\varepsilon_{av} = \frac{\varepsilon_{\|} + 2\varepsilon_{\perp}}{3}$, are shown in Fig. 5(a)-5(g). The dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ of all the seven compounds are also presented in Fig. 5(a)-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 higher in comparison to other compounds mainly due to the strong dipole moment of C-F bond and the phenyl ring (Fig. 5(g)) at the terminal position. 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 [34].

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

$\varepsilon_{\|}$ **f>a>b>d~e>c>g**
$\varepsilon_{\perp}$ **f>a>b>d~e>c>g**
$\Delta\varepsilon$ **g>a>c>b>d~e>f**


Compound **a**
Dielectric parameters
2.65
2.60
2.55
2.50
2.45
2.40
0.3
0.2
0.1
0.0
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{NI}
ε_{iso}
(a)
60
65
70
75
80
85
90
T in ^{o}C
Compound **b**
Dielectric parameters
2.42
2.40
2.38
2.36
2.34
2.32
2.30
0.15
0.10
0.05
0.00
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{SmB-N}
T_{NI}
ε_{iso}
(b)
30
40
50
60
70
80
90
T in ^{o}C
Compound **c**
Dielectric parameters
1.60
1.55
1.50
1.45
0.15
0.10
0.05
0.00
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{NI}
ε_{iso}
(c)
55
60
65
70
75
80
85
T in ^{o}C
Compound **d**
Dielectric parameters
2.26
2.24
2.22
2.20
2.18
2.16
2.14
0.15
0.10
0.05
0.00
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{NI}
ε_{iso}
(d)
20
25
30
35
40
45
50
55
T in ^{o}C
Compound **e**
Dielectric parameters
2.56
2.54
2.52
2.50
2.48
0.12
0.08
0.04
0.00
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{NI}
ε_{iso}
(e)
50
60
70
80
90
T in ^{o}C
Compound **f**
Dielectric parameters
2.98
2.96
2.94
2.92
2.90
2.88
0.12
0.08
0.04
0.00
Δε
$\varepsilon_{||}$
Δε
ε_{av}
$\varepsilon_{\perp}$
T_{NI}
ε_{iso}
(f)
30
40
50
60
70
T in ^{o}C

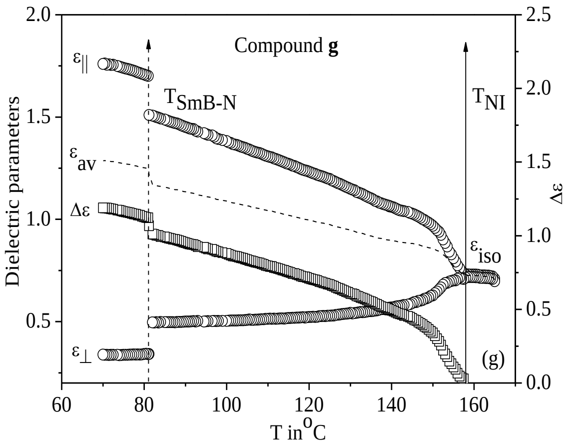


Fig. 5. Variation of dielectric permittivities ($\varepsilon_{||}$ and $\varepsilon_{\perp}$), dielectric anisotropy ($\Delta\varepsilon$) and average value of dielectric permittivity (ε_{av}) with temperature for (a) compound **a**, (b) compound **b**, (c) compound **c**, (d) compound **d**, (e) compound **e**, (f) compound **f** and (g) compound **g**. Solid arrow and dashed arrow denote the nematic-isotropic (T_{NI}) and nematic-smectic B (T_{SmB-N}) phase transition temperatures respectively. Key to symbols: o $\varepsilon_{||}$ and $\varepsilon_{\perp}$,□ $\Delta\varepsilon$ and **- - -** ε_{av}.

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 $\varepsilon_{||}$ and $\varepsilon_{\perp}$ than other compounds. It is observed that by decreasing the length of the terminal hydrocarbon CH_3 to C_2H_5 in compound **e** the $\varepsilon_{||}$ and $\varepsilon_{\perp}$ 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 π bonds) in compounds **a** leads to $\varepsilon_{||}$ and $\varepsilon_{\perp}$ values close to the ester compounds **d**, **e** and **f**. In case of phenylbicyclohexane fluorinated compound **g** value the $\varepsilon_{\perp}$ is lowest, hence it shows the highest dielectric anisotropy as there is no polar atom attached in the transverse direction. In the compounds **b** and **g** with polar terminal end, an increase in the $\Delta\varepsilon$ values is observed during the SmB-N transition (Fig. 5(b) and 5(g)). An opposite trend in the values of $\Delta\varepsilon$ for the ester compounds is observed. This is not surprising since in case of compounds **d, e** and **f**, the dipole moment of the oxygen atoms of ester linkage are pointing in the opposite directions with respect to the molecular long axis.

4. 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. The mesophases given by 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 electro-dynamical phenomena which are present in dielectrics in general, and in liquid crystals in particular, without the effects resulting from coupling between applied electric fields and molecular dipoles. All the compounds belong to the non-polar bicyclohexane liquid crystal class exhibits pronounced nematic mesophases. These materials can be used in a minute amounts in the vertically aligned mode negative dielectric nematic mixtures primarily to lower the birefringence of the same.

The difference in the terminal molecule or chain markedly affects the behavioral change in different compounds. Compound **g** exhibits higher birefringence (Δn) and dielectric anisotropy ($\Delta\varepsilon$) in comparison to others as it is the only compound which possesses highly negative fluorine atom and benzene ring at the terminal position. The $\langle P_2 \rangle$, Δn and density (ρ) 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 the SmB 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 2–3%. Interestingly, the high resolution Δn 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 β 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 β values. Moreover, by analyzing the temperature behavior of the orientational order parameter both from optical birefringence (Δn) directly (OT data) and also from density and individual refractive indices, it has been found that temperature dependent behavior of the order parameter agree quite well upto 10^oC below the nematic-isotropic transition and deviates on the average around 2% far from the clearing temperature. Possible cause may be due to unrealistic manifestation of the optical characteristics of a liquid crystalline media arising for a precise reckoning of the local field surrounding a molecule far from the nematic-isotropic transition.

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