## X-ray diffraction, optical birefringence, dielectric and phase transition properties of the long homologous series of nematogens 4-(trans -4'- n -alkylcyclohexyl) isothiocyanatobenzenes

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# X-ray diffraction, optical birefringence, dielectric and phase transition properties of the long homologous series of nematogens 4-(*trans*-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes†

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The temperature dependence of density, refractive indices, apparent molecular length and intermolecular distance of 11CHBT, are reported, together with the static dielectric permittivities, $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\varepsilon_{iso}$ of 11CHBT and 12CHBT; the effect of chain length on various physical properties of the CHBT series is also discussed. All the temperatures $T_m$, $T_{NI}$ and $T_{NCr}$ show an odd–even (OE) effect, but transition enthalpies $\Delta H_m$ and $\Delta H_C$ show no such behaviour. $T_m$, $T_{NI}$, $T_{NCr}$ and $\Delta H_m$ are found to increase with chain length, while $\Delta H_C$ shows a maxima at $n = 6$. At the common reduced temperature $T^* = 0.98 T_{NI}$, the density of the compounds are found to decrease with increasing chain length while the polarizability parameters $\alpha_e$, $\alpha_o$ and $\bar{\alpha}$ increase. However, the volume expansion coefficient, polarizability anisotropy and normalized polarizability anisotropy show a distinct OE effect. Similarly, $n_e$ decreases smoothly with chain length but $n_o$ and $\Delta n$ show an OE effect like $\varepsilon_{\perp}$ and $\Delta\varepsilon$. The ratio $\ln\langle P_2\rangle / \ln\langle P_4\rangle$ remains closer to Faber theory than MS theory. Effective dipole moments are found to be approximately constant in the series; antiparallel association is observed in all the members. Kirkwood correlation factors $g_{\perp}$ and $\Delta g$ are found to exhibit an OE effect like $\varepsilon_{\perp}$ and $\Delta\varepsilon$, but $g_{\parallel}$ and $\varepsilon_{\parallel}$ show no such effect. The effects of substitution in the core and end polar group on these properties are also discussed.

## 1. Introduction

The simplest molecules of low molecular mass liquid crystals (LCs) usually consist of a two-ring rigid core (mesogenic core) and two adjoining flexible (often alkyl or alkenyl) terminal groups, or one polar and one flexible group. The flexible end chain attached to the central rigid core of the LC molecules does not merely 'take up space' [1], rather end chains actually 'take an active part' in the anisotropic interactions [2]. The aliphatic chain of typical mesogenic molecules is essential for the creation and stabilization of mesophases, especially the nematic phase. If the chain length is below some critical value (usually propyl), the N–I transition (clearing point) is drastically lowered and no mesophase is observed.

The mesophase stability and many of its physical properties (transition temperature, enthalpies, elastic constants,

densities, polarizabilities, birefringence, orientational order parameters, dielectric permittivities, dipole correlation factors, conductivities, activation energies of conductivities and viscosities) are found to depend on the extent of flexible chain. Such macroscopic physical parameters of liquid crystals, if compared at a common reduced temperature (say at $T^* = 0.98 T_{NI}$ where $T_{NI}$ is the nematic–isotropic transition temperature) however show an overall increasing or decreasing trend. A significant alternation in the values of the parameters is also observed as a function of the number of carbon atoms (*n*) in the chain and is popularly known as the odd–even (OE) effect [3].

Since the physical properties depend strongly upon the type of LC phase, the effect of alkyl chain length can be discussed freely if the series studied contains a single phase, e.g. nematics only. In this context we have chosen the series 4-(*trans*-4′-*n*-alkylcyclohexyl)isothiocyanatobenzenes, *n*CHBT. They have unique properties among the LC families, the members $n = 2$–12 of the series show only the nematic phase. Therefore they may be considered

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Table 1.    Molecular structures of *n*CHBT and related compounds.

| Short Name | Structure | Phase |
|---|---|---|
| *n*CB | N≡C—⟨◯⟩—⟨◯⟩—C$_n$H$_{2n+1}$ | Nematic for $n < 8$ and SmA for $n \geqslant 8$ |
| *n*PCH | N≡C—⟨◯⟩—⟨H⟩—C$_n$H$_{2n+1}$ | Nematic for $n < 10$ and SmA for $n \geqslant 10$ |
| *n*CHBT | S=C=N—⟨◯⟩—⟨H⟩—C$_n$H$_{2n+1}$ | Nematic for $n \leqslant 12$ |

as a more typical nematic medium without local smectic organization in comparison with other polar nematic families.

In previous communications the following results have been discussed for the *n*CHBT series: phase transition temperatures and transition enthalpies for $n = 3$–10 [4]; density, refractive indices and dielectric constants for $n = 3$–10 [5]; X-ray diffraction (XRD) studies for $n = 3$ [6] and $n = 10, 12$ [7]; dielectric permittivity, conductivity anisotropy and activation energy of ionic movements for $n = 3$–10 [8, 9]; molecular dipole moments for $n = 5, 6$ [10–13]; optical birefringence, elastic constant and magnetic susceptibility studies for $n = 10, 12$ [7], and viscosities for $n = 0$–12 [14]. Several physical and molecular properties from XRD studies have been described for $n = 4$–9 [15, 16]. In this paper we discuss in detail the effect of chain length on different physical properties of the nematic phase for homologues of as large as possible ($n = 2$–12). We used existing data in revised form (tested again, if found doubtful), or made new measurements. The results of XRD and optical birefringence studies on 11CHBT and dielectric studies on 2CHBT, 11CHBT and 12CHBT, which were not reported earlier, are presented. We also compared the physical properties of the CHBT series with two other related series: the 4′-*n*-alkyl-4-cyano-biphenyls (*n*CB) and *trans*-4-alkyl-(4′-cyanophenyl)-cyclohexanes (*n*PCH). A strongly polar cyano group (dipole moment 4.06 D) is replaced by the less polar isothiocyanato group (dipole moment 3.06 D), and the rigid phenyl group by a more flexible cyclohexyl group for the *n*CB → *n*CHBT transformation. But for the *n*PCH → *n*CHBT transformation only the cyano group is replaced by the isothiocyanato group. The molecular structural formulae of the three series of compounds are given in table 1.

## 2.    Experimental

The *n*CHBT compounds were synthesized by the procedure described previously by Dabrowski *et al.* [4]. Transition temperatures (accuracy $\pm 0.1°$C) and enthalpies were determined by optical microscopy using a Mettler FP82HT hot stage and differential scanning calorimeter SETARAM 141 and are given in table 2 for the members not reported earlier.

0CHBT and 1CHBT are only virtual nematics with very low N–I transitions. Although 2CHBT is a monotropic nematic with an easily seen N–I transition at $-4°$C, it was studied only in the isotropic phase since no low temperature facility was available. The ordinary and extraordinary ($n_o$, $n_e$) refractive indices of 11CHBT were measured by the thin prism method, for three different wavelengths ($\lambda_V = 4758$ Å, $\lambda_G = 5461$ Å, $\lambda_Y = 5780$ Å). We used wedge-like cells made of two thin glass substrates treated with PVA solution and one glass spacer. A monochromatic beam from a Hg-lamp was made incident normal to one of the cell surfaces. Angles of refraction were determined by a precision spectrometer and the prism angle found to be 0.84°. Details of the measurement procedure were reported earlier [17]. Densities of 11CHBT were also measured with an accuracy of 0.1%, at various temperature, using a capillary-type dilatometer.

The dielectric constants of 11CHBT and 12CHBT, in the nematic as well as the isotropic phase, and of 2CHBT in the isotropic phase, were measured using an LCR

Table 2.    Phase transition temperatures ($°$C) and the enthalpies [in square brackets] of transition (kJ mol$^{-1}$) for some members of the *n*CHBT homologous series.

| 0CHBT | Cr 29.1 (N*[b]–150)[a] I |
| | [12.9] |
| 1CHBT | Cr 46.0 (N*–43) I |
| | [15.6] |
| 2CHBT | Cr 23 (N–4) I |
| | [12.0] |
| 11CHBT | Cr 48.1 {39.4} N 53.6 I |
| | [41.7]    [1.2] |
| 12CHBT | Cr 51.0 {44.0} N 52.8 I |
| | [56.7]    [1.3] |

[a] ( ) Monotropic transition.
*[b] Virtual transition estimated by extrapolation of clearing points of 6CHBT solutions.
{ } Supercooled crystallization temperatures.

bridge at 10 kHz. The frequency was low enough to ensure static dielectric behaviour of the compounds, and high enough to avoid effects due to ionic conductivity of the samples. The LCs were placed in cells made from ITO-coated conducting glass plates (thickness 7000 Å, conductivity 10.5–11.1 $\Omega/\square$) with a 190 μm gap. Care was taken not to introduce air bubbles while filling the cell by capillary action. The samples were aligned with a magnetic field of about 5 kG. The parallel component of permittivity $\varepsilon_\parallel$ was measured with the nematic director aligned homeotropically in the cell; for perpendicular component $\varepsilon_\perp$, the nematic director was aligned homogeneously. The amplitude of the applied constant voltage across the cell plates was about 300 mV, which was too small to disturb the alignment of the LC molecules.

Low angle X-ray photographs of magnetically aligned 11CHBT samples were taken throughout the mesomorphic range using Ni filtered CuK$_\alpha$ radiation. The experimental details have been reported earlier [18].

### 3. Results and discussion

The temperature variation of the refractive indices ($n_o$, $n_e$ and $\bar{n}$) and birefringence $\Delta n$ of 11CHBT are shown in figures 1 and 2, respectively. The extraordinary refractive index $n_e$ slowly decreases with increasing temperature while ordinary refractive index $n_o$ shows the opposite behaviour, as observed with other members of the series [5] and also in 5PCH, 7PCH [19] and the $n$CB series [20]. In the case of 3PCH [19], however, $n_o$ is found to decrease with temperature, though an increasing trend is present near $T_{NI}$. It is observed that both $n_o$ and $n_e$ and birefringence $\Delta n$ decrease with wavelength in a typical manner, though the effect is more prominent in case of $n_e$. The average refractive index $\bar{n}$ remains almost constant with temperature in the nematic phase as in the case of the shorter members, but decreases slowly in the case of $n$CB and $n$PCH. The optical birefringence decreases with temperature; the value at $0.98\,T_{NI}$ is found to be comparable with $n$CB but much higher than for $n$PCH.

The variation of density $\rho$ of 11CHBT with temperature is shown in figure 3; it decreases linearly in both the nematic and isotropic phases and remains constant in the solid phase. Fitted coefficients are $\rho_o = 1.0067$ gm cc$^{-1}$, $\rho_1 = -10.200 \times 10^{-4}$ gm cc$^{-1}$ °C$^{-1}$ in the nematic phase and $\rho_o = 0.9761$ gm cc$^{-1}$, $\rho_1 = -5.277 \times 10^{-4}$ gm cc$^{-1}$ °C$^{-1}$ in the isotropic phase. A small pretransitional effect is also observed on both sides of $T_{NI}$. The calculated volume expansion coefficient $\chi$ at $0.98\,T_{NI}$ is found to be $-10.660 \times 10^{-4}$ °C$^{-1}$ which is close to that of the $n$CB homologue but less than that of the $n$PCH homologue. Using refractive index and density values, the principal polarizabilities $\alpha_o$ and $\alpha_e$ in the nematic phase of 11CHBT for the three wavelengths were calculated following the methods of Neaugebauer [21] and Vuks [22]. The orientational order parameter $S$ was calculated using the relation $S = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp)$. The value of $(\alpha_\parallel - \alpha_\perp)$, the polarizability anisotropy in the crystal phase, was calculated by Haller's extrapolation method [23]. Although the anisotropy of molecular polarizability in the solid and mesophase, calculated by the Neaugebauer
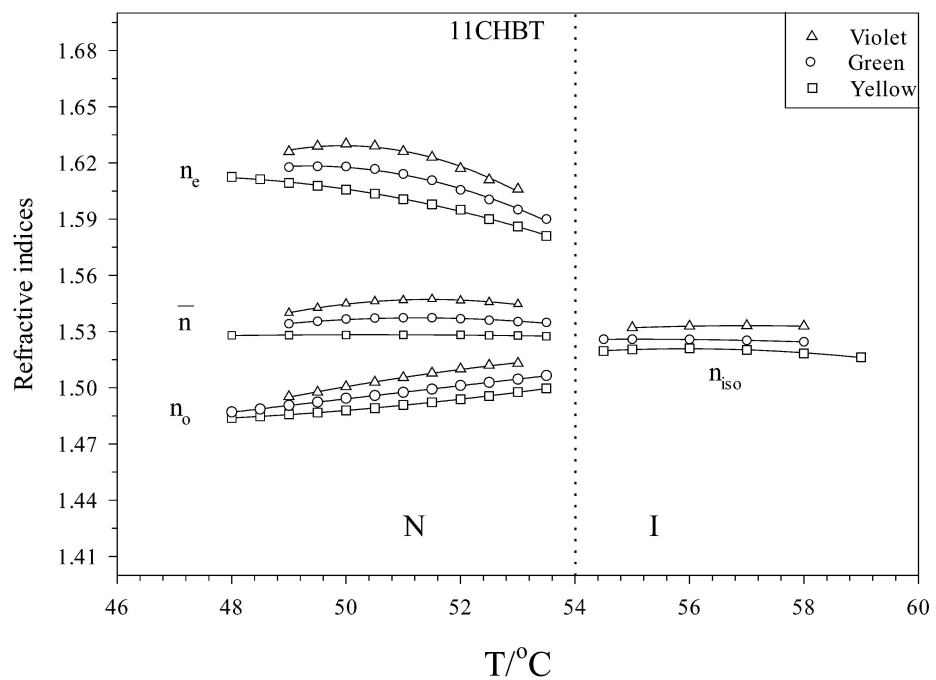


Figure 1.   Temperature variation of refractive indices of the compound 11CHBT at different wavelengths ($\lambda_V = 4758$ Å, $\lambda_G = 5461$ Å, $\lambda_Y = 5780$ Å).
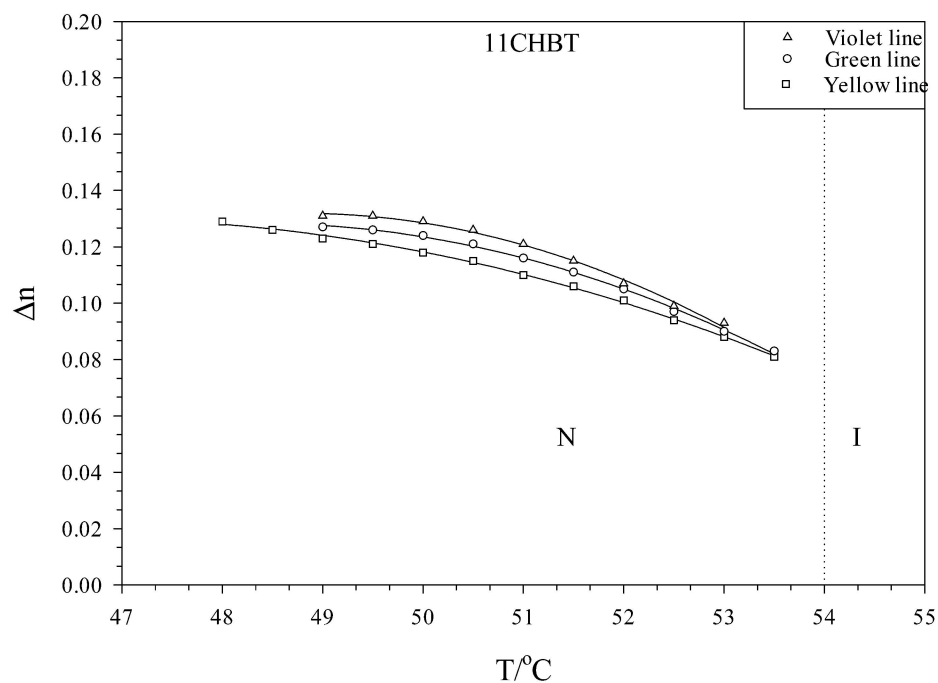
Figure 2. Variation of optical birefringence ($\Delta n$) with temperature for 11CHBT.
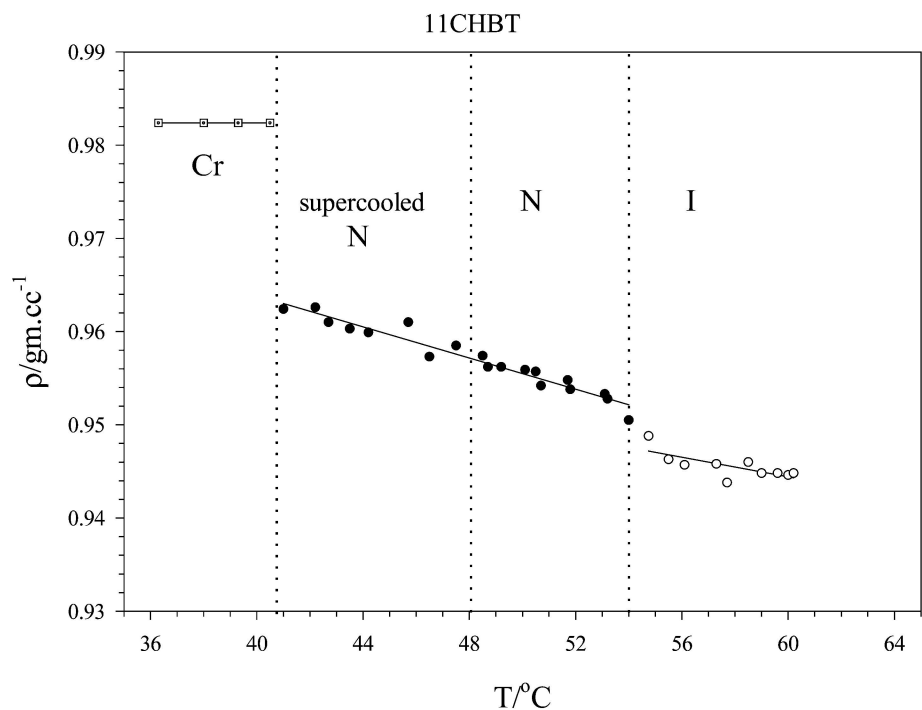


Figure 3. Density of 11CHBT as function of temperature.

and Vuks methods, differ from each other (since the assumed internal field model is different in the two cases [24]), the average polarizability $\bar{\alpha}$ and the order parameter values are very similar. So an average value of $S$ obtained from the two methods was taken. As expected, the order parameter values do not depend upon wavelength. The temperature variation of $S$ is shown in figure 4; at higher temperature region its value is found

to be much less than Maier–Saupe theoretical values [25] unlike for other members of the CHBT series [6, 7].

Values of dielectric permittivities, $\varepsilon_\parallel$, $\varepsilon_\perp$, $\bar{\varepsilon}$, $\Delta\varepsilon$ and $\varepsilon_{iso}$ for 11CHBT and 12CHBT, and only $\varepsilon_{iso}$ for 2CHBT, are shown in figures 5–7. In both cases $\varepsilon_{iso}$ is almost independent of $T$. $\varepsilon_\parallel$ decreases with increasing temperature, as expected for a polar Debye-type liquid, and all the members show positive dielectric anisotropy.
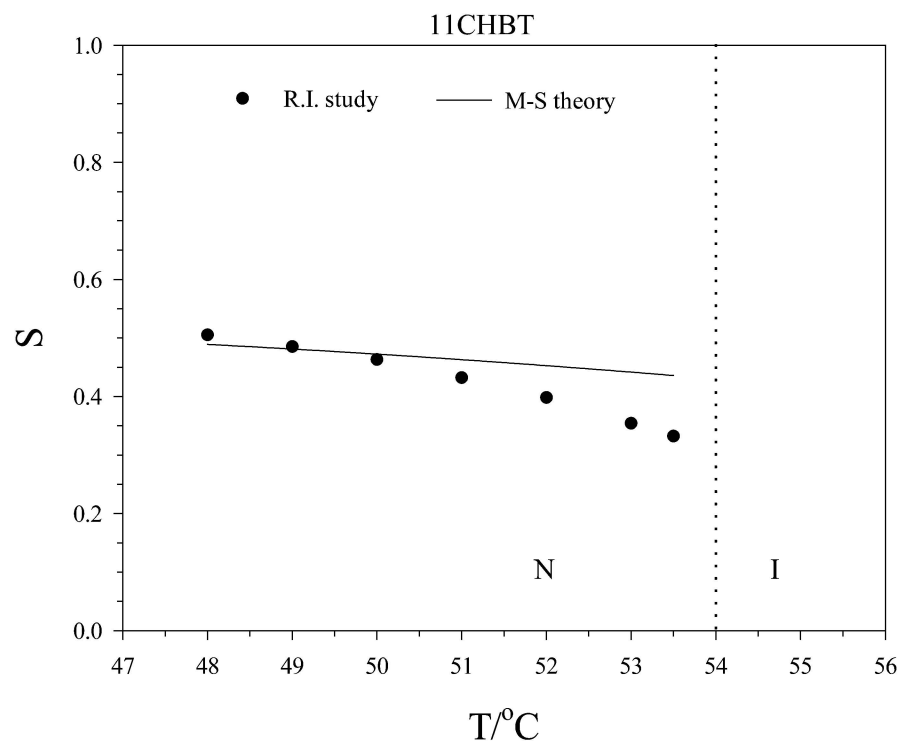
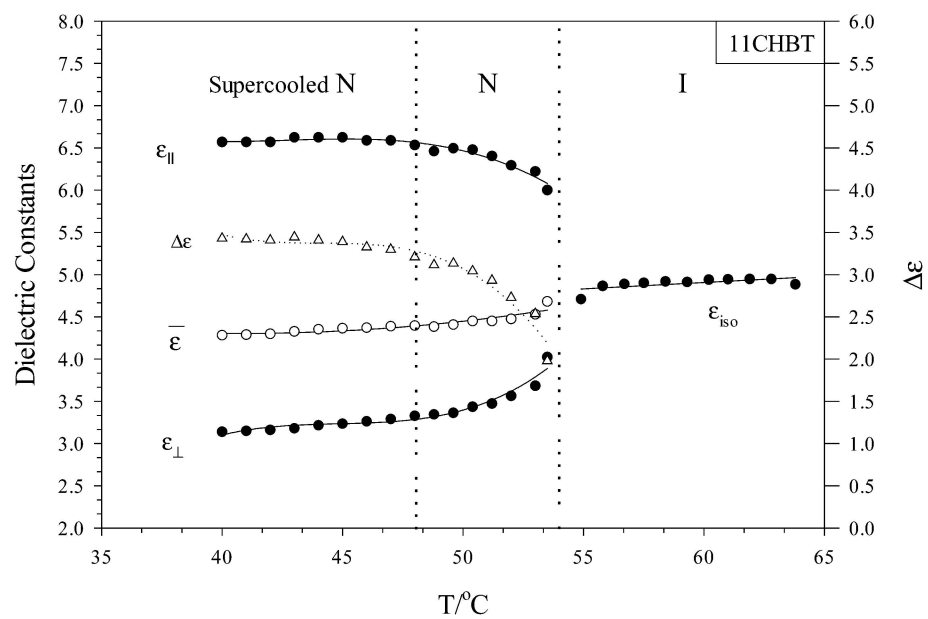Figure 4. Dependence of order parameter on temperature for 11CHBT.



Figure 5. Temperature variation of dielectric constants for 11CHBT.

However, the average dielectric constant $\bar{\varepsilon}$ is less than the extrapolated value of $\varepsilon_{iso}$ at $T < T_{NI}$ in both 11CHBT and 12CHBT. These results are in agreement with results for other members of the series [5, 8, 9] and with other axial polar molecules [26, 27]. Non-polar molecules do not show such behaviour [28]. This suggests the existence of short range antiferroelectric order in the nematic phase [29, 30]. In both cases dielectric anisotropy decreases

with increased temperature, at first slowly and then rapidly near the N–I transition, as with other members of the series [8]. Some of the dielectric parameters at selected temperatures are given in table 3.

The effective dipole moment $\mu$ of molecules in the nematic phase, and its inclination angle $\beta$ with the long molecular axis, were calculated for the members ($n = 3$–12) of the $n$CHBT series using the Maier–Meier [31, 32]
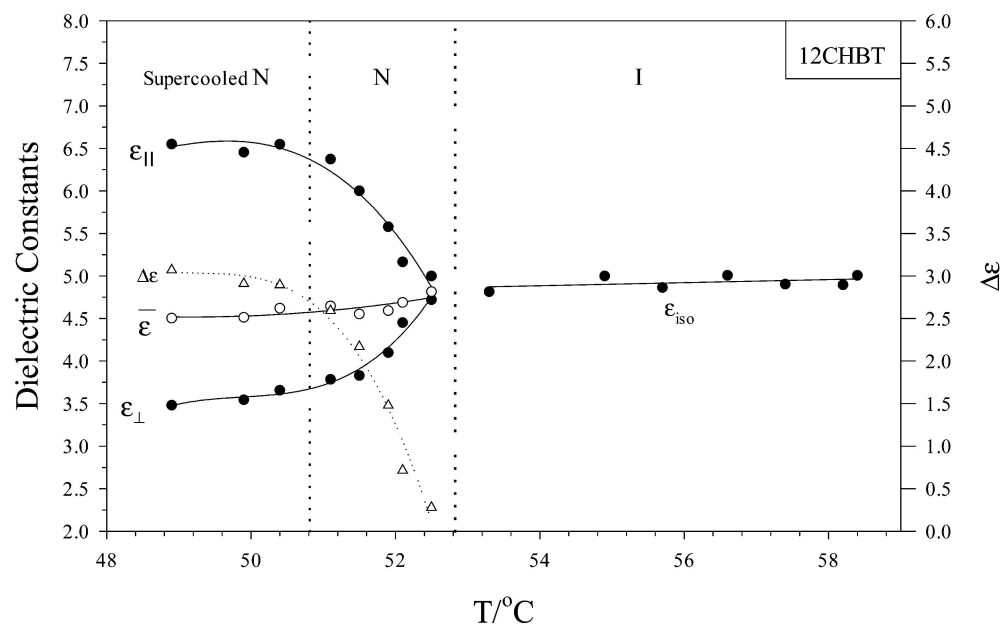
Figure 6.    Temperature variation of dielectric constants for 12CHBT.
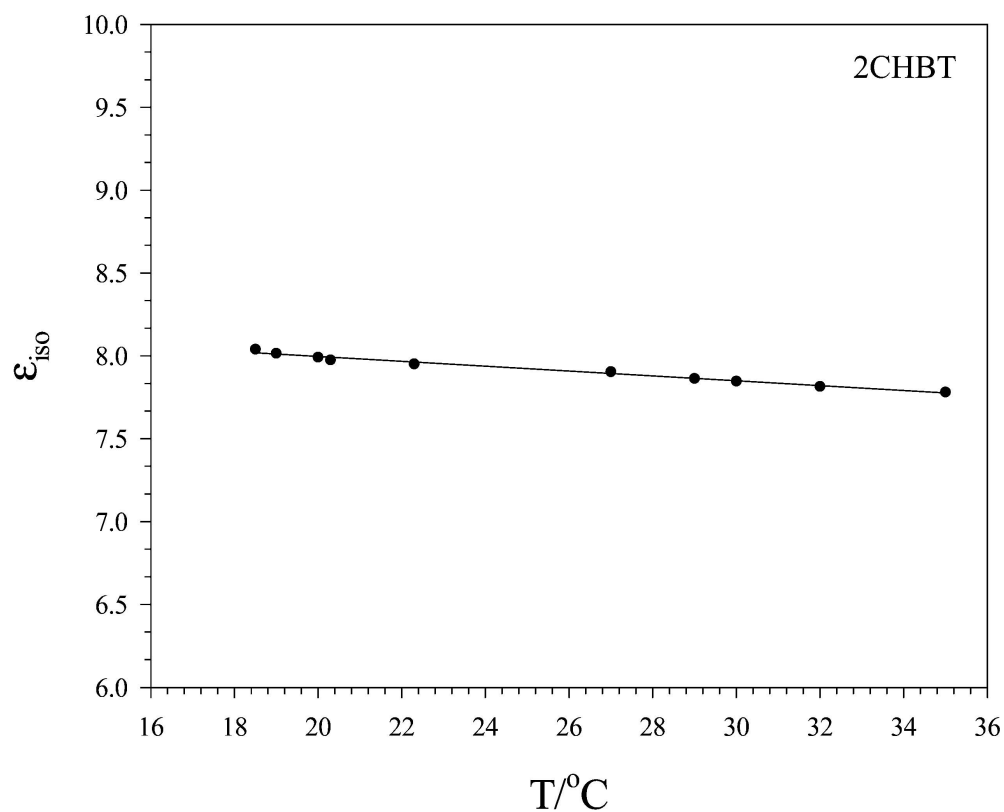


Figure 7.    Variation of dielectric constant with temperature for 2CHBT.

expressions for $\varepsilon_\parallel$ and $\varepsilon_\perp$. The values of optical polarizability and order parameter obtained from the birefringence study were used in the calculation. Since free molecular dipole moment values for 11CHBT and 12CHBT were not available, we used the value 3.50 D for 6CHBT [11, 12]. It has been shown previously for the *n*CB series that with changing length, the free molecular dipole moment does not vary appreciably [33, 34]. The

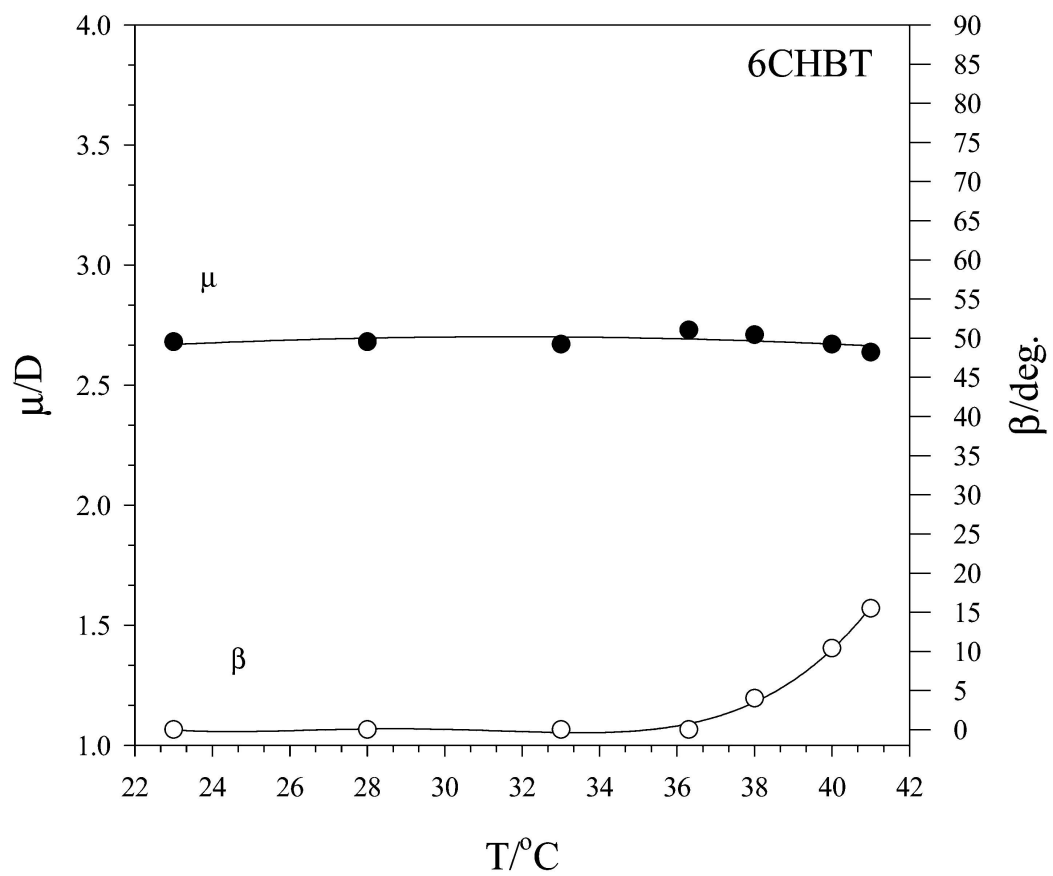Figure 8.   Effective molecular dipole moments and their orientation with molecular axis, as a function of temperature.
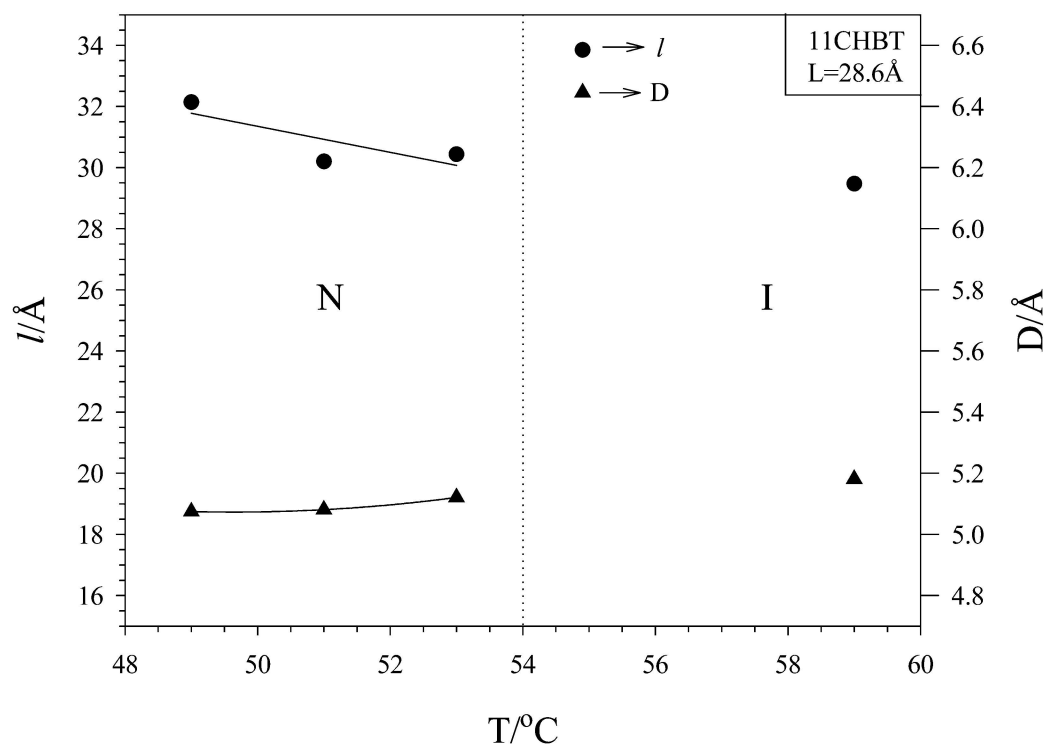


Figure 9.   Variation of apparent molecular length *l* and intermolecular distance *D* with temperature for 11CHBT.

effective values of dipole moments in nematic phase are found to be 70% of the free molecular dipole moment. This further indicates that antiparallel correlation exists between nearest dipoles in the nematic phase [29], and it was also observed in $CCl_4$ solution [12]. The dipole moment $\mu$ and orientation angle $\beta$ do not vary significantly with temperature. The temperature dependence of $\mu$ and $\beta$ is shown in figure 8 for 6CHBT; similar

behaviour was observed in other members of the series. $\beta$-values suggest that the molecular dipoles are approximately on-axis, though appreciable values of tilt angle are observed near $T_{NI}$ which may be a pretransition effect.

The XRD patterns of 11CHBT confirm that it possesses an ordinary nematic phase like other members of the series [6, 7, 15]. The average intermolecular distance $D$ at different temperatures is calculated from the peak positions
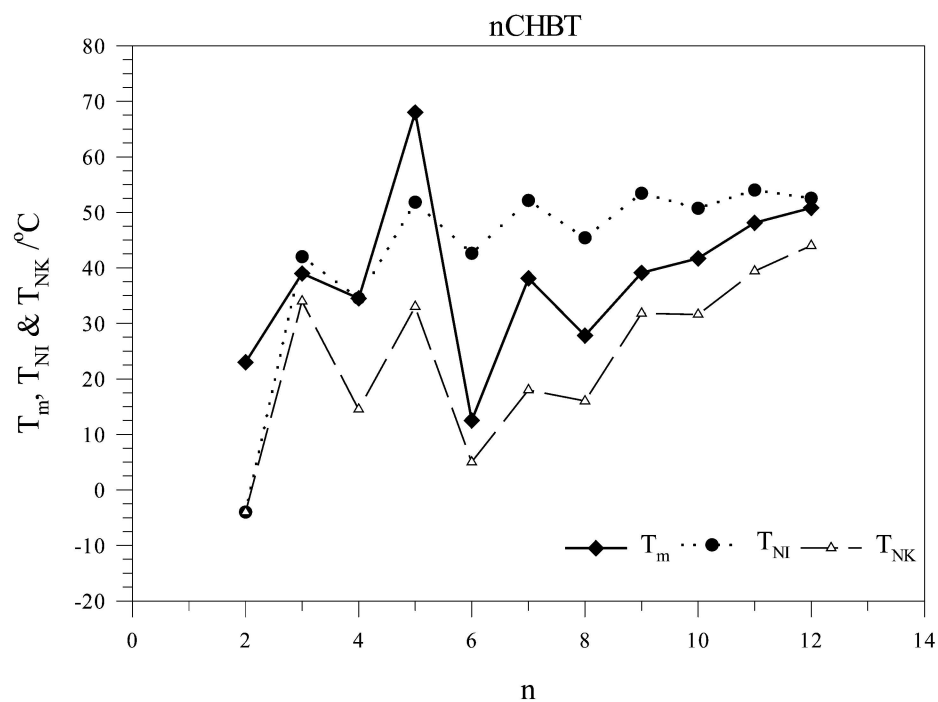


Figure 10. Variation of melting point $T_m$, nematic–isotropic transition $T_{NI}$ and crystallization $T_{NCr}$ temperatures of the $n$CHBT series with the number of carbon atoms $n$ in the alkyl chain.
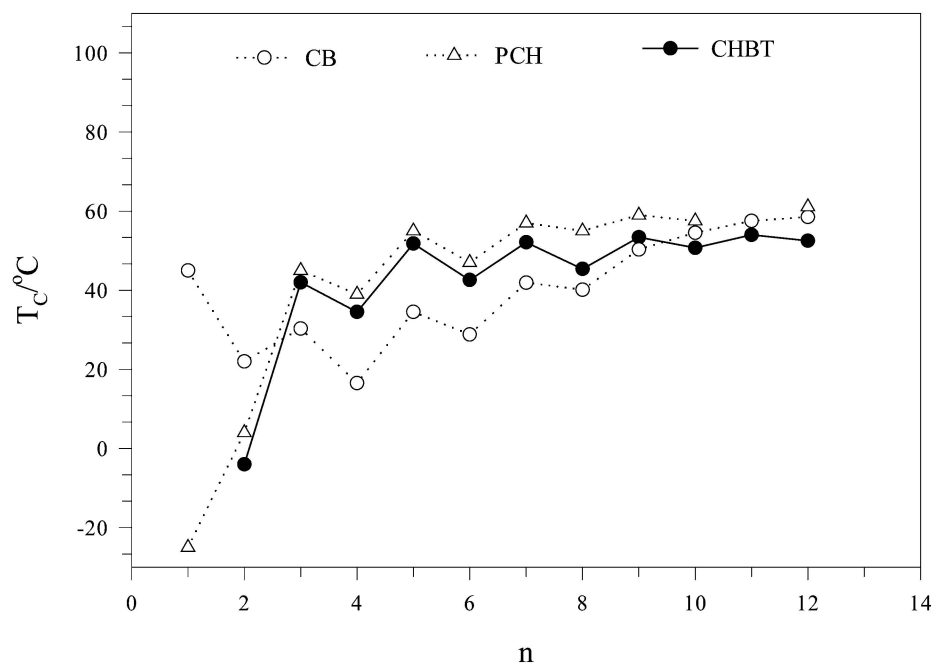


Figure 11. Variation of clearing temperatures $T_C$ of different series with the number of carbon atoms $n$ in the alkyl chain.

of the outer equatorial arc in the diffraction pattern, using the modified Bragg formula $D = 1.117\lambda/2 \sin \theta$ derived on the basis of cylindrical symmetry [35]. D-values slightly increase with temperature (figure 9) signifying a decrease in density of molecular packing; this is supported by density studies (figure 3).

The apparent molecular lengths $l$, determined from the meridional diffraction peak using the Bragg relation, are found to be slightly greater than the calculated molecular length ($L = 28.57$ Å) in the all-*trans*-configuration in 11CHBT, and are found to decrease with temperature (figure 9) as in the other homologues of the series [15]. The observed $l/L$ ratio is about 1.15, similar to that in other homologues. This again indicates that some bimolecular association exists in $n$CHBT compounds.

The extent and nature of the short range associations are found to depend on the molecular structure; its quantitative measurement was made by calculating the
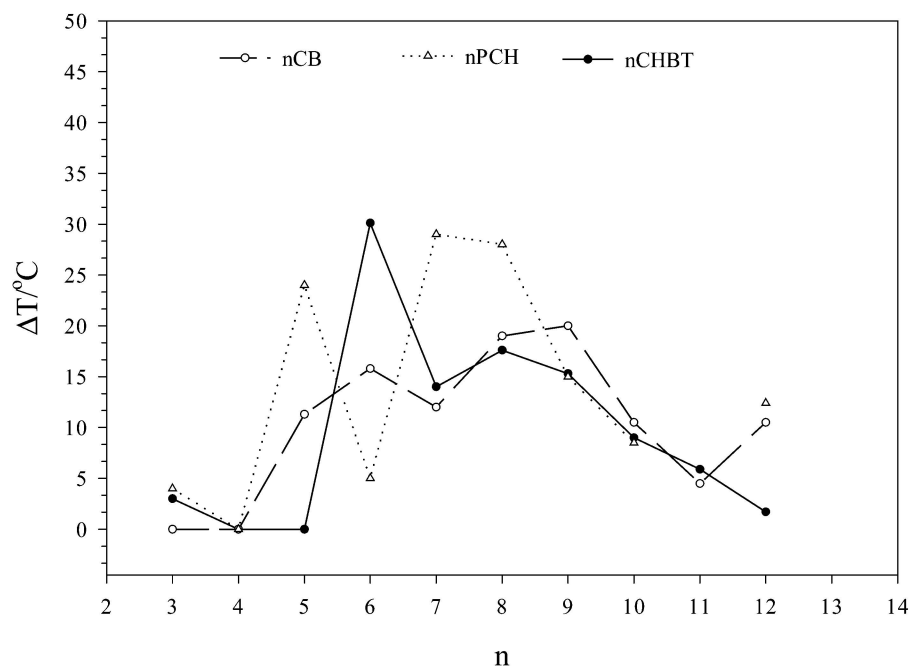


Figure 12. Variation of meso-morphic range $\Delta T$ with $n$ for the CB, PCH and CHBT series.
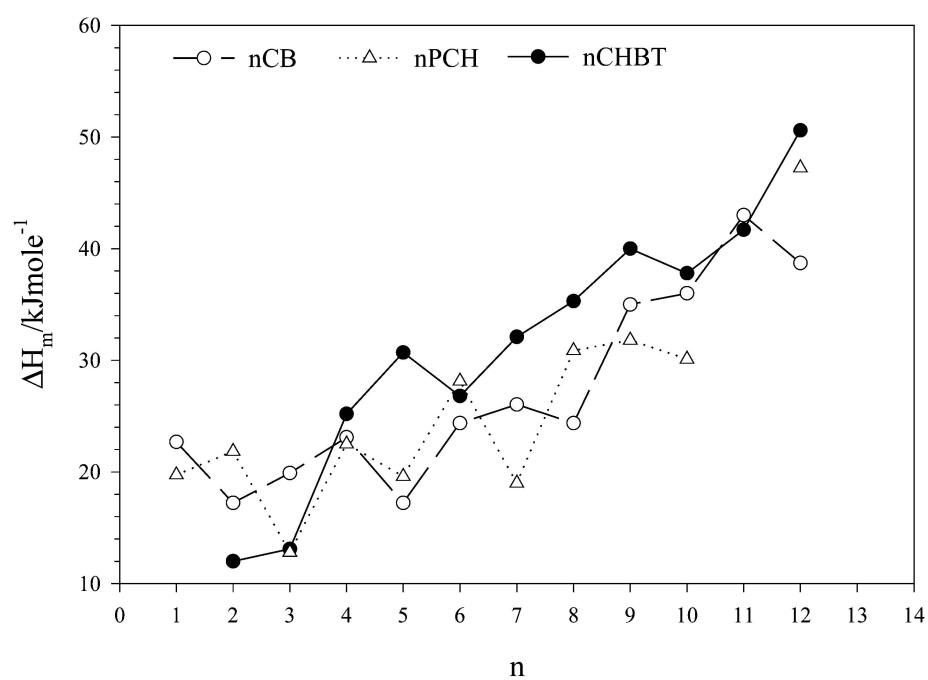


Figure 13. Variation of melting enthalpies $\Delta H_{\mathrm{m}}$ with $n$ for the CB, PCH and CHBT series.

Kirkwood correlation factor $g_\lambda$, where $\lambda$ refers to axes parallel and perpendicular to the nematic director. The calculation was made using the Bordewijk [37] theory of anisotropic dielectrics and following the procedure of Bata and Buka [38]. The necessary computer program

was developed. Here $g_\lambda = 1$ means no correlation at all and $g_\lambda < 1$ means antiparallel associations. In the case of 11CHBT and 12CHBT, both the $g_\parallel$ and $g_\perp$ values, shown in table 3, are found to be less than 1; and $g_\parallel < g_\perp$ indicating more antiparallel correlation along


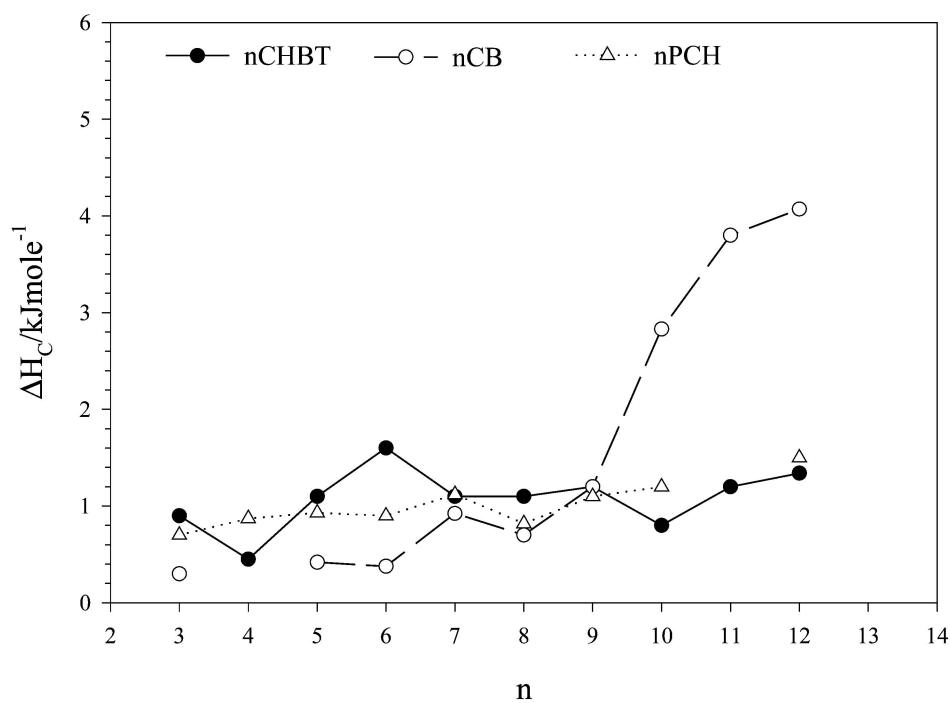
Figure 14.   Variation of clearing enthalpies $\Delta H_C$ with $n$ for the CB, PCH and CHBT series. $\Delta H_C = \Delta H_{NI}$ except for higher $n$CB and $n$PCH homologues, for which $\Delta H_C = \Delta H_{SI}$.
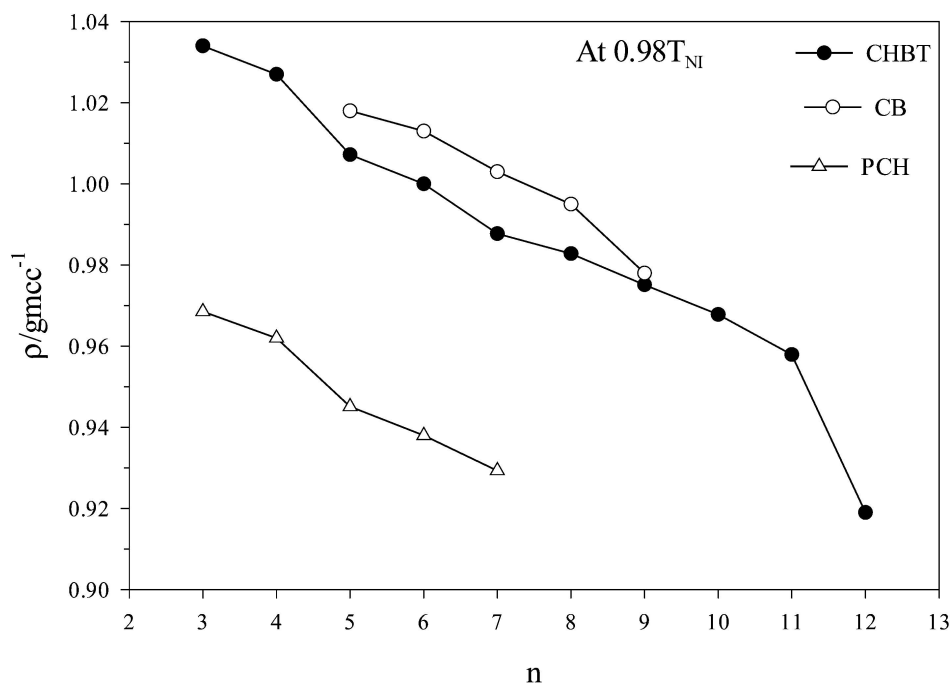


Figure 15.   Alkyl chain length dependence of density for the CB, PCH and CHBT series.

Table 3. Selected dielectric parameters of 11CHBT and 12CHBT.

| Compound | $T/°C$ | $\varepsilon_\parallel$ | $\varepsilon_\perp$ | $\Delta\varepsilon$ | $\mu/D$ | $\beta/°$ | $g_\parallel$ | $g_\perp$ | $T_\parallel$ |
|----------|--------|------|------|------|------|------|------|------|------|
| 11CHBT | 48[a] | 6.56 | 3.28 | 3.28 | 2.37 | 0 | 0.34 | 0.52 | 0.19 |
|  | 50 | 6.46 | 3.40 | 3.07 | 2.41 | 0 | 0.36 | 0.53 | 0.20 |
|  | 52 | 6.28 | 3.62 | 2.66 | 2.46 | 0 | 0.39 | 0.55 | 0.21 |
|  | 59 (iso) | $\varepsilon_{iso} = 4.89$ | | 0 | 2.73 | — | $g_{iso}^b = 0.61$ | | 0.17 |
| 12CHBT | 49[a] | 6.54 | 3.50 | 3.04 | 2.53 | 0 | 0.42 | 0.61 | 0.21 |
|  | 50 | 6.57 | 3.59 | 2.98 | 2.57 | 0 | 0.42 | 0.64 | 0.21 |
|  | 51 | 6.25 | 3.74 | 2.51 | 2.58 | 16.9 | 0.39 | 0.73 | 0.22 |
|  | 54 (iso) | $\varepsilon_{iso} = 4.88$ | | 0 | 2.81 | — | $g_{iso}^b = 0.64$ | | 0.18 |

[a] Temperature corresponds to $0.98 T_{NI}$.
$g_{iso}^b$ from Kirkwood–Fröhlich equation [36].

the molecular axis than in the perpendicular direction. As expected, the correlation in the isotropic phase is less than in the mesophase.

## 4. Effect of alkyl chain length on the mesogenic properties

To see how the different physical properties vary with the number of carbon atoms in the chain of the $n$CHBT molecules, we have considered the parameter values at the common reduced temperature $T^* = 0.98 T_{NI}$. Values of the relevant physical parameters of the $n$CHBT series are given in table 4. The parameters for other related homologous series are taken from reference [39].

Variation of melting point $T_m$, nematic–isotropic transition temperature $T_{NI}$ and crystallization temperature $T_{NCr}$ as a function of $n$ for the CHBT series is shown

in figure 10. Although all the parameters show an overall increasing trend, a strong OE effect is present which is more significant at lower values of chain length. It is also observed that odd members exhibit higher values than even members. A similar behaviour of $T_C$ (N–I or Sm–I) is observed in the $n$CB and $n$PCH series (figure 11). $T_{NI}$ increases with $n$ more strongly in the homologous series $n$CB and $n$PCH; here the smectic phase $A_d$ is more dominating than in the $n$CHBT series, where only the nematic order is observed. The observed tendency results probably from a higher degree of dimerization in the $n$CB and $n$PCH series, which increases the value of apparent molecular length $l$. Therefore in a LC medium real existing bodies are larger and the mesophase is better stabilized. It is also seen that for $n = 4–12$ the $T_C$ is maximum in the $n$PCH series, closely followed by the
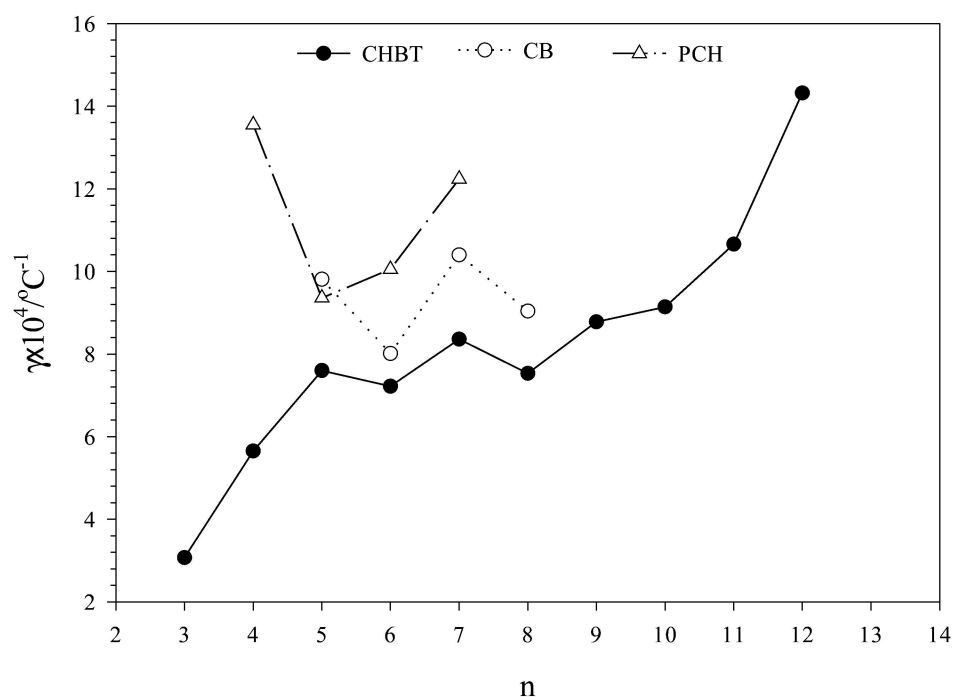


Figure 16. The dependence of volume expansion coefficient $\chi$ on alkyl chain length for the CB, PCH and CHBT series.

Table 4.   Some physical properties of the *n*CHBT series. Temperature-dependent properties correspond to $T^* = 0.98T_{NI}$. See text for details.

| $n$ | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|
| $T_m/°C$ | 39 | 34 | 68 | 12.5 | 38.1 | 27.8 | 39.1 | 41.7 | 48.1 | 50.8 |
| $T_c/°C$ | 42 | 34 | 51.8 | 42.6 | 52.1 | 45.4 | 53.4 | 50.7 | 54 | 52.8 |
| $T_{NCr}/°C$ | 34.0 | 14.5 | 33.0 | 5.0 | 18.0 | 16.0 | 31.8 | 31.6 | 39.4 | 44.0 |
| $\Delta T = T_c \sim T_m/°C$ | 3 | 0 | 0 | 30.1 | 14 | 17.6 | 14.3 | 9 | 5.9 | 1.7 |
| $T^* = 0.98T_{NI}/°C$ | 35.7 | 27.4 | 45.3 | 36.28 | 45.6 | 39.0 | 46.9 | 44 | 47.5 | 46 |
| $\Delta H_m/kJ\ mol^{-1}$ | 13.1 | 25.2 | 30.7 | 26.80 | 32.1 | 35.3 | 40.0 | 37.80 | 41.7 | 56.7 |
| $\Delta H_{NI}/kJ\ mol^{-1}$ | 0.90 | 0.45 | 1.10 | 1.60 | 1.10 | 1.10 | 1.20 | 0.80 | 1.2 | 1.3 |
| $n_o$ | 1.52 | 1.53 | 1.51 | 1.522 | 1.51 | 1.51 | 1.50 | 1.508 | 1.484 | 1.51 |
| $n_e$ | 1.69 | 1.67 | 1.67 | 1.654 | 1.64 | 1.63 | 1.63 | 1.627 | 1.612 | 1.61 |
| $\bar{n}$ | 1.58 | 1.58 | 1.57 | 1.567 | 1.55 | 1.55 | 1.55 | 1.548 | 1.528 | 1.544 |
| $n_{iso}$ | 1.57 | 1.57 | 1.56 | 1.559 | 1.55 | 1.54 | 1.54 | 1.540 | 1.516 | 1.549 |
| $\Delta n = n_e - n_o$ | 0.17 | 0.14 | 0.15 | 0.132 | 0.13 | 0.12 | 0.12 | 0.119 | 0.128 | 0.10 |
| $\rho/g\ cc^{-1}$ | 1.03 | 1.02 | 1.00 | 1.001 | 0.98 | 0.98 | 0.97 | 0.968 | 0.957 | 0.919 |
| $\chi \times 10^4/°C^{-1}$ | 3.07 | 5.65 | 7.60 | 7.22 | 8.36 | 7.53 | 8.78 | 9.14 | 10.66 | 14.32 |
| $\alpha_o/N_{eug}/Å^3$ | 30.1 | 32.3 | 33.8 | 35.97 | 37.6 | 39.6 | 41.1 | 43.15 | 43.45 | 47.82 |
| $\alpha_e/N_{eug}/Å^3$ | 39.9 | 41.1 | 43.7 | 45.15 | 47.3 | 49.1 | 51.5 | 53.39 | 55.14 | 59.68 |
| $\Delta\alpha/Å^3$ | 9.77 | 8.71 | 9.94 | 9.18 | 9.71 | 9.52 | 10.3 | 10.24 | 11.69 | 11.86 |
| $(\alpha_\parallel - \alpha_\perp)/Å^3$ | 15.3 | 16.1 | 16.1 | 14.91 | 16.7 | 16.0 | 17.1 | 20.96 | 23.63 | 23.90 |
| $\alpha/Å^3$ | 33.4 | 35.2 | 37.1 | 39.03 | 40.9 | 42.7 | 44.6 | 46.56 | 47.34 | 51.77 |
| $\Delta\alpha/\alpha$ | 0.29 | 0.24 | 0.26 | 0.235 | 0.23 | 0.22 | 0.23 | 0.220 | 0.247 | 0.229 |
| $N_C = 4\pi N\bar{\alpha}/3$ | 0.33 | 0.33 | 0.32 | 0.327 | 0.32 | 0.32 | 0.32 | 0.318 | 0.308 | 0.310 |
| $S = \langle P_2 \rangle_{optical}$ | 0.64 | 0.54 | 0.62 | 0.61 | 0.58 | 0.58 | 0.59 | 0.48 | 0.505 | 0.52 |
| $l/Å$ | 21.9 | 22.7 | 22.2 | 23.3 | 26.5 | 27.4 | 28.6 | 31.81 | 32.14 | 33.9 |
| $L_{MNDO}/Å$ | 18.9 | 19.7 | 21.4 | 22.24 | 23.4 | 24.8 | 26.4 | 27.30 | 28.55 | 29.83 |
| $l/L_{MNDO}$ | 1.16 | 1.15 | 1.04 | 1.05 | 1.13 | 1.11 | 1.08 | 1.16 | 1.13 | 1.14 |
| $D/Å$ | 5.09 | 5.06 | 5.08 | 5.08 | 5.09 | 5.12 | 5.10 | 5.08 | 5.07 | 5.08 |
| $\langle P_2 \rangle_{XRD}$ | 0.54 | 0.51 | 0.60 | 0.559 | 0.54 | 0.55 | 0.56 | 0.502 | — | 0.51 |
| $\langle P_4 \rangle_{XRD}$ | 0.14 | 0.17 | 0.21 | 0.149 | 0.14 | 0.17 | 0.15 | 0.167 | — | 0.142 |
| $R = \ln\langle P_2 \rangle/\ln < P$ | 0.31 | 0.37 | 0.33 | 0.305 | 0.31 | 0.33 | 0.30 | 0.385 | — | 0.335 |
| $\mu_{free}/D$ | 4.21 | 3.50 | 3.37 | 3.50 | 3.50 | 3.50 | 3.50 | 3.50 | 3.50 | 3.50 |
| $\varepsilon_\parallel$ | 12.7 | 11.2 | 10.5 | 10.74 | 8.76 | 8.28 | 8.89 | 8.2 | 6.561 | 6.541 |
| $\varepsilon_\perp$ | 4.80 | 4.86 | 4.4 | 4.30 | 4.6 | 3.96 | 4.18 | 3.88 | 3.284 | 3.503 |
| $\varepsilon_{iso}$ | 6.7 | 6.4 | 6.5 | 6.32 | 5.7 | 5.2 | 5.1 | 4.9 | 4.892 | 4.885 |
| $\varepsilon$ | 7.45 | 6.99 | 6.43 | 6.45 | 5.99 | 5.40 | 5.76 | 5.32 | 4.376 | 4.516 |
| $\Delta\varepsilon$ | 7.96 | 6.38 | 6.1 | 6.44 | 4.16 | 4.32 | 4.71 | 4.32 | 3.277 | 3.038 |
| $\mu/D$ | 2.66 | 2.66 | 2.67 | 2.71 | 2.70 | 2.53 | 2.78 | 2.67 | 2.37 | 2.53 |
| $\beta/°^a$ | 0 | 11.0 | 15.6 | 4.05 | 23.8 | 13.2 | 1.6 | 0 | 0 | 0 |
| $\mu_{iso}/D$ | 2.59 | 2.52 | 2.76 | 2.753 | 2.68 | 2.53 | 2.60 | 2.573 | 2.73 | 2.81 |
| $g_\parallel$ | 0.50 | 0.50 | 0.49 | 0.55 | 0.49 | 0.45 | 0.49 | 0.53 | 0.34 | 0.42 |
| $g_\perp$ | 0.76 | 0.77 | 0.86 | 0.79 | 0.93 | 0.73 | 0.95 | 0.71 | 0.52 | 0.61 |
| $g_{iso}(Kirk–Fröh)$ | 0.59 | 0.56 | 0.67 | 0.667 | 0.63 | 0.56 | 0.59 | 0.583 | 0.61 | 0.64 |
| $\Delta g = g_\perp \sim g_\parallel$ | 0.26 | 0.27 | 0.37 | 0.24 | 0.44 | 0.28 | 0.46 | 0.18 | 0.18 | 0.19 |
| $T_\parallel$ | 0.11 | 0.12 | 0.13 | 0.12 | 0.15 | 0.16 | 0.15 | 0.16 | 0.19 | 0.21 |

[a] Well below $T_c$ for all members, $\beta$ values are almost zero; large $\beta$ values for some members at $T^*$ may be due to a pre-transitional effect.

*n*CHBT series. The variation of thermal stability of the mesophase, $\Delta T = T_C - T_m$, as a function of *n* is shown in figure 12. $\Delta T$ shows a maximum at $n = 6$ in the *n*CHBT series, but does not show odd–even behaviour like other related series.

The variation of transition enthalpies $\Delta H_m$ and $\Delta H_C$ with number of $-CH_2-$ segments is displayed in figures 13 and 14. $\Delta H_m$ increase with *n* for all the compounds but only the *n*PCH series shows a distinct OE effect, with higher value for even *n* than for odd *n*. However,

$\Delta H_C$ shows no OE effect in any series. In the case of the *n*CB series we observe a strong increase of $\Delta H_C$ values for longer members, because the smectic phase appears.

The density at $0.98T_{NI}$ decreases monotonically with chain length in the *n*CHBT series like the *n*CB [20] and *n*PCH [19] series (figure 15). Members ($n = 3–12$) of the *n*OCB series also show similar behaviour [40]. The densities of corresponding *n*CHBT and *n*CB members are nearly equal, but that of *n*PCH members is much less. Thus when a flexible voluminous cyclohexyl group

is introduced into the core region in place of the rigid flat phenyl group ($n$CB→$n$PCH), the density decreases considerably, and the introduction of the heavy element S ($n$PCH → $n$CHBT) almost compensates the above effect. The decrease of $\rho$ in going from even to odd is greater than that in going from odd to even, although this effect gradually vanishes with higher homologues. The crystal phase is denser than the nematic phase, which in turn is denser than the isotropic liquid. So, as the degree of molecular order decreases the molecular packing density

also decreases. Within a homologous series the decrease of density with chain length suggests that the higher homologues are less ordered than the lower ones. Calculated volume expansion coefficients $\chi$ have also been found to exhibit an OE effect (figure 16) except for $n = 3, 12$.

Variation of refractive indices ($n_o$, $n_e$ and $\bar{n}$) with chain length at $0.98T_{NI}$, is shown in figure 17. All the refractive indices decrease slowly but monotonically with increasing chain length, except for 11CHBT for which minimum
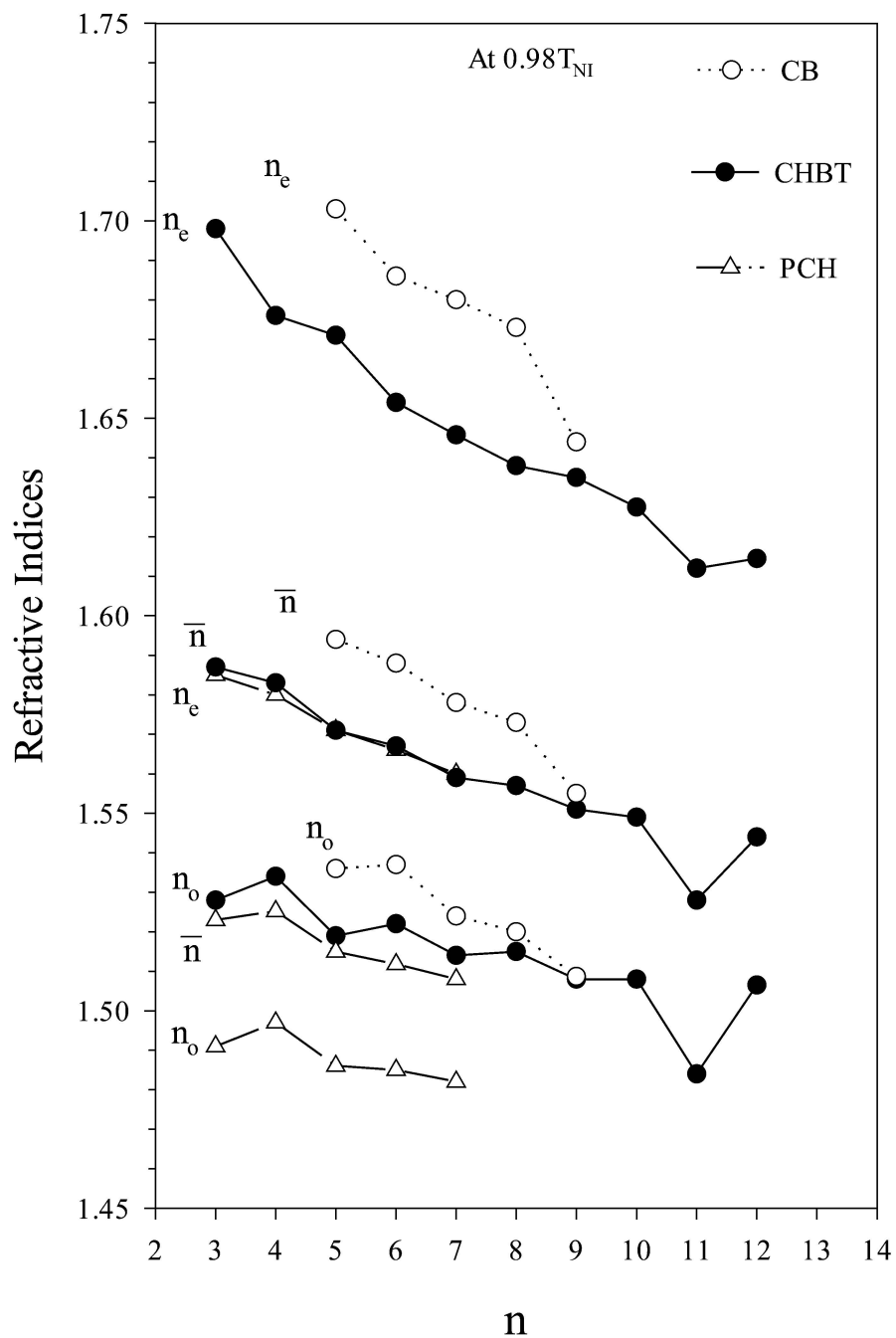


Figure 17. Variation of refractive indices with $n$ for the CB, PCH and CHBT series.

values are found. As displayed in figure 18 the optical birefringence $\Delta n$ reveals a distinct OE effect, though the refractive index $n_e$, measured along the director, decreases smoothly with increasing chain length, and $n_o$, the perpendicular component, reveals a weak OE effect; however, $\Delta n$ has higher values for odd $n$, while $n_o$ has higher values for even $n$. The alternation in $\Delta n$ is obviously the result of the alternating change in molecular polarizability anisotropy $\Delta\alpha$ caused by the alternation in the C–C bond angle in the terminal aliphatic chains (figure 19). The optical birefringences of $n$CHBT and $n$CB series members are nearly equal, but that for the $n$PCH series is much less, as has been observed in density and refractive indices values. Since aromatic rings have a higher polarizability anisotropy than alicyclic rings; the replacement of aromatic rings by alicyclic rings leads to a decrease in polarizability anisotropy and refractive index values and thus to the decrease of birefringence (CB → PCH), however this effect is compensated by the replacement of the –CN group by –NCS (PCH → CHBT).

The mean polarizability values, $\bar{\alpha}$, calculated by Neugebaur's method, are shown in figure 20 and found to increase smoothly with chain length. Similar behaviour is exhibited by the $n$CB and $n$PCH series [19, 20]. It is found that $\bar{\alpha}$ varies by about 5% between successive members of the series, as also observed in the $n$CB series

[20]. The polarizability anisotropy $\Delta\alpha$ shows an overall increasing trend (figure 19) and an OE effect. Higher values are found in odd members, as with $\Delta n$, but the values of $(\alpha_\parallel - \alpha_\perp)$ in the crystalline state show an overall increasing trend (figure 21); no systematic variation with chain length is observed.

In figure 22 the chain length variation of $\Delta\alpha/\bar{\alpha}$ (the anisotropy of molecular polarizability normalized against the average polarizability) is shown, and an overall decreasing trend with distinct OE effect is observed, odd members having higher values. This suggests that the contribution to $\Delta\alpha$ comes mainly from the core (–Cy–Ph–) part. The covalent bond electrons in the alkyl chains contribute more to $\bar{\alpha}$ than to $\Delta\alpha$. Therefore, the addition of carbon atoms in the alkyl chain increases $\bar{\alpha}$ more than $\Delta\alpha$. Similar behaviour has been observed in $n$CB [41] and in other polar compounds [42, 43]. Moreover, the average polarizability incorporated with number density of molecules $N_c = 4\pi N_A \rho \bar{\alpha}/3M = 4\pi N\bar{\alpha}/3$ decreases with $n$, as does density $\rho$ itself (figure 23). This suggests that $\rho$ decreases more rapidly with increase of chain length than $\bar{\alpha}$ increases with it.

A comparison of the ratio of the average value of apparent molecular length $l$, in the nematic phase (or smectic layer thickness), to the molecular model length $L$, for members of the $n$CB, $n$PCH, and $n$CHBT series
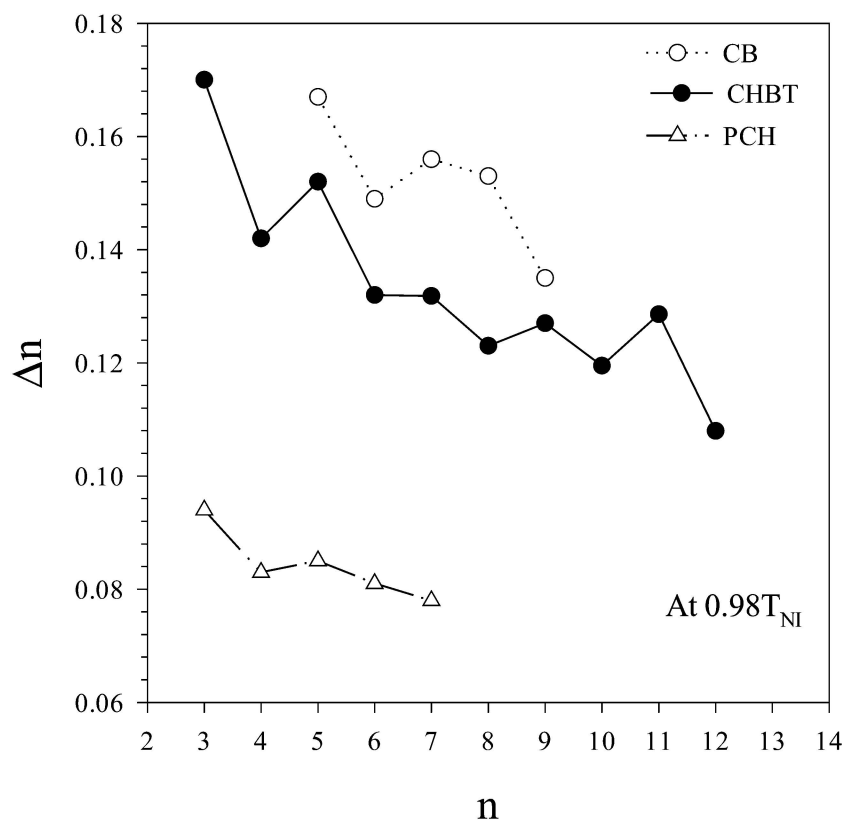


Figure 18. Alkyl chain length dependence of the optical birefringence at a common reduced temperature $T^* = 0.98T_{NI}$ for the CB, PCH and CHBT series.
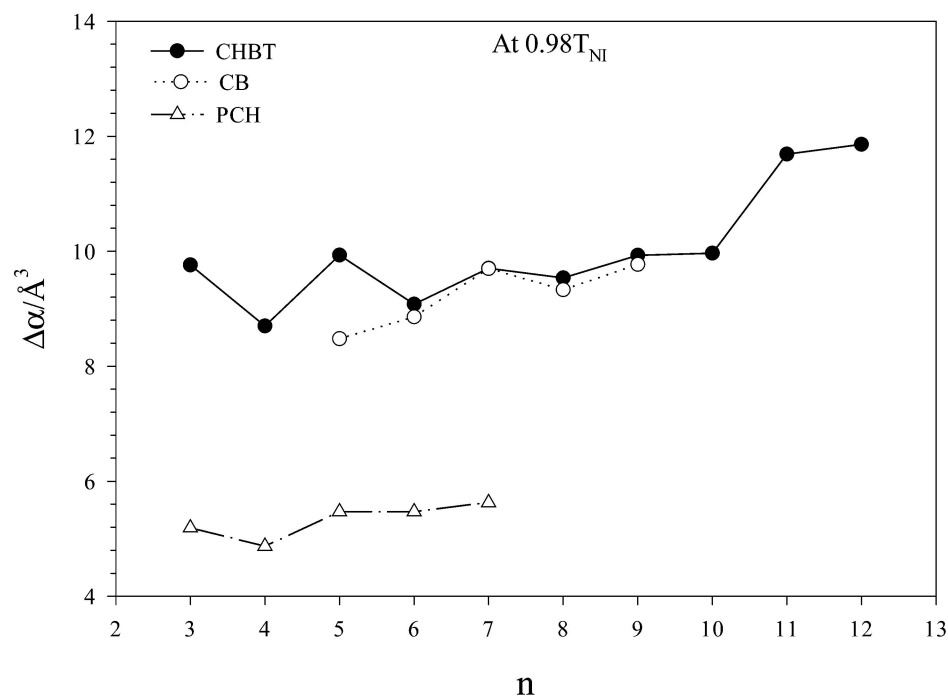
Figure 19. Variation of polarizability anisotropy with the alkyl chain length for the CHBT, CB and PCH series.
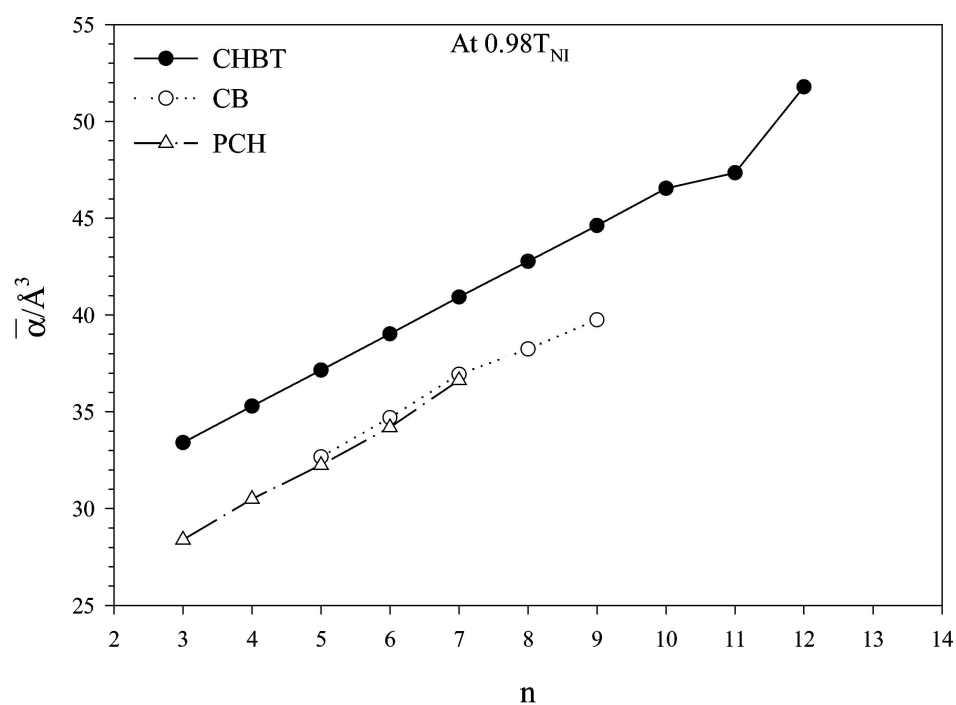


Figure 20. Variation of average polarizability with *n* for the CB, PCH and CHBT series.

is shown in figure 24; it can be seen that the *l*/*L* ratio is greater than unity, suggesting the existence of some sort of bimolecular association in all cases. It is evident that the overlap of association decreases when the cyclohexyl group is replaced by phenyl (*n*PCH → *n*CB) or −NCS is replaced by −CN (*n*CHBT → *n*PCH); the effect is additive when both groups are changed simultaneously (*n*CHBT → *n*CB). However a lower dimer concentration may also reduce the *l*/*L* ratio in *n*CHBT, as observed in a solution study [12].
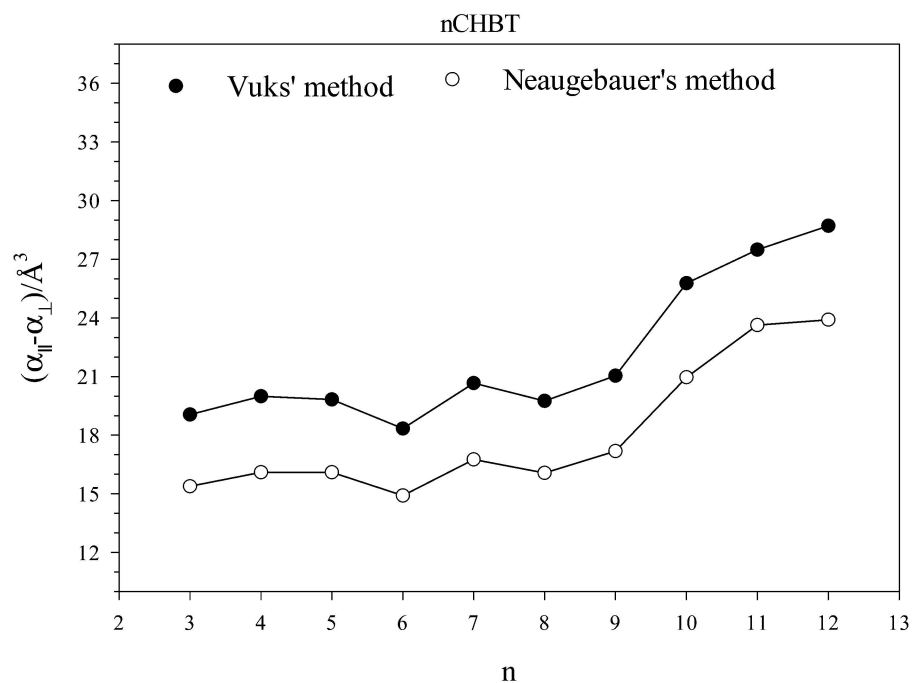
Figure 21. Chain length dependence of polarizability anisotropy in the solid phase for the CHBT series.
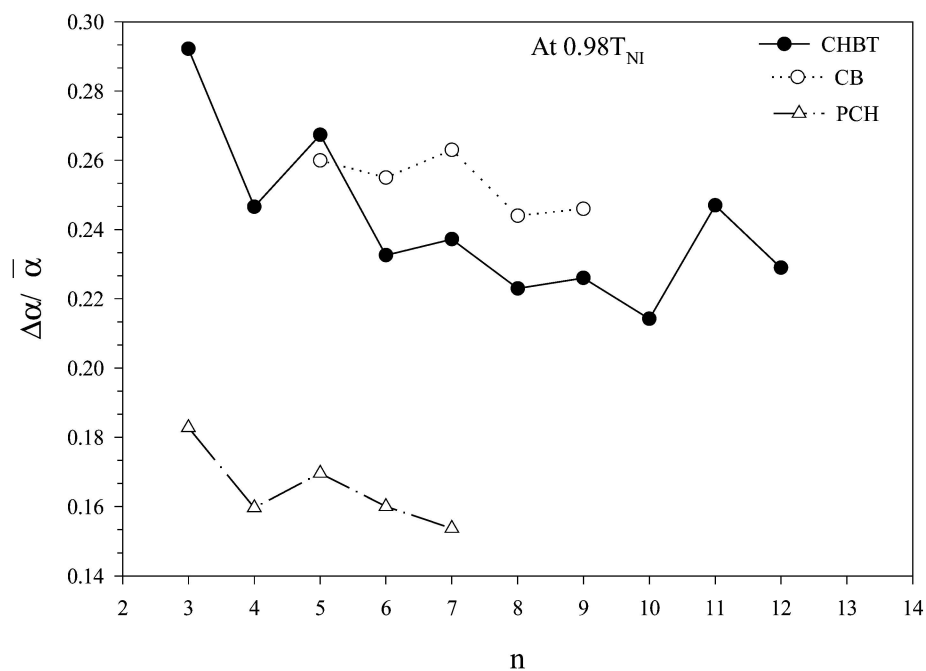


Figure 22. Variation of normalized polarizability anisotropy with alkyl chain length for the CB, PCH and CHBT series.

The orientational order parameter $\langle P_2 \rangle$ for the $n$CHBT and $n$PCH series, determined from X-ray and refractive index data, exhibits an overall, small decreasing trend with increase in chain length, but no distinct OE effect is seen (figure 25). The $n$CB series, however, shows a clear OE effect [20, 41]. The order parameter $\langle P_4 \rangle$, determined from X-ray studies, also shows no OE effect. Moreover if one plots $R = \ln\langle P_2 \rangle / \ln\langle P_4 \rangle$ as a function of chain length (figure 26) it is observed that $R$ remains

closer to the values predicted by the Faber continuum theory [45] than by the Maier–Saupe mean field theory. Paul also reported such good agreement with the Faber theory for many compounds [46].

It has been reported by Jadzyn *et al.* [8], in case of the $n$CHBT series, that $\varepsilon_\parallel$ shows no OE effect, but that $\varepsilon_\perp$ and $\Delta\varepsilon$ show, respectively, a distinct or weak OE effect. However, an overall decrease with $n$ is noted for all the above parameters (figures 27 and 28). Thus the
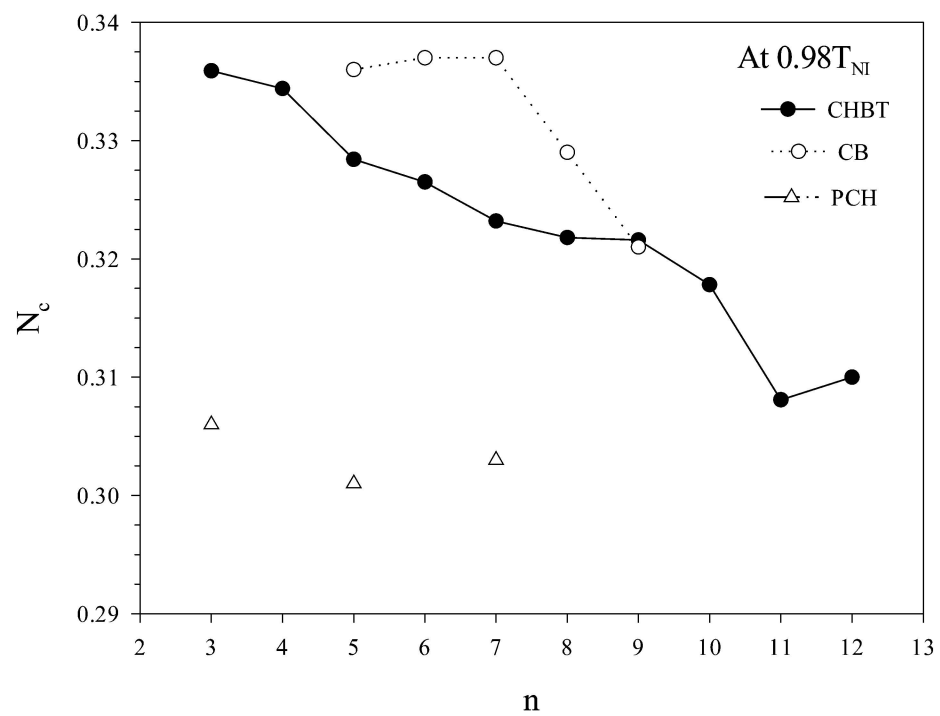
Figure 23. Variation of average polarizability incorporated with density, $N_c$ with the alkyl chain length for the CB, PCH and CHBT series.
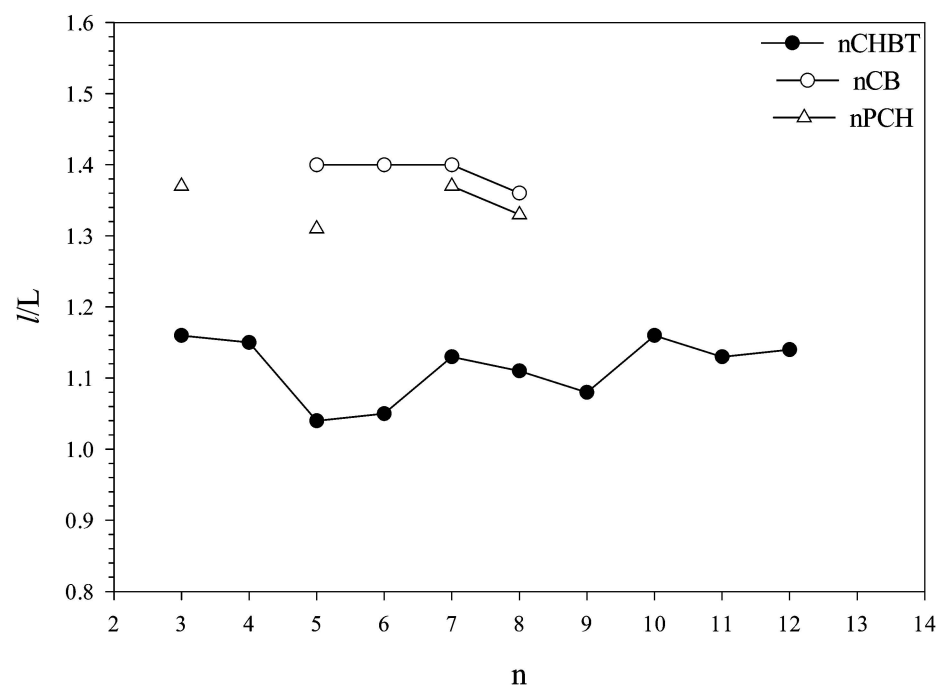
Figure 24. Chain length dependence of $l/L$ for the CB, PCH and CHBT series. For 8CB smectic data is given [44], nematic phase data is not available.

dielectric behaviour is similar to the optical birefringence behaviour. The same type of behaviour was found earlier in the homologous series of $n$CB [47, 48], $n$PCH [19], 4-$n$-alkyl-4′-thiocyanatobiphenyl ($n$BT) [49] di-alkylazo-benzenes [50], *trans-p-n*-alkoxy-α-methyl-*p*′-cyanophenyl cinnamates [48], alkyl/alkoxy-cyanophenyl pyrimidines [51] and cyanoalkoxy Schiff's bases [26, 27]. The cyano

compounds, $n$CB and $n$PCH, have considerably larger permittivities than the corresponding isothiocyanato analogues, $n$BT [49] and $n$CHBT. However, larger permittivities are observed for the substances having two benzene rings. According to Maier and Meier [31, 32] the dielectric anisotropy is given by $\Delta\varepsilon = 4\pi NhF[\Delta\alpha - F\mu^2(1 - 3\cos^2\beta)/2kT]S$. Since $\Delta\alpha$ increases, number density $N$ and order
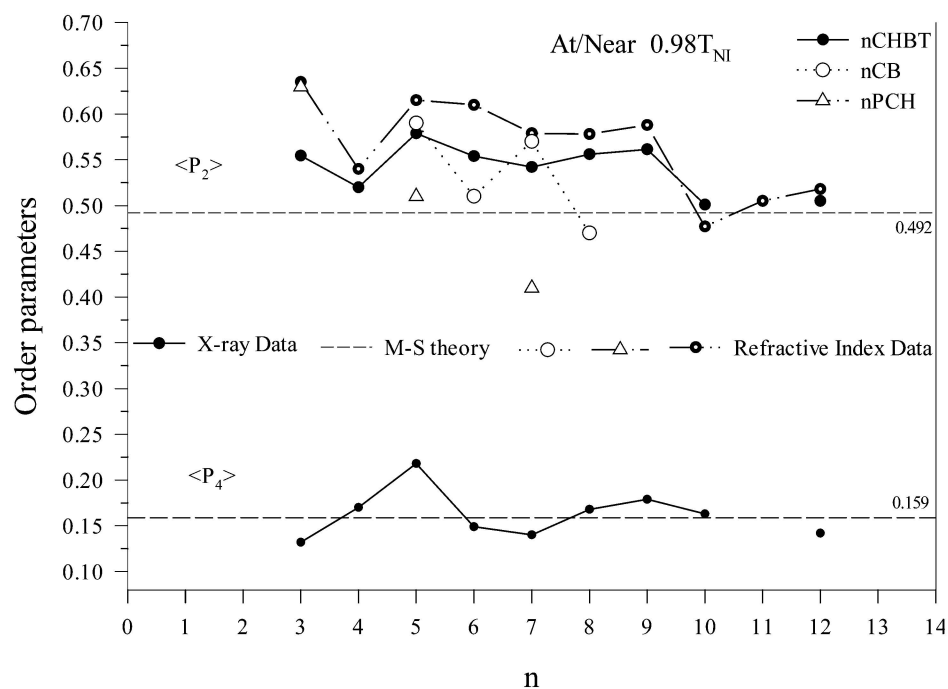
Figure 25. Orientational order parameters as function of alkyl chain length for the CB, PCH and CHBT series.
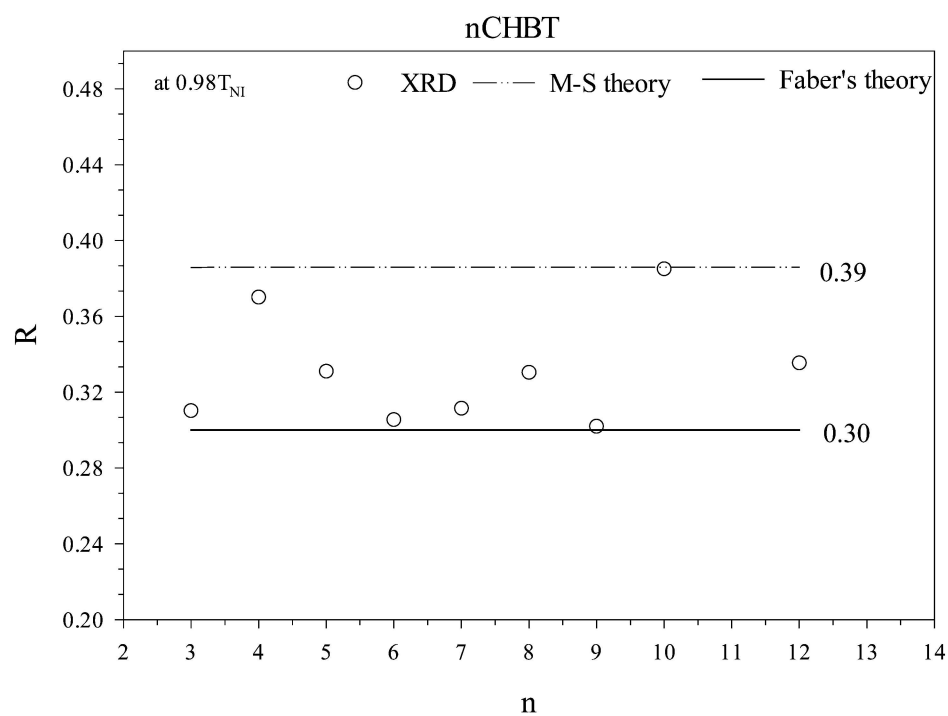


Figure 26. Alkyl chain length dependence of the factor $R = \ln\langle P_2 \rangle / \ln\langle P_4 \rangle$ for CHBT homologues.

parameter $S$ decrease and $\mu$ remains almost constant with $n$, $\Delta\varepsilon$ should decrease with chain length. However, for a molecule with zero dipole moment $\Delta\varepsilon$ is directly proportional to $\Delta\alpha$, hence $\Delta\varepsilon$ is found to exhibit a distinct OE effect like $\Delta\alpha$. It is also observed that the

calculated Kirkwood correlation factor $g_{\parallel}$ does not show an OE effect, but $g_{\perp}$ and $\Delta g$ do show such behaviour for $n = 4$–$10$ (figures 29 and 30).

Finally it might be pointed out that Marcelja [2, 52] and Pink [53] explained the OE effect in $T_{NI}$ and $\Delta H_{NI}$
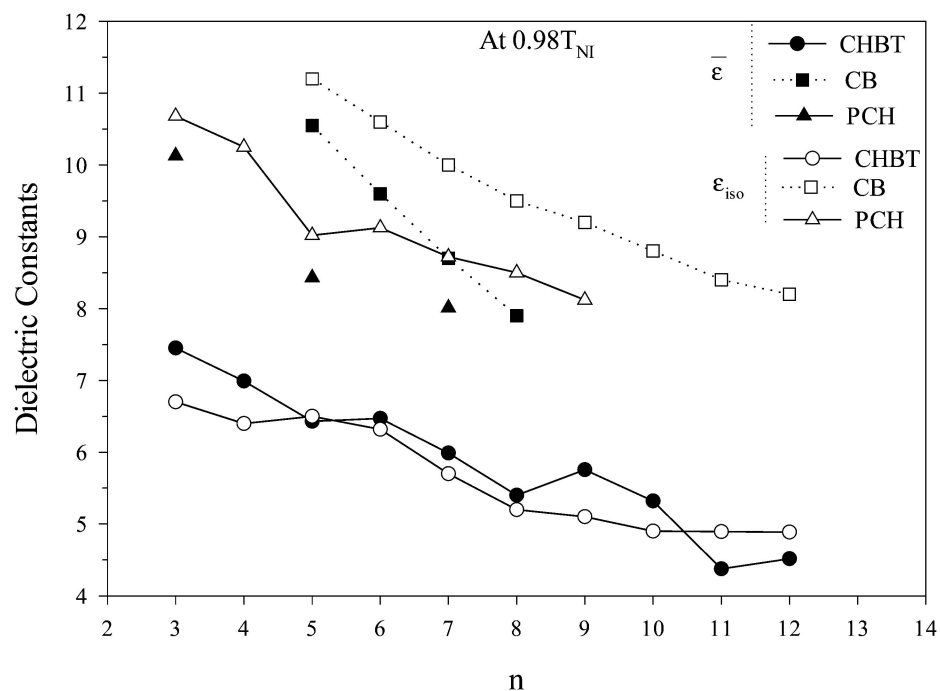
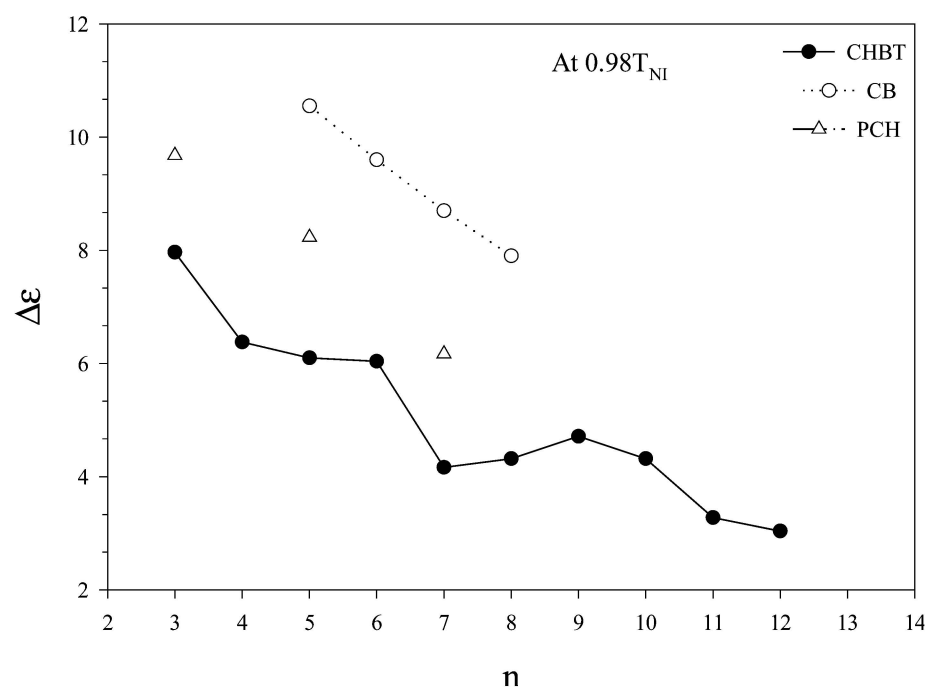Figure 27. Dielectric constants as a function of alkyl chain length for the CB, PCH and CHBT series.



Figure 28. Dielectric anisotropy as function of the alkyl chain length for some series.

in 4,4′-di-*n*-alkoxyazobenzenes assuming that addition of the first C atom to the alkyl chain results in the increase of anisotropy of the molecule and helps the ordering process; subsequent addition of C atoms increases the width of the molecule and hinders the ordering. As the chain becomes longer its flexibility progressively reduces the effect, and for long end chains it becomes unnoticeable. The same explanation is valid for the OE effect observed in many other physical properties such as optical birefringence [54], magnetic susceptibility and order parameter [55, 56] and deuterium quadrupole splittings [57]. De Jeu *et al.* [58], however, qualitatively explained
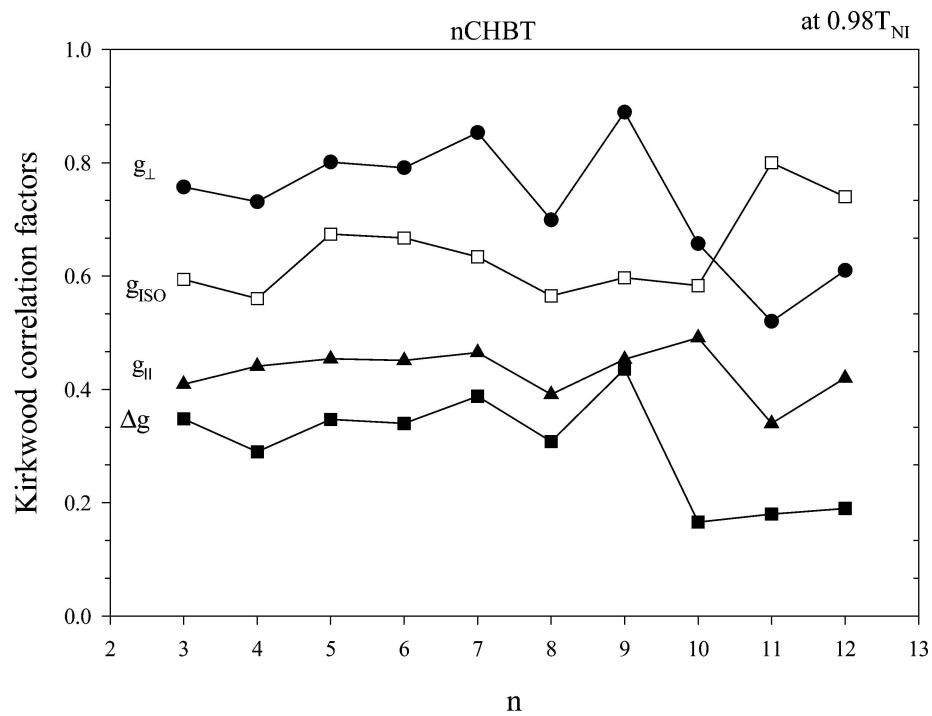
Figure 29. Chain length depend-
ence of Kirkwood correlation
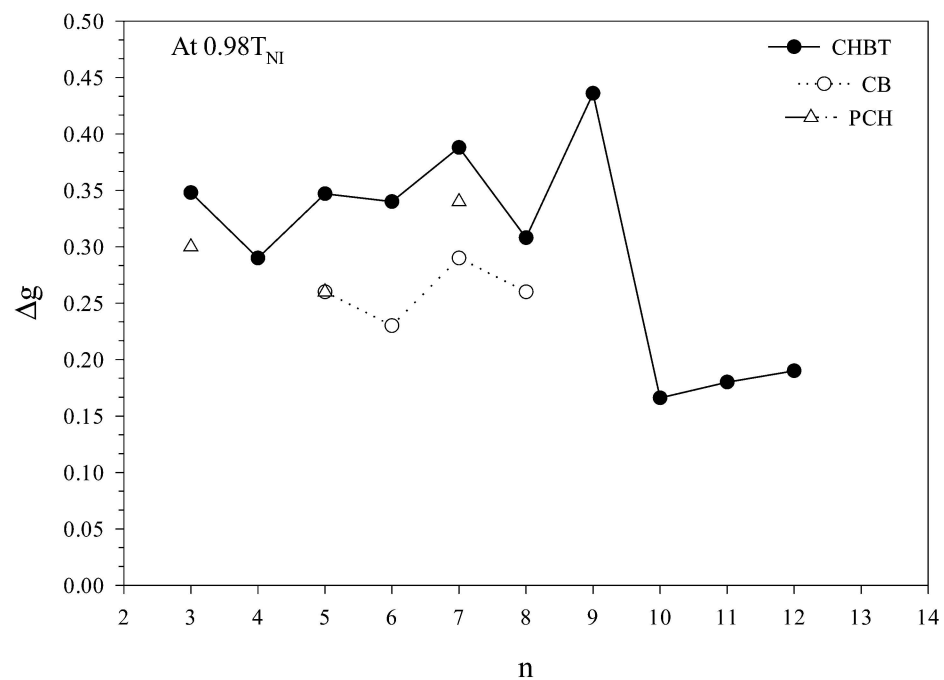factors for the CHBT series.



Figure 30. Chain length depend-
ence of anisotropy of dipole
correlation factors for the CB,
PCH and CHBT series.

clearing temperature dependence on chain length on
the basis of free energy, which takes into account the
attractive forces and the excluded volume effects. So it
can be inferred that the alkyl chain part of the mesogenic
molecules does not merely take up space but also plays an
active role in exhibiting and modifying various physical
properties of liquid crystals.

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