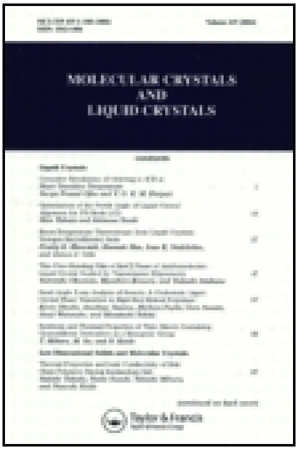


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Kerr Effect Investigations in Liquid Crystals Containing the Isothiocyanato and Cyano Groups with Identical Flexible Tails

H. Khoshsima [a], H. Tajalli [a], A. Ghanadzadeh [a b] & R. Dabrowski [c]

[a] Research Institute for Applied Physics and Astronomy, Tabriz University, Tabriz, Iran

[b] Department of Chemistry, Faculty of Science, Guilan University, Rasht, Iran

[c] Institute of Chemistry of the Military Technical Academy, Warsaw, Poland

Version of record first published: 20 Dec 2006

To cite this article: H. Khoshsima, H. Tajalli, A. Ghanadzadeh & R. Dabrowski (2006): Kerr Effect Investigations in Liquid Crystals Containing the Isothiocyanato and Cyano Groups with Identical Flexible Tails, Molecular Crystals and Liquid Crystals, 460:1, 93-106

To link to this article: http://dx.doi.org/10.1080/15421400600912761

Mol. Cryst. Liq. Cryst., Vol. 460, pp. 93–106, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600912761

Kerr Effect Investigations in Liquid Crystals Containing the Isothiocyanato and Cyano Groups with Identical Flexible Tails

H. Khoshsima
H. Tajalli
Research Institute for Applied Physics and Astronomy, Tabriz University, Tabriz, Iran

A. Ghanadzadeh
Research Institute for Applied Physics and Astronomy, Tabriz University, Tabriz, Iran and Department of Chemistry, Faculty of Science, Guilan University, Rasht, Iran

R. Dabrowski
Institute of Chemistry of the Military Technical Academy, Warsaw, Poland

Electro-optical Kerr effect data have been obtained for 6CB, 6CHBT, 6PCH, and 6BOBT at temperatures greater than the nematic–isotropic transition temperature. Using these data, the real parts of the third-order nonlinear susceptibility $\chi^{(3)}$ *are determined for all the liquid crystals. All the compounds had a positive Kerr constant, which increased with decreasing of temperature. The second-order phase-transition temperatures,* T^**, were determined for these compounds. The replacement of aromatic ring by a flexible cyclohexyl group or a bulkier bicyclooctane has a marked effect on the birefringence. Hexyl 4-(4-isothiocyanato-phenyl) bicycle [2,2,2] octane, 6BOBT, with the highest transition temperature, had the lowest Kerr constant. In contrast, hexyl cyanobiphenyl, 6CB, showed the largest Kerr constant* ($6BOBT \longrightarrow 6CHBT \approx 6PCH \longrightarrow 6CB$)*. The effect of the rigid core and polar head group of the liquid crystals was investigated.*

Keywords: electric birefringence; Kerr effect; liquid crystals; pretransition behavior; third-order nonlinear susceptibility

Address correspondence to A. Ghanadzadeh, Department of Chemistry, Faculty of Science, Guilan University, Rasht, Iran. E-mail: aggilani@guilan.ac.ir

1. INTRODUCTION

The relationship between optical anisotropy and molecular properties has long been an objective of electro-optical studies [1–3]. The current interest in organic materials that have very large optical nonlinearities, such as liquid crystals, is due to their desirable optical properties that are required in the design and application of many opto-electronic devices. Liquid-crystalline materials are currently considered best candidates for devices based on nonlinear optical effects. Therefore, investigations of the influence of molecular structure on the optical properties of the liquid crystals are needed.

The optical anisotropy (a tensor quantity) is one of the most convenient and sensitive parameters for investigating and characterizing the molecular anisotropy and intermolecular ordering in liquid crystals because the value of this parameter is strongly related both to the chemical structure of a molecule and to intermolecular interactions. The induction of double refraction or birefringence in a fluid by application of an external electric field is known as electro-optical Kerr effect [4], which depends both on polarity and polarizability (optical and electrical) of the molecules. Measurements of the temperature dependence of electric Kerr effect and third-order nonlinear susceptibility in the isotropic phase and pretransitional behavior, related to order parameter fluctuations, of many nematic liquid crystals have been studied [5–12]. In the majority of publications, a good agreement between experimental and mean-field theory for nematic compounds was reported and discussed [13–15].

The main aim of this work is to present and discuss electro-optic Kerr results and third-order nonlinear susceptibility $\chi^{(3)}$ obtained for four nematic liquid crystals in the isotropic phase. To investigate the role of the polar-end group (-CN and -NCS) and rigid core in electro-optical properties, static Kerr effect studies have been carried out for four biring compounds containing the isothiocyanato and cyano groups. All the chosen compounds have a hexyl end group in common.

2. EXPERIMENTAL

2.1. Materials

The liquid-crystalline materials (6CB, 6PCH, 6CHBT, and 6B0BT) were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland. The chemical structure of these compounds is shown in Fig. 1. The clearing points or nematic to isotropic transition temperatures for 6CB, 6PCH, 6CHBT, and 6BOT

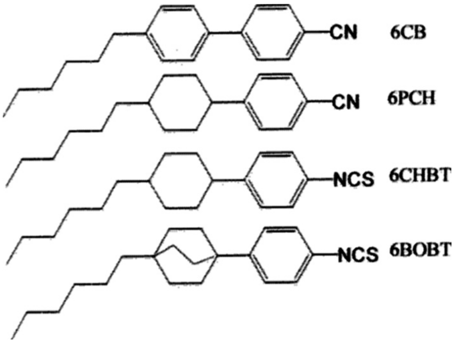


FIGURE 1 Chemical structures of the compounds.

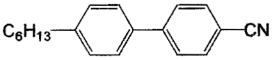
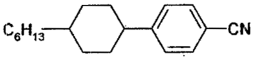
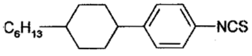
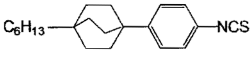
were measured using differential scanning calorimetry (DSC) and polarizing microscopy methods and were found to be 28.9°C, 47.2°C, 43.0°C, and 88.5°C, respectively (Table 1).

2.2. Kerr Effect Apparatus

A diagram of the apparatus (optical component) used to measure the electrically induced phase difference is shown in Fig. 2. All the optical components were mounted on a 2-m optical bench enclosed in a light-proof cabinet.

A Spectra physics He-Ne laser emitting at a wavelength of 632.8 nm with a power of 5 mW was used as a probe beam. For the electro-optical investigation in the isotropic phase, a sample holder similar to that described by O'Konski and Haltner [16] was constructed. The

TABLE 1 Clearing Temperature, T_C, and Pretransitional Temperature, T^*, of 6CB, 6PCH, 6CHBT, and 6BOBT

Material	Structure	T_C (°C)	T^* (°C)
6CB	 C_6H_{13} … CN	28.9	27.9
6PCH	 C_6H_{13} … CN	47.2	46.2
6CHBT	 C_6H_{13} … NCS	43.0	42.1
6BOBT	 C_6H_{13} … NCS	88.5	86.8

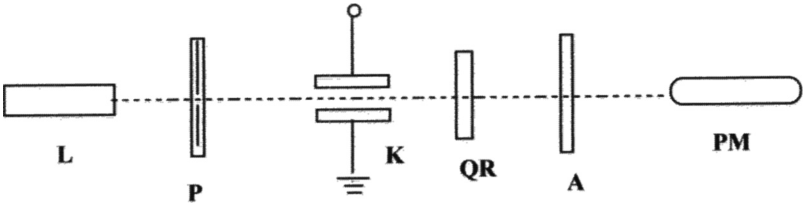


FIGURE 2 Diagram of apparatus used to measure the electro-optical Kerr effect. Principle components are L, laser; P, Polarizer; K, Kerr cell; QR, quarter-wave retarder; A, analyzer; and PM, photomultiplier.

sample holder was a quartz spectrophotometer cell with a path length of 10 mm. The stainless steel electrodes were inserted into the Kerr cell, leaving an active column of liquid $2 \times 2 \times 10$ mm. A Teflon® spacer was used to provide insulation between the electrodes and to maintain an electrode gap of 2 mm. The lower part of the Kerr cell fitted into a thermostated metal jacket, which was cut away to allow passage of the light beam. The temperatures were determined with a copper constantan thermocouple. The estimated accuracy in the measurement of temperature is $\pm 0.1o°C$.

The detection of the Kerr signal was achieved using a photomultiplier tube, type E.M.I. 9816B. The optical signal from the photomultiplier was displayed using a digital storage oscilloscope (Tektronix 300 MHz, model TDS3032B) and a personal computer. The polarizer and analyzer were Glan-Thompson double-refraction-type prisms of commercial origin and adjusted such that they crossed each other and made an angle of 45° with respect to the applied ac electric field (1 kHz). The quarter wave plate used in these experiments was mica cut specifically for use at 632.8 nm and mounted between glass discs.

The electric field is generated by means of a high-voltage power supply that was applied, as a 1-KHz ac field, to the electrodes of the Kerr cell. The refractive indices of the samples in different temperatures have been measured using an Abbe refractometer model (Abbe 60/ED Bellingham + Stanley Ltd. Company).

2.3. Measurements of Experimental Kerr Constants (B)

All measurements of the Kerr constant were made using the nulled intensity method [17,18], which involves the nulling of an optical response resulting from the application of electric field across the Kerr cell.

The electric birefringence of the medium is defined as the difference between the refractive indices for light polarized parallel ($n_{\|}$) and perpendicular ($n_\perp$) to the orienting field direction and is related to optical retardation or optical phase difference, δ,

$$\delta = 2\pi lBE^2 = \frac{2\pi l(n_\parallel - n_\perp)}{\lambda} \tag{1}$$

where λ is the wavelength of the light, l is the optical path length, and B is called the Kerr constant of the substance and is used to denote the magnitude of the Kerr effect. The electrically induced birefringence, Δn, may also be conveniently defined by (Kerr law) as

$$\Delta n = \lambda BE^2. \tag{2}$$

For the nulled intensity method of measuring Kerr effect, the rotation of the plane of polarization, α, is related to the phase difference, δ, by

$$\alpha = \frac{\delta}{4} \tag{3}$$

Eliminating δ from Eqs. (3) and (4) and rearranging gives

$$\alpha = \frac{\pi LBE^2}{2} \tag{4}$$

If the Kerr law is observed, a plot of α *versus* the square of applied electric field (E^2) also should give a straight-line graph passing through the origin with a gradient of ($\pi LB/2$), from which the Kerr constant B may be determined.

To investigate the third-order optical nonlinearity of the medium, it may be shown that there is a relation between Kerr constant B and third-order nonlinear susceptibility $\chi^{(3)}$. By applying the symmetry properties [19], the nonvanishing elements of third-order nonlinear susceptibility tensor $\chi^{(3)}$ in an isotropic media are related as

$$\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221}. \tag{5}$$

Also, by applying the Klienmann symmetry [20], we get

$$\frac{1}{3}\chi_{1111} = \chi_{1122} = \chi_{1212} = \chi_{1221}. \tag{6}$$

Thus, there is only one nonvanishing element of the third-order nonlinear susceptibility tensor, which can be related to the Kerr constant as [21]

$$B = \frac{24\pi}{n\lambda}[\chi_{1221}(-\omega_1, \omega_1, 0, 0)]. \tag{7}$$

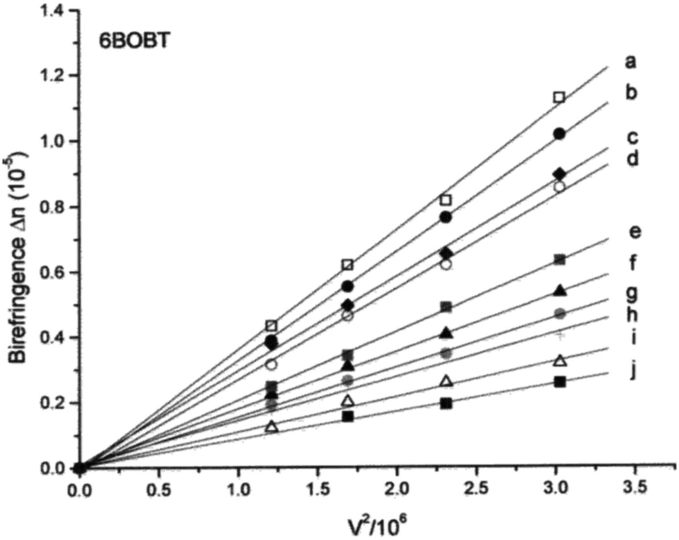


FIGURE 3 Induced birefringence, Δn, as a function of applied field for 6BOBT at several temperatures: a) 89.4°C, b) 89.7°C, c) 90.1°C, d) 90.3, e) 91.4°C, f) 92.5°C, g) 93.6, h) 94.7°C, i) 95.8, and j) 96.9°C.

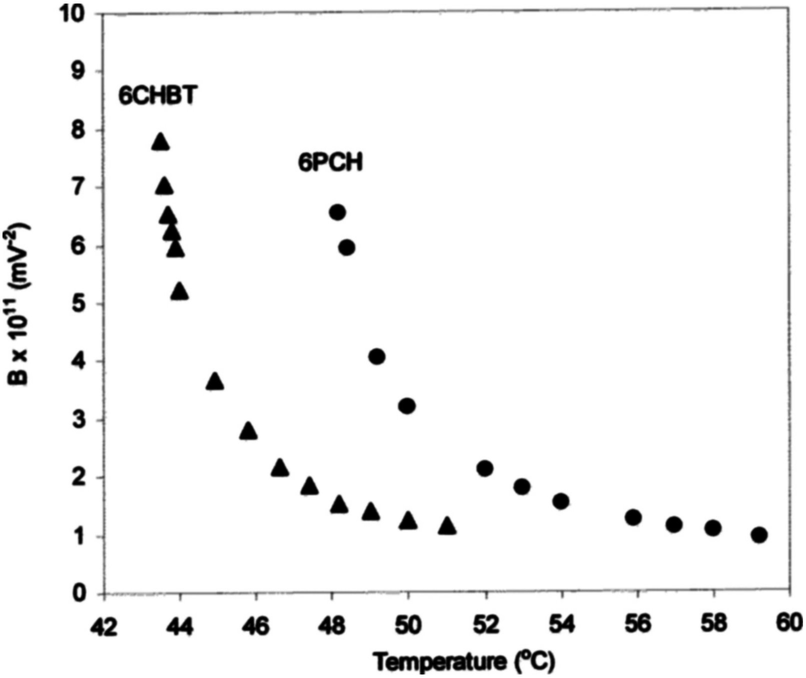


FIGURE 4 Temperature dependence of B for 6CHBT and 6PCH obtained using the ac field method ($f = 1\,\mathrm{kHZ}$).

2.4. Dielectric Measurement

The electrical capacitance of the dielectric cell was measured using a Wayne Kerr model 6425B Digibridge. Measurements of the capacitance required for calculating the static dielectric permittivity were performed at a frequency of 10 kHz. A three-terminal dielectric cell was constructed for measurements on small volumes of solutions.

3. RESULTS AND DISCUSSION

The Kerr constant, B, of a material at a given temperature may be obtained from the gradient of a graph of induced birefringence, Δn, plotted against the square of applied electric field (*i.e.*, $\Delta n = \lambda BE^2$). This is illustrated for hexyl 4-(4-isothiocyanato-phenyl) bicycle [2,2,2] octane (6BOBT) in Fig. 3. For each of the materials, the electrically induced birefringence was found to be a linear function of the square of the applied electric field and is positive in all cases ($\Delta n > 0$).

The dependences of the Kerr constant, B, and the third-order nonlinear susceptibility, $\chi^{(3)}$, on temperature for the compounds are shown in Figs. 4–7. These data show that the values of B and hence

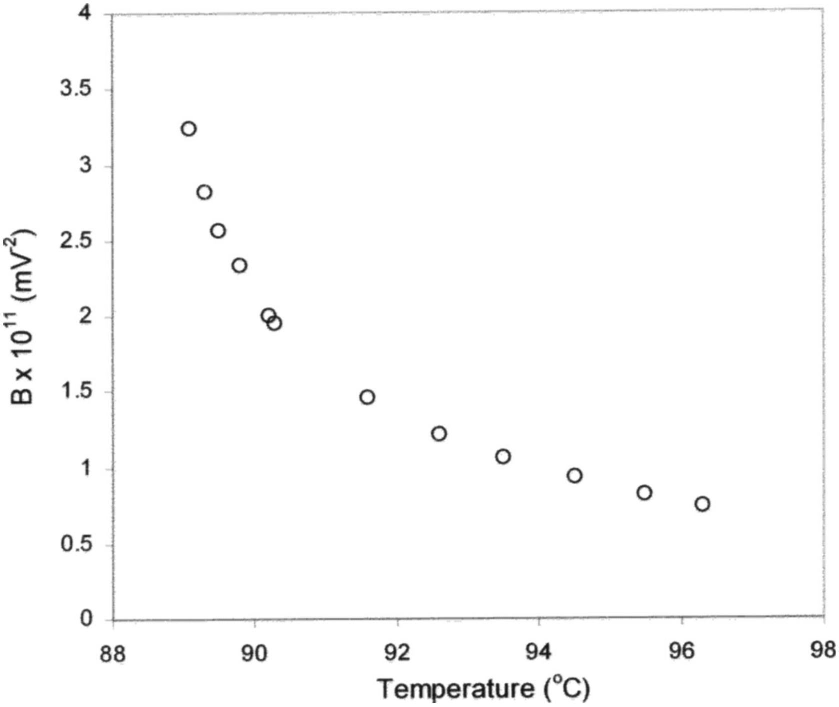


FIGURE 5 Temperature dependence of B for 6BOBT obtained using the ac field method ($f = 1\,\mathrm{kHZ}$).

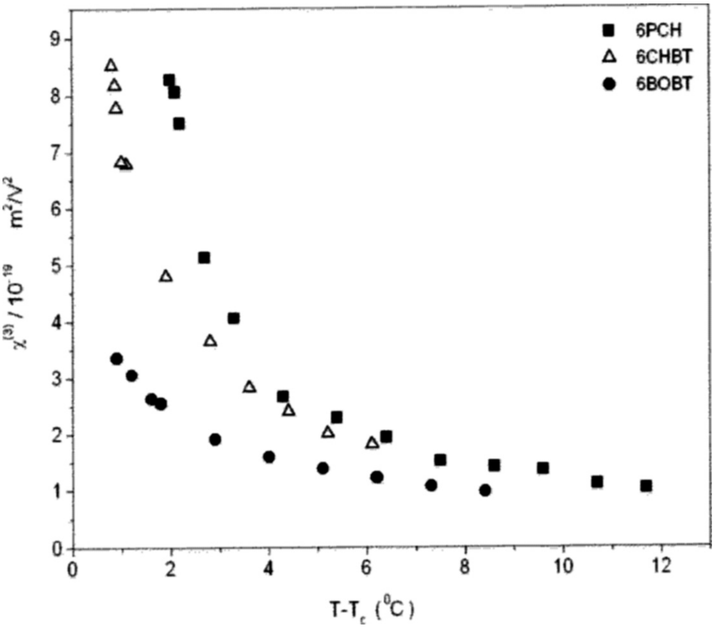


FIGURE 6 Temperature dependence of $\chi^{(3)}$ for 6PCH, 6CHBT, and 6BOBT obtained using their Kerr constants and refractive indices in the same temperatures.

$\chi^{(3)}$ depend strongly on temperature and molecular structure (nematic core). The temperature dependence of the induced birefringence increases with decreasing temperature as the nematic transition temperature is approached. However, the highest value of the Kerr constant obtained for 6BOBT is less than that for other compounds. In contrast, 6CB shows the highest Kerr constants in the range of temperatures studied in this work.

In general, the Kerr constants of these liquid-crystalline materials as well as their third-order susceptibility are found to be very high at the nematic–isotropic transition temperatures. The high Kerr constant of these materials in the isotropic phase (close to phase-transition temperatures), which leads to high third-order optical nonlinearity, can be due to the existence of the highly intermolecular ordering and molecular association [22]. The origin of the molecular association in these materials is due to several factors but is mainly due to the strong polar groups, that is, Isothiocyanato (NCS) and Cyano (CN), and the van der Waal's interactions involving the rigid core.

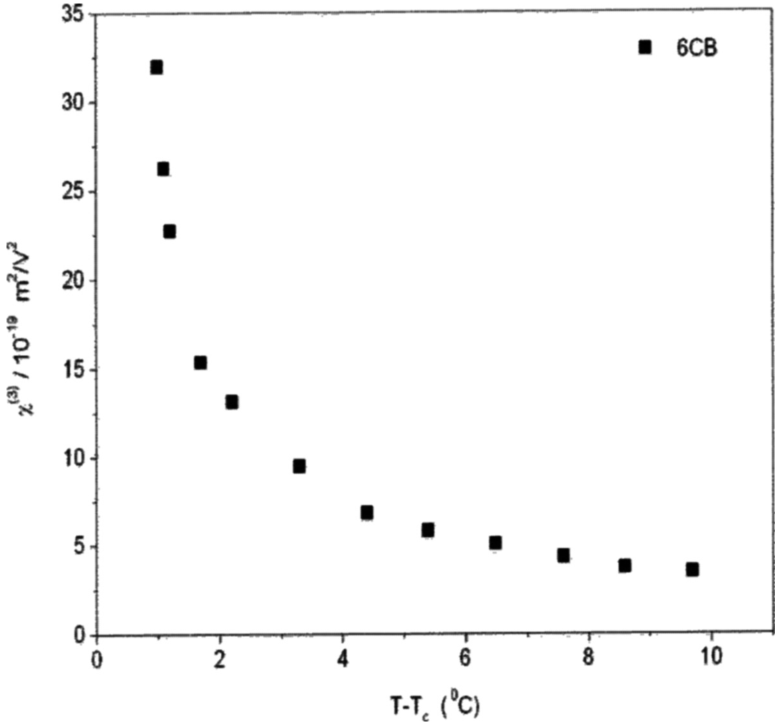


FIGURE 7 Temperature dependence of $\chi^{(3)}$ for 6CB obtained using its Kerr constants and refractive indices in the same temperatures.

By using dipole moment measurements on the isotropic phases of liquid crystals over a range of temperatures, it is possible to obtain valuable information about the molecular association and dipole–dipole interactions. The relation between the effective dipole moment, (μ^2_{eff}, and the dipole moment value of the isolated molecule, μ^2, is expressed by the Kirkwood dipole–dipole correlation factors, $g = \mu^2_{\text{eff}}/\mu^2$. The isotropic g-values of 6CB at several temperatures are shown in Fig. 8. The g-factors at different temperatures for 6CB are less than 1, indicating a high degree of antiparallel dipole association. As it can be seen from Fig. 8, the g-value decreases with decreasing temperature just above clearing point, T_c. This suggests increasing antiparallel association as the temperature is increased. Figure 9 shows that the Kerr constant of 6CB decreased with decreasing of g-factor. The pretransitional effect in the electric permittivity of cyano compounds have been observed and discussed by the earlier investigators [22,23].

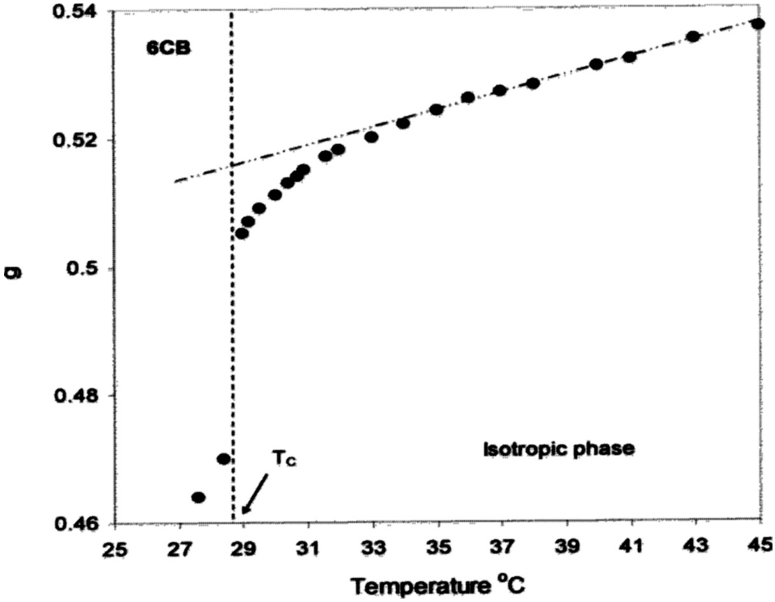


FIGURE 8 Temperature dependence of Kirkwood correlation factors (g) for 6CB in the isotropic phase.

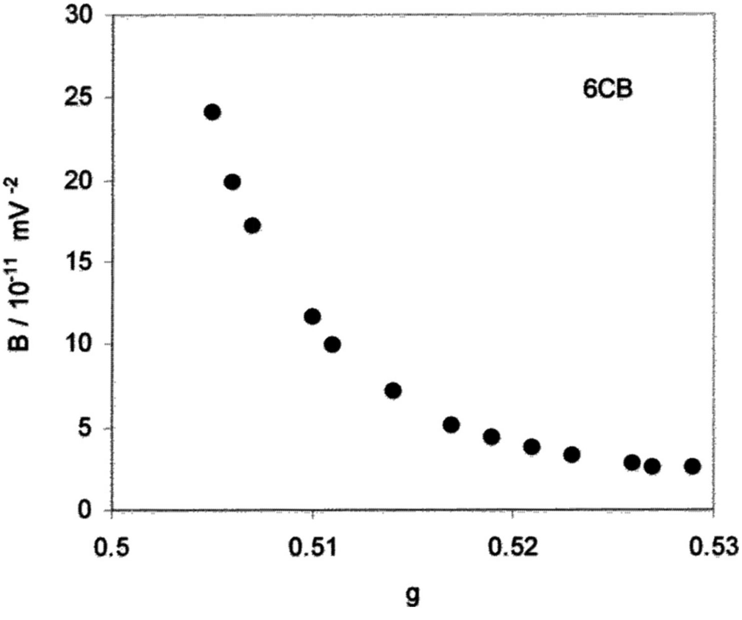


FIGURE 9 Variation of B with Kirkwood correlation factors (g) for 6CB.

The pretransitional Kerr effect is exhibited by liquid-crystalline materials that are in their isotropic phase at a temperature that is close to the nematic–isotropic transition temperature. The theory of Landau–De Gennes [24] has been used to describe the pretransitional behavior in the isotropic phase of liquid crystals. According to this model, the Kerr constant in the isotropic phase is given by

$$B = \frac{\varepsilon_o \Delta n_o \Delta\varepsilon_o}{4a\lambda\sqrt{\bar{\varepsilon}}(T - T^*)}, \tag{8}$$

where a is the temperature independent coefficient, T* is the second-order pretransitional temperature, which is an extrapolated temperature just below the isotropic–nematic phase transition, and $\Delta\varepsilon_o$ is the low-frequency dielectric anisotropy in the completely ordered phase. From this equation, it is clear that there is a reciprocal relationship between the Kerr constant, B, and temperature, that is,

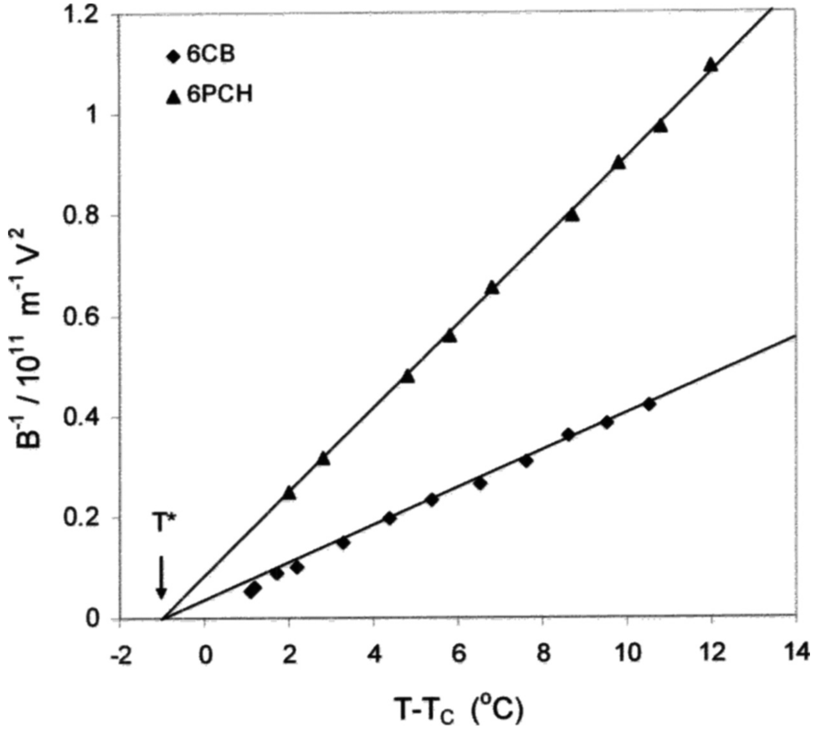


FIGURE 10 Temperature dependence of B^{-1} for 6CB and 6PCH obtained using the ac field method.

$$\Delta n \propto (T - T^{*})^{-1}. \tag{9}$$

The linear dependence of $(T - T^{*})^{-1}$ on the Kerr constant has been discussed in detail elsewhere. The temperature T^{*} can be obtained by a linear extrapolation of the Ken-constant (B^{-1}) *versus* temperature. In the pretransition region, the short-range order leads to pseudo-nematic domains of highly correlated molecules in the isotropic phase.

The variation of B^{-1} (inverse of Kerr constant) with temperature for the compounds is shown in Figs. 10 and 11. The extrapolated temperatures T^{*} for these liquid crystals are just below the isotropic phase transitions T_{NI} (*i.e.*, approx. 0.9–1.7°C), where T_{NI} for the compounds obtained using the optical microscopy are in degrees centigrade. For the samples studied the graphs of B^{-1} *versus* T are linear. However, close to the transition temperature, a systematic deviation from the mean-field theory is usually observed [25–28].

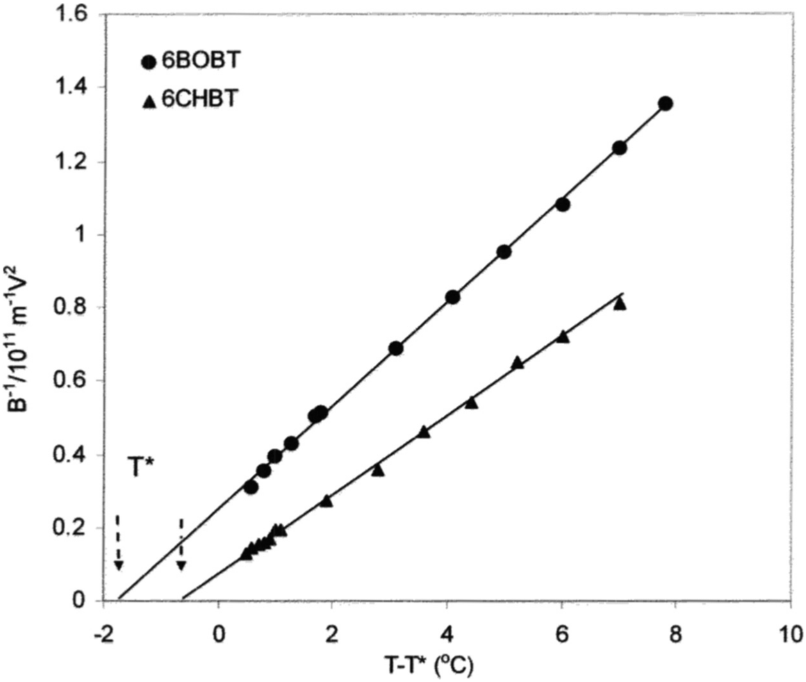


FIGURE 11 Temperature dependence of B^{-1} for 6CHBT and 6BOBT obtained using the ac field method.

TABLE 2 Values of Kerr Constant and Third-Order Nonlinear Susceptibility at a Temperature of 1°C above the Clearing Temperatures

Material	$B/10^{-11}$ m/v^2	$\chi^{(3)}/10^{-19}$ m^2/v^2
6CB	24.126	31.948
6CHBT	6.515	8.522
6PCH	6.522	8.266
6BOBT	2.553	3.346

4. CONCLUSION

The highly molecular association and intermolecular ordering have been found to influence the isotropic values close to the clearing temperature of some physical properties such as Kerr constant, permittivity, and third-order nonlinear susceptibility, $\chi^{(3)}$. The experimental results show a significant variation in the magnitude of the Kerr constant and susceptibility among the different liquid crystals, with 6CB showing the largest effect and 6BOBT the smallest. This effect can be due to the difference in the molecular polarizability and molecular packing in these materials.

The values of the Kerr constants and third-order nonlinear susceptibility obtained for 6CB, 6CHBT, 6PCH, and 6B0BT, at a temperature of 1°C greater than the clearing temperatures, is shown in Table 2. The replacement of the high polarizable phenyl ring by a flexible cyclohexyl group (*i.e.*, $6CB \longrightarrow 6PCH$) leads to a decrease in polarizability anisotropy and therefore to a decrease of birefringence. The substitution of an aromatic ring by a bulkier bicyclooctane group has a marked effect on the physical properties such as birefringence, and then the lowest value for the Kerr constant was obtained for this material. However, the Kerr constant values for 6CHBT with -NCS group and 6 PCH with a -CN group are nearly identical.

The pretransitional behavior and small deviations from mean-field theory, at temperatures close to T_{NI}, for these liquid crystals with polar end groups (cyano and isothiocyanato) have been observed. The pretransitional temperature of 6BOBT with much a bulkier ring system is found to be about 1.7°C below the clearing temperature, whereas the second-order pretransitional temperature for other compounds studied here are found to be approximately 1°C less than the first-order nematic–isotropic transition temperatures.

REFERENCES

[1] Fiaz, M. & Beevers, M. S. (2000). *Eur. Polym. J.*, *36*, 1943.
[2] Mumby, S. J. & Beevers, M. S. (1989). *Polymer*, *30*, 860.
[3] Coles, H. J. & Jennings, B. R. (1976). *Mol. Phys.*, *31*, 571.
[4] Kerr, J. (1875). *Phil. Mag.*, *50*, 337.
[5] Beevers, M. S. (1975). *Mol. Cryst. Liq. Cryst.*, *31*, 333.
[6] Davies, M., Moutran, R., Price, A. H., Beveers, M. S., & Williams, G. (1976). *J. Chem. Soc. Faraday Trans.*, *2*(72), 1447.
[7] Philip, J. & Prasada Rao, T. A. (1992). *Phys. Rev. A*, *46*, 2163.
[8] Pouligny, J. P., Marcerou, J. R., & Lalanne, H. J. *Coles*, (1983). *Mol. Phys.*, *49*, 583.
[9] Coles, H. J. & Kershaw, S. V. (1985). *Mol. Cryst. Liq. Cryst. Lett.*, *2*(1–2), 29.
[10] Coles, H. J. & Kershaw, S. V. (1988). *J. Chem. Soc. Faraday Trans.*, *2*(84), 987.
[11] Philip, J. & Prasada Rao, T. A. (1991). *J. Mol. Liq.*, *50*, 215.
[12] Sinha, A. & Prasada Rao, T. A. (2000). *Liquid Crystals*, *27*(2), 191.
[13] Philip, J. & Prasada Rao, T. A. (1992). *J. Phys. D: Appl. Phys.*, *25*, 1231.
[14] Ghanadzadeh, A. & Beevers, M. S. (2003). *J. Mol. Liq.*, *107*, 77.
[15] Ghanadzadeh, A. & Beevers, M. S. (2004). *J. Mol. Liq.*, *112*, 141.
[16] O'Konski, C. T. & Haltner, A. J. (1956). *J. Am. Chem. Soc.*, *78*, 3604.
[17] Beevers, M. S. & Khanarian, G. (1979). *Aus. J. Chem.*, *3*, 263.
[18] Beevers, M. S. & Mumby, S. J. (1984). *Polym. Commun.*, *25*, 173.
[19] Butcher, P. N. & Cotter, D. (1990). *The Elements of Nonlinear Optics*, Cambridge University Press: Cambridge, 141.
[20] Klienmann, D. A. (1962). *Phys. Rev.*, *152*, 1977.
[21] Wang, C. C. (1966). *Phys. Rev.*, *152*, 149.
[22] Ghanadzadeh, A. & Beevers, M. S. (2002). *J. Mol. Liq.*, *100*(1), 47.
[23] Bradshaw, M. J. & Raynes, E. P. (1981). *Mol. Cryst. Liq. Cryst. Lett.*, *72*, 73.
[24] de Gennes, P. G. (1971). *Mol. Cryst. Liq. Cryst.*, *12*, 193.
[25] Malraison, B., Poggi, Y., & Filippini, J. C. (1979). *Solid State Commun.*, *31*, 843.
[26] Coles, H. J. (1978). *Mol. Cryst. Liq. Cryst.*, *49*, 67.
[27] Dunmur, D. A. & Tomes, A. E. (1981). *Mol. Cryst. Liq. Cryst.*, *76*, 231.
[28] Ghanadzadeh, A. & Beevers, M. S. (2001). *J. Mol. Liq.*, *92*, 217.