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Kerr effect of low melting nematic liquid crystals with negative dielectric anisotropy

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The two low melting nematic liquid crystals, 2-chloro-4-heptylphenyl 4-pentylbicyclo[2,2,2]octane-1-carboxylate (7CP5BOC) and 2-chloro-4-heptylphenyl 4-heptylbicyclo[2,2,2]octane-1-carboxylate (7CP7BOC) have been investigated to determine their electro-optical behaviour and third order non-linearity by the static Kerr effect method. Both liquid crystals are laterally substituted by a single chlorine atom located close to the ester linking group. The temperature dependence of the electric Kerr constant in the isotropic phase and the pretransitional behaviour have been investigated for these low birefringence nematic liquid crystals in the isotropic phase. Both the compounds, with negative dielectric anisotropy, have a positive Kerr constant. The Landau–de Gennes model was obeyed for these compounds.

1. Introduction

Liquid crystal materials are unique in their properties and uses. Most technical applications of nematic liquid crystals (NLCs) are based on their optical properties. The wide range of optical phenomena manifested by liquid crystals has inspired many investigations on these materials. Many researchers have investigated various classes of room temperature NLCs with positive dielectric anisotropy, such as cyanobiphenyls, in order to understand and provide further information about the optical and electro-optical behaviour of such systems [1–7].

However, NLCs that possess negative dielectric anisotropy are much less numerous. The most studied nematic compound with negative dielectric anisotropy is MBBA [8], which is chemically and thermally unstable. The electro-optical behaviour of this nematogen has been reported in the literature [9].

In this investigation we are concerned with liquid crystals of the low melting nematic type with negative dielectric anisotropy, low birefringence and high chemical and thermal stability, and in which the long axes of the molecules have a strong tendency to align parallel to one another. Aromatic esters are known to be thermally stable. The replacement of a phenyl ring with a bulkier bicyclooctane group leads to an additional stability. However, this replacement has a marked effect on physical properties such as birefringence. This new class of room temperature nematics, the *2-chloro-4-alkylphenyl esters of 4-alkylbicyclooctane-1-carboxylic acids*, has been recently reported by Dabrowski *et al.* [10].

The induction of double refraction or birefringence in a fluid by application of an external electric field is known as the electro-optical Kerr effect [11]; it depends both on polarity and polarizability of the molecules. The electric birefringence (Δn) 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. The electro-optical Kerr effect has been demonstrated to be an effective technique for studying optical anisotropy and pre-transitional effect of liquid crystals in the isotropic phase [12–15]. The extent of the Kerr effect depends both on polarity and polarizability of the molecules. The electro-optical behaviour is strongly related both to the molecular structure and to intermolecular interactions.

The investigation reported here is concerned with the determination of the Kerr constant and the third order non-linear optical susceptibility, in the isotropic state, of two of a new class of stable low melting NLCs containing an ester linking group between *bicyclooctane* and *phenyl* rings. Both compounds have an additional chlorine atom located in the neighbourhood of the *ester* linking group. While the alkyl chain and *chlorine* lateral group reduce the melting point of these liquid crystalline compounds, the mesogenic rigid cores provide the

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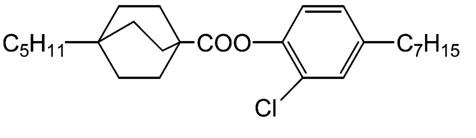
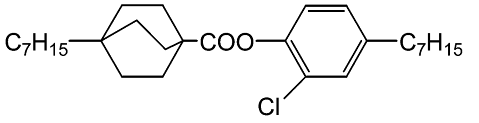


7CP5BOC



7CP7BOC

Figure 1. Chemical structures of the compounds studied.

anisotropic interactions necessary for liquid crystal formation. The two compounds exhibit only a nematic phase with high thermal stability due to the bicyclooctane ring. The presence of a chlorine atom in the lateral position leads a good solubility for polar and also for non-polar compounds. Therefore, these compounds are suited as anisotropic solvents for polarizing spectroscopy.

2. Experimental procedure

2.1. *Materials*

The liquid crystalline materials were synthesized by Dabrowski *et al.* in the Institute of chemistry of the Military Technical Academy, Warsaw, Poland [10]. The chemical structure of these compounds is shown in figure 1. The clearing points or nematic-to-isotropic transition temperatures for these nematogens were measured using differential scanning calorimetry (DSC) and polarizing optical microscopy, and are given in table 1.

2.2. *Kerr effect apparatus*

A diagram of the apparatus used to measure the phase difference is shown in figure 2. A parallel, plane-polarized beam of monochromatic light is passed through the Kerr cell such that the plane of polarization of the light is at angle of 45° relative to the direction of the applied electric field. In the presence of an electric field the light leaving the cell is generally elliptically polarized. After passing through an oriented quarter-wave plate the light can be extinguished by the analyser. The light source was a Spectra Physics He-Ne laser emitting at a wavelength of 632.8 nm.

Table 1. The melting point T_{Cr}, clearing temperature T_C, and pre-transitional temperature T^*, of the nematic compounds.

Compound	T_{Cr}/°C	T_C/°C	T^*/°C
2-Chloro-4-heptylphenyl-4-pentylbicyclo[2,2,2]octane-1-carboxylate (7CP5BOC)	18.2	43.6	42.7
2-Chloro-4-heptylphenyl-4-heptylbicyclo[222]octane-1-carboxylate (7CP7BOC)	14.1	47.3	46.0

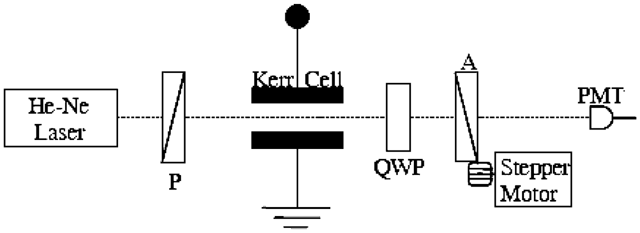


Figure 2. Apparatus used to measure the electro-optical Kerr effect. The components are: P, Polarizer; QWP, quarter-wave plate; A, analyser; PMT, photomultiplier.

A sample holder similar to that described by O'Konski and Haltner [16] was constructed; it consisted of a quartz spectrophotometer cell with a path length of 10 mm. Stainless steel electrodes were inserted into the Kerr cell, leaving an active column of liquid of size $2 \times 2 \times 10\,\text{mm}^3$. Temperatures were determined with a copper-constantan thermocouple, with an estimated accuracy of ± 0.1°C.

Detection of the Kerr signal was achieved using a photomultiplier tube, type EMI 9816B. The optical signal from the photomultiplier was displayed using a digital storage oscilloscope (Tektronix 300 MHz, model TDS3032B) and a PC. The polarizer and analyser were commercial Glan–Thompson double refraction type prisms, and were adjusted such that they crossed each other, making an angle 45° with respect to the applied a.c. 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.

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 an external electric field across the Kerr cell with rotating of the analyser.

2.3. *Refractive index measurements*

The refractive indices of the samples in the isotropic phase were determined at a wavelength of 632.8 nm using an Abbe Refractometer (Abbe 60/ED Bellingham and Stanley Ltd.). The temperature of the refractometer was controlled by circulation of water.

3. Results and discussion

The electrically induced birefringence, Δn, may be conveniently defined by (Kerr law):

$$\Delta n = \lambda B E^2 \tag{1}$$

Table 2. Kerr constants B, susceptibility $\chi^{(3)}$, and refractive index n, of 7CP5BOC and 47CP7BOC for λ=632.8 nm.

7CP5BOC				7CP7BOC			
Temp./°C	$B\times10^{12}$/m V^{-2}	$\chi^{(3)}\times10^{-20}$/m^2 V^{-2}	n	Temp./°C	$B\times10^{12}$/m^2 V^{-2}	$\chi^{(3)}\times10^{-20}$/m^2 V^{-2}	n
43.9	3.01	3.80	1.5029	47.6	3.44	2.62	1.4993
44.0	2.66	3.36	1.5028	47.8	3.24	2.37	1.4992
44.1	2.56	3.23	1.5028	48.0	2.86	2.09	1.4991
44.7	1.91	2.41	1.5025	48.1	2.60	1.98	1.4991
45.2	1.37	1.73	1.5023	48.4	2.24	1.76	1.4990
46.2	0.98	1.24	1.5019	48.9	1.94	1.47	1.4988
47.3	0.79	1.00	1.5015	49.4	1.64	1.22	1.4986
48.3	0.69	0.87	1.5011	50.5	1.36	0.93	1.4981
49.4	0.58	0.73	1.5007	51.5	1.03	0.77	1.4977
50.4	0.49	0.62	1.5003	52.6	0.86	0.65	1.4973
51.4	0.39	0.50	1.4999	53.6	0.71	0.56	1.4969
				54.7	0.64	0.48	1.4965
				55.7	0.60	0.44	1.4961
				56.8	0.53	0.39	1.4956
				57.8	0.48	0.37	1.4952

where λ is the wavelength of the light, l is the optical path length, and B is called the 'Kerr constant' of the substance. The values of B of the compounds, above the transition temperatures, were obtained from the gradients of graphs of induced birefringence, Δn, plotted against the square of applied electric field.

In the samples examined, the electrically induced birefringence was found to be directly proportional to the square of the applied electric field, and is positive in both cases ($\Delta n>0$). For comparison, the Kerr constants and third order non-linear susceptibility data of the samples, measured at different temperatures in the isotropic phase, are summarized in table 2.

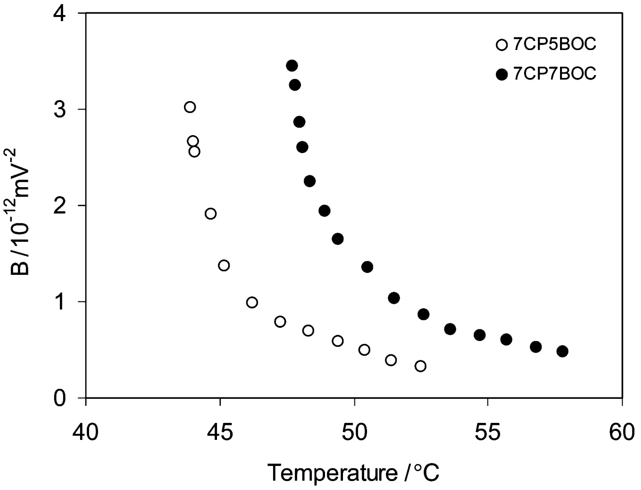


Figure 3. Temperature dependence of B for 7CP5BOC and 7CP7BOC obtained using the nulled intensity method (f=1 kHz).

The strong dependence of the Kerr constant on temperature for the nematogens in the isotropic phase is shown in figure 3. The Kerr constants of these liquid crystalline materials are found to be low in the isotropic phase. This may be due to the presence of the ester linking group and the *bicyclooctane* groups, which greatly decrease the conjugation length, leading to a marked effect on physical properties such as birefringence and susceptibility in theses liquid crystal; i.e. the reduction of conjugation length is conductive to low optical anisotropy.

On the other hand, the lack of a polar head group such as –CN or –NSC in these compounds leads a high reduction in dielectric permittivity and permanent dipole moment. The values of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ for 7CP5BOC have been reported to be 3.0 and 3.7, respectively [10]. The highest values of the Kerr constant obtained in this work for 7CP5BOC and 7CP7BOC at a temperature of 0.3°C above the clearing temperatures were 3.01×10^{-12} and 3.44×10^{-12} m V^{-2}, respectively.

In figure 4 the reciprocal of the Kerr constant, B^{-1}, for the compounds is shown and compared as a function of temperature. For the samples studied the inverse of the Kerr constant varies linearly with temperature, i.e. γ=1, as predicted by the Maier–Saupe mean-field theory for liquid crystals [19]. The extrapolated temperatures T* for these liquid crystals are just below the isotropic phase transitions T_C (i.e. approximately 1.2°C).

The electro-optical Kerr effect is used to determine the third order non-linear susceptibility, $\chi^{(3)}$. The Kerr constant can be related to the third order non-linear susceptibility, an important material parameter for isotropic media. By applying the symmetry properties,

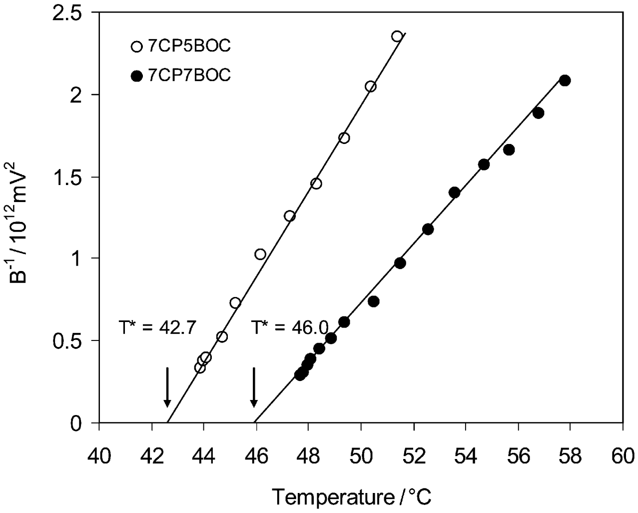


Figure 4. Temperature dependence of B^{-1} for 7CP5BOC and 7CP7BOC obtained using the nulled intensity method (f=1 kHz).

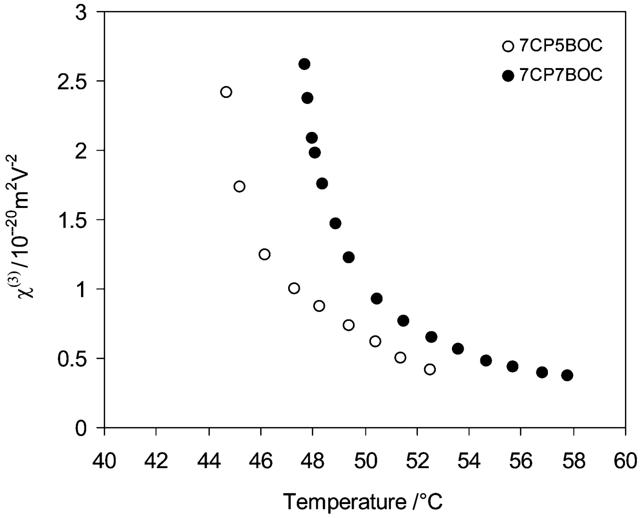


Figure 5. Variation of susceptibility, $\chi^{(3)}$,with temperature for 7CP5BOC and 7CP5BOC.

the non-vanishing elements of third order non-linear susceptibility tensor $\chi^{(3)}$ in an isotropic medium are related as:

$$\chi^{(3)}_{1111}=\chi^{(3)}_{1122}+\chi^{(3)}_{1212}+\chi^{(3)}_{1221}. \tag{2}$$

Using the Klienmann symmetry for this system, it is clear that:

$$\frac{1}{3}\chi^{(3)}_{1111}=\chi^{(3)}_{1122}=\chi^{(3)}_{1212}=\chi^{(3)}_{1221}. \tag{3}$$

Thus, there is only one non-vanishing element of the third order non-linear susceptibility tensor, which can be related to the Kerr constant as [20]:

$$B=\frac{24\pi}{n\lambda}\left[\chi^{(3)}_{1221}(-\omega_1,\omega_1,0,0)\right] \tag{4}$$

where n is the refractive index of the liquid crystal at a given temperature and λ is wavelength of the light.

Figure 5 shows the variation of the susceptibility with temperature for the compounds in the isotropic phase. It can be seen that the compounds exhibit similar non-linearity behaviour due to their similar structure.

4. Conclusions

The values of the Kerr constants and susceptibilities were obtained for 7CP5BOC and 7CP5BOC in the isotropic phase. In general, these compounds exhibit low birefringence and non-linear susceptibility. A low value of $\Delta n=(n_e\text{–}n_o)=0.064$ for 7CP5BOC at 22°C was reported in the earlier study [10].

Nematogens of this class have no polar head group, and are therefore low birefringent materials. In addition, the presence of an ester linking group and bulky *bicyclooctane* ring leads to a decrease in conjugation length; the induced dipole moment and polarizability are responsible for the low birefringence and susceptibility of these nematics. Since the use of low birefringence liquid crystals in light trough modification in an optical fibre is now well established, our electro-optical data may be useful in optical fibre technology.

Pretransitional behaviour at temperatures close to T_C for has been observed in these liquid crystals. The observed linear dependence of $(T\text{–}T^*)^{-1}$ on the Kerr constant (B^{-1}) in this investigation is closely consistent with the Landau–de Gennes model.

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