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## Liquid Crystals

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# Kerr effect investigations in a liquid crystal

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Measurements are reported for the d.c. Kerr response and the pretransitional behaviour of a new liquid crystal, 4-cyanophenyl 4-pentylbenzoate at and above the nematic–isotropic phase transition temperature. The real parts of the third order nonlinear susceptibilities  $\chi^{(3)}$  at and above the nematic–isotropic transition temperatures are determined for the new liquid crystal from the electro-optic Kerr effect (EOKE) experiments. The variation of the Kerr constant with temperature is discussed on the basis of the Landau–de Gennes model of the nematic–isotropic phase transition. The susceptibility values are also compared with that of the well known liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB). The effect of the linking group of the liquid crystal on the susceptibility value is also discussed.

## 1. Introduction

The current interest in organic materials having very large optical non-linearities [1] is a result of the promising potential applications of such materials in a wide variety of opto-electronic devices. Organic compounds such as liquid crystals (LCs) [2, 3] are currently considered best candidates for devices based on non-linear optical effects. Phase transition regions in liquid crystals are regions of giant optical non-linearity.

The optimization of non-linear optical behaviour depends to a large extent on the design of active molecular elements. Thus, to engineer liquid crystal molecules showing large non-linear optical effects, it is of interest to study the influence of structure on the non-linear optical properties of the liquid crystals.

In this paper we investigate the third order non-linear effect in a new liquid crystal 4-cyanophenyl 4-pentylbenzoate, at and above its nematic–isotropic transition region. To determine the potential of a particular liquid crystal, it is important to determine its non-linearity, of which the susceptibility tensor is an important material parameter. The electro-optic Kerr effect is used to determine the third order nonlinear susceptibility tensor. The results are compared with that of a well-studied liquid crystal 4'-pentyl-4-cyanobiphenyl 5CB [4–6]. Since the new liquid crystal differs from 5CB by having an addi-

tional ester linking group, it is of interest to see how this linking group affects the nonlinear properties of the LC.

Since the non-linearity is studied in the nematic–isotropic phase transition region, the validity of the Landau–deGennes theory [7] for the nematic–isotropic phase transition has also been studied. The hypothetical second order phase transition temperature has also been determined.

## 2. Theory

The Kerr law is given by [8]:

$$\Delta n = B\lambda E^2 \quad (1)$$

where  $\Delta n$  is the induced birefringence,  $B$  is the Kerr constant,  $\lambda$  is the probe wavelength and  $E$  is the electric field applied to the isotropic media.

By applying the symmetry properties [9], the non-vanishing elements of the third order susceptibility tensor  $\chi^{(3)}$  in an isotropic media are related as:

$$\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221} \quad (2)$$

Also, applying the Klienmann symmetry [10] we get:

$$1/3\chi_{1111} = \chi_{1122} = \chi_{1212} = \chi_{1221} \quad (3)$$

Thus, there is only one non-vanishing element of the third order susceptibility tensor, which can be related to

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the Kerr constant as [11]:

$$B = 24\pi/n\lambda[\chi_{1221}(-\omega_1, \omega_1, 0, 0)]. \quad (4)$$

By Landau–deGennes theory [7] for a nematic–isotropic phase transition in a conventional LC, the free energy can be expanded as a function of the nematic order parameter  $Q$  as:

$$F = F_0 + (1/2)a(T - T^*)^\gamma Q^2 - (1/3)bQ^3 + (1/4)cQ^4 - (1/2)\Delta\epsilon_0/4\pi E^2 Q + \dots \quad (5)$$

where  $\gamma$  is the critical exponent which takes a value of 1 in any mean field treatment and  $a, b, c$  are the phenomenological constants characteristic of the transition and are assumed to be independent of temperature.  $T^*$  is the hypothetical second order transition temperature the system could have in the absence of the weak first order

transition temperature;  $F_0$  is the free energy when there is no external field. There is no linear term in  $Q$  in zero field. This ensures that the state of minimum  $F$  in the absence of an electric field is a state of zero  $Q$ . The anisotropy in the dielectric constant in the fully ordered phase is given as  $\Delta\epsilon_0$ . Neglecting higher order terms in  $Q$  and by minimizing the free energy with respect to the field and using equation (1) we get [12]:

$$B_{dc} = \Delta n_0 \Delta\epsilon_0 / 3a\lambda(T - T^*). \quad (6)$$

Thus according to the Landau–deGennes model of the nematic–isotropic phase transition, the variation of the inverse of the Kerr constant with temperature is linear, with an intercept on the temperature axis giving the value of the hypothetical second order transition temperature ( $T^*$ ).

### 3. Experimental procedure

The phase transition temperature for the sample was determined by differential scanning calorimetry (DSC) measurements. The structure of the sample studied is shown in figure 1 along with 5CB.

The schematic diagram of the experimental set-up is shown in figure 2. The liquid crystal sample was contained in Kerr cells consisting of polished aluminum electrodes of 10 mm path length and 2 mm electrode

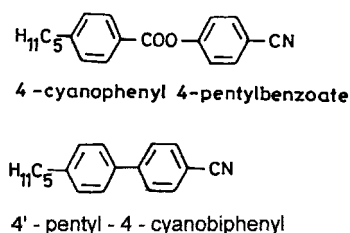


Figure 1. Structural formulae of the liquid crystals studied.

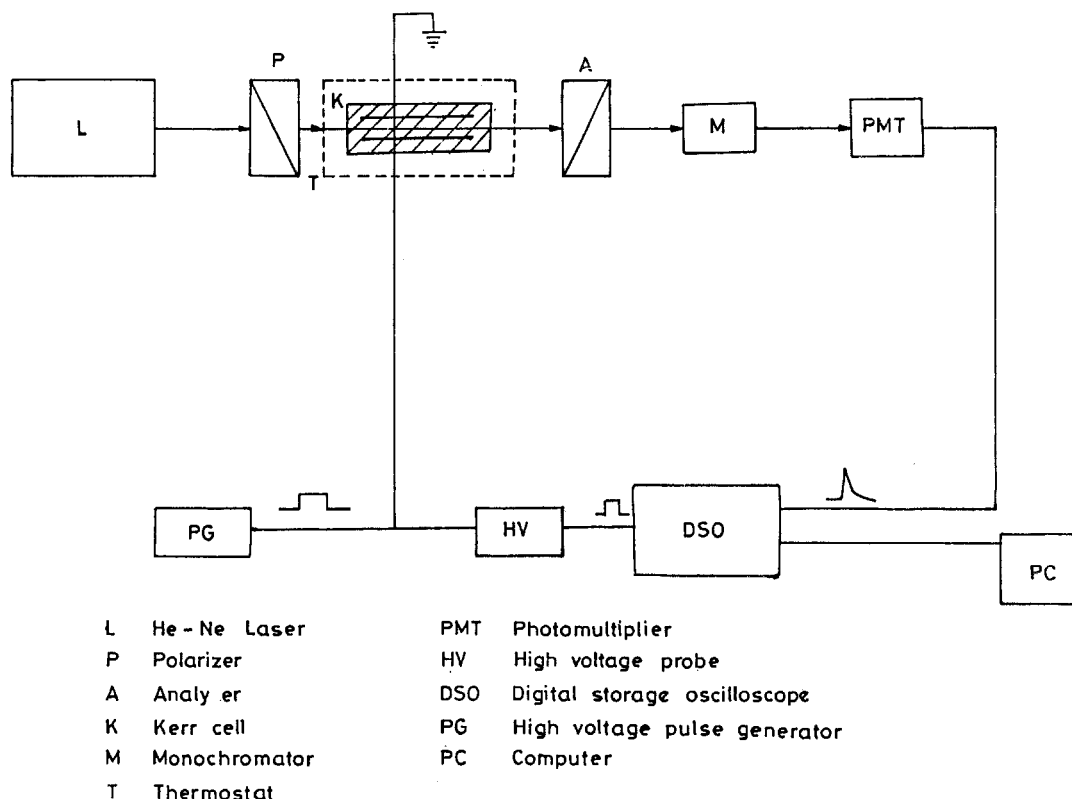


Figure 2. Experimental set-up for the electro-optic Kerr effect.

separation. The electrodes themselves formed the sides of the Kerr cells. The Kerr cells were designed such that minimum quantities of LC samples could be used without wastage. The LC samples were heated directly by a proportional integral differential (PID) controller; the temperature could be maintained to an accuracy of  $\pm 0.1^\circ\text{C}$ . The sample was maintained in the cell at the desired temperature for about 40 min before taking measurements.

A helium-neon laser of 5 mW power was used as a probe beam. A photomultiplier tube (RCP IP-28) was the detector. High voltage pulses up to 8 kV were used to induce birefringence in the medium. The high voltage electric pulses that cause birefringence in the medium were measured using a Tektronix P6015 high voltage probe with 1:1000 attenuation. Both the Kerr signal and the high voltage pulses were acquired on a Digital storage oscilloscope (Tek 2440) with 350 MHz bandwidth and a sampling rate of  $500 \text{ MS sec}^{-1}$ . The polarizer and the analyser were adjusted such that they are crossed with each other, making an angle of  $45^\circ$  with the direction of the electric field.

The phase difference can be obtained from the experiment by using the relation [13, 14]:

$$I = I_0 \sin^2(\delta/2). \quad (7)$$

The induced birefringence ( $\Delta n$ ) which is related to the phase difference ( $\delta$ ) induced by the electric field is given by [12]:

$$\delta = 2\pi l \Delta n / \lambda, \quad (8)$$

where  $l$  is the length of the Kerr cell. The values of  $B$  and hence  $\chi^{(3)}$  for various temperatures were obtained by using the above equations.

#### 4. Results and discussion

The phase transition temperature for the nematic LC is found to be  $63.9^\circ\text{C}$  from DSC measurements. The values of the Kerr constant ( $B$ ), at the transition temperature and above, were determined from the plot of induced birefringence with respect to the square of the electric field as shown in figure 3. Figure 4 shows the variation of the Kerr constant with temperature. The maximum value of the Kerr constant obtained at the transition temperature was  $95.37 \times 10^{-12} \text{ m V}^{-2}$ . Figure 5 shows the variation of the susceptibility with temperature. The highest value of  $\chi^{(3)}$  measured was  $124.44 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$  at the transition temperature. Figure 6 shows the variation of the inverse of the Kerr constant with temperature.

#### 5. Conclusions

The liquid crystal 4-cyanophenyl 4-pentylbenzoate has been studied for the first time to determine its third order nonlinearity by the EOKE method. The highest

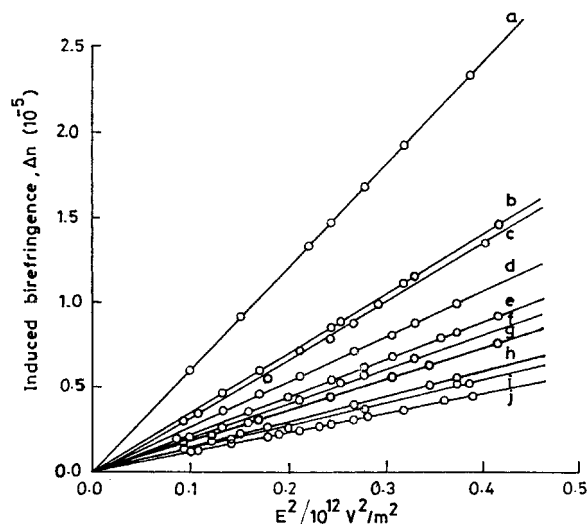


Figure 3. Variation of the induced birefringence ( $\Delta n$ ) with  $E^2$  at (a)  $T = 63.9^\circ\text{C}$ , (b)  $T = 64.5^\circ\text{C}$ , (c)  $T = 65^\circ\text{C}$ , (d)  $T = 65.8^\circ\text{C}$ , (e)  $T = 66.4^\circ\text{C}$ , (f)  $T = 67^\circ\text{C}$ , (g)  $T = 68.5^\circ\text{C}$ , (h)  $T = 69.8^\circ\text{C}$ , (i)  $T = 71.1^\circ\text{C}$ , (j)  $T = 72.9^\circ\text{C}$ .

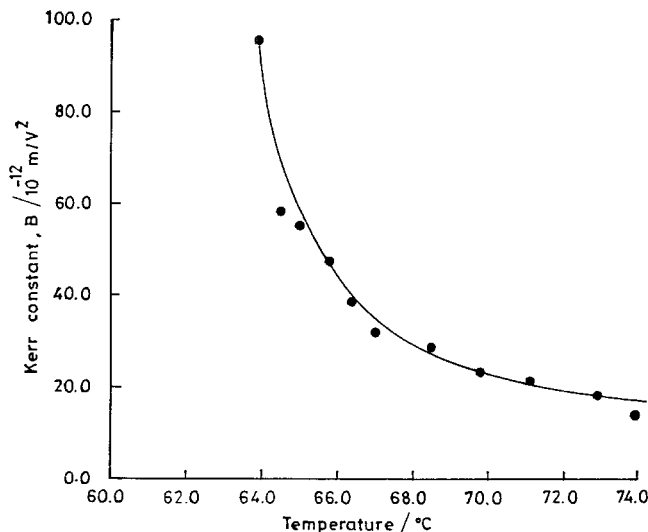


Figure 4. Variation of Kerr constant with temperature.

value of  $\chi^{(3)}$  obtained was  $124.44 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$  at the nematic–isotropic phase transition temperature ( $T_{\text{NI}}$ )  $63.9^\circ\text{C}$ . This corresponds to the highest value of the Kerr constant ( $95.37 \times 10^{-12} \text{ m V}^{-2}$ ) at the same temperature.

The high nonlinearity in the transition region is due to pre-transitional effects occurring in a nematic–isotropic transition region. The value of  $\chi^{(3)}$  of the new liquid crystal has been compared with that of 5CB at the phase transition temperatures, as these two LCs have the same structures except for the linking group shown in figure 1. The highest value of  $\chi^{(3)}$  obtained is less than that for 5CB which is  $172.5 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$  [3]. The additional ester linking group decreases the conjugation length,

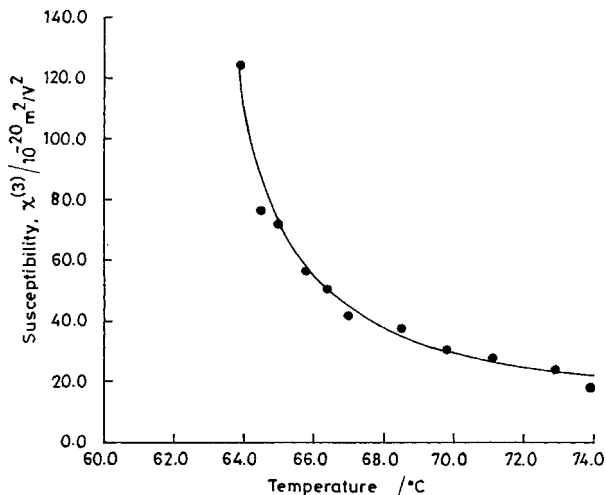


Figure 5. Variation of susceptibility with temperature.

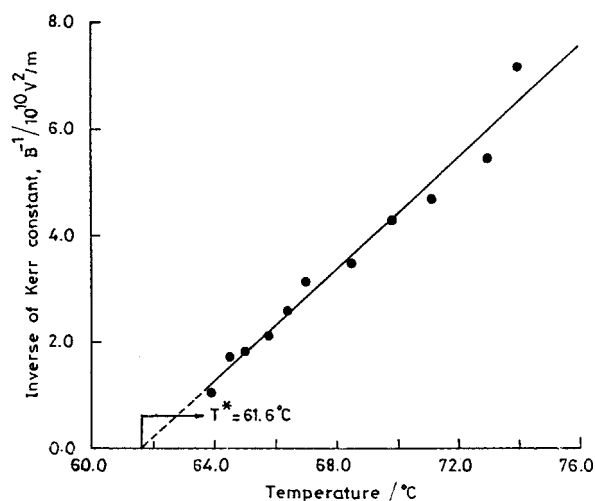


Figure 6. Variation of the inverse of the Kerr constant with temperature.

resulting in the reduction of the freedom of movement of electrons along the length of the molecule. The non-linearity is manifested because of the dipolar orientation of the molecules. Since both LCs have the same terminal group (–CN) they both have the same permanent dipole moment. Due to the reduction in polarizability because of the decrease in the conjugation length, the induced dipole is less in the case of the new liquid crystal, which results in a decrease in its non-linear parameters.

The variation of the Kerr constant with temperature has been found to be linear, thus proving the validity of the Landau–deGennes theory for the nematic–isotropic transition region. The hypothetical second order transition temperature is found to be 61.7°C.

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