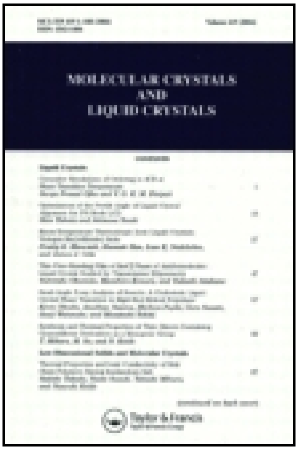

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Magnetic and Electric Birefringence in the Isotropic Phase of a Nematic of Large Positive Dielectric Anisotropy

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Magnetic and Electric Birefringence in the Isotropic Phase of a Nematic of Large Positive Dielectric Anisotropy

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Magnetic (Δn_H) and electric birefringence (Δn_E) in the isotropic phase of strongly positive ($\Delta\varepsilon \approx 8$)*trans-p-n*-octyloxy α-methyl-*p*′-cyanophenyl cinnamate (8 OMCPC) have been measured. It is established that they both exhibit a $(T - T^*)^{-1}$ dependence, $T_{NI} - T^*$ being 1.4 K. Also, the induced birefringence is found to be proportional to the square of the applied field, magnetic or electric.

INTRODUCTION

The pretransitional effects observed in the isotropic phase of a nematic liquid crystal are well described by the phenomenological model[1] based on the Landau theory of phase transitions. It is well established that, as expected from this model, the magnetic birefringence Δn_H in the isotropic phase diverges as $(T - T^*)^{-1}$, where T^* is a hypothetical second order transition point slightly below T_{NI}. However, the electric birefringence Δn_E shows a complex behaviour. Madhusudana and Chandrasekhar[2] showed theoretically that the behaviour of Δn_E can be explained by taking into account the contributions of the polarizability and the permanent dipole of the molecule; Δn_E may be positive or negative depending on the angle which the dipole moment makes with the long molecular axis, and indeed may even exhibit a reversal of sign[3] as the temperature is varied. When the dipole is more or less along the long molecular axis, the electric and magnetic birefringence should both vary as $(T - T^*)^{-1}$. This prediction[4] was confirmed experimentally by us for 4′-*n*-hexyl 4-cyanobiphenyl (6 CB)[5] and by Filippini and Poggi[6] for 5 CB and 7 CB.

The induced birefringence (Δn_H or Δn_E) is expected to vary linearly as the square of the applied field. Coles[7,8] has observed a linear behaviour of Δn_E with E^2 for fields as high as 10 kV/cm for 4'-*n*-pentyl and 4'-*n*-pentyloxy 4-cyanobiphenyls. However recently Muta *et al.*[9] have reported that for the 4'-*n*-alkoxy 4-cyanobiphenyls a linear dependence of Δn_H with H^2 is obtained only for the even members of the series and not for the odd ones. Here we present measurements of both Δn_H and Δn_E of *trans*-*p*-*n*-octyloxy-α-methyl-*p*'-cyanophenyl cinnamate (8 OMCPC) as functions of temperature and for various field strengths. This compound has a large positive dielectric anisotropy[10] of ≈8 owing to the presence of the strongly polar $C \equiv N$ end group. As a consequence it exhibits a large electric birefringence also.

EXPERIMENTAL

8 OMCPC, synthesized in our chemistry laboratory,[11] exhibits nematic phase between 58°C and 71.7°C. The low electrical conductivity ($\approx 10^{-10}$ ohm^{-1} cm^{-1}) of the sample precluded any heating effects on application of strong electric fields.

Light from a He–Ne laser polarized at an angle of 45° to the field direction was allowed to pass through the sample. The phase retardation introduced in the sample due to the application of the external field was measured as a rotation of the plane of polarization using a quarter-wave plate whose principal axes were inclined at an angle of 45° to the field direction. The rotation was measured with a graduated analyzer to an accuracy of 0.02°. When light of wavelength λ passes through L cm of the sample, the induced birefringence

$$\Delta n = \frac{\lambda R}{\pi L},$$

where R is the rotation measured in radians. The position of the minimum intensity was located using a photomultiplier tube and a lock-in-amplifier. For measuring Δn_H, the incident light was modulated using a variable speed chopper operating at 500 Hz. An electromagnet with 15 cm diameter pole pieces was used at 4 cm pole separation. At each temperature the rotations were measured for two magnetic field strengths, viz., 5600 and 6520 gauss. In the case of Δn_E measurements the AC electric field itself served for modulation. A sine wave generator with a matched step-up transformer gave a maximum voltage of 1 kV at 500 Hz. Δn_E was measured at two field strengths, viz., 2.98 and 3.92 kV/cm.

The magnetic birefringence cell consisted of a 6.95 cm long non-magnetic stainless steel tube with an internal diameter of 3 mm. A 3 mm wide slot made along the length of the tube helped in filling the cell with the sample.

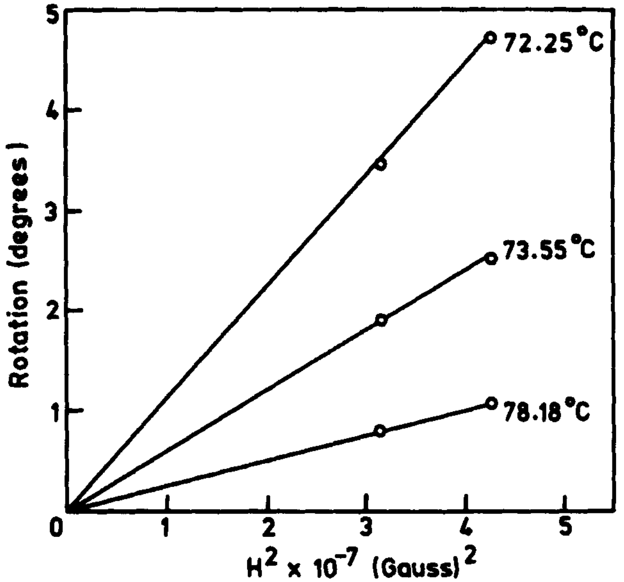

FIGURE 1 Rotation versus square of the magnetic field at different temperatures.

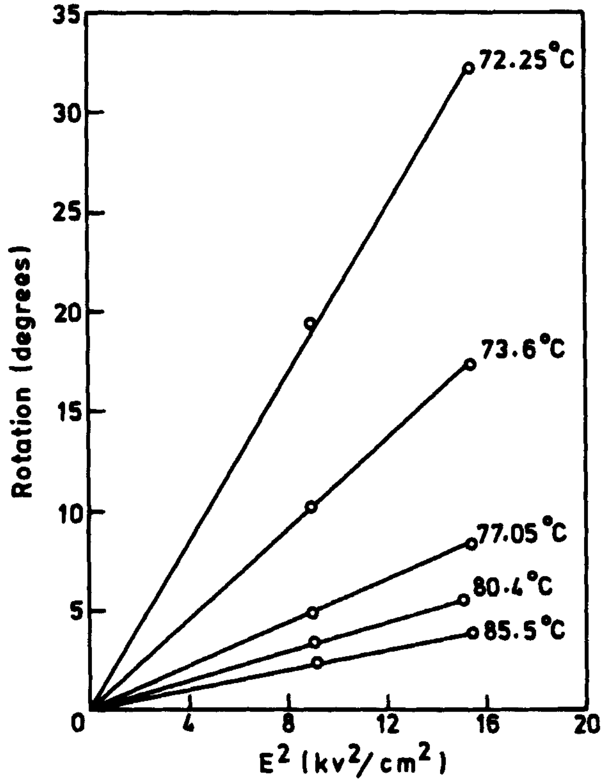

FIGURE 2 Rotation versus square of the electric field at different temperatures.

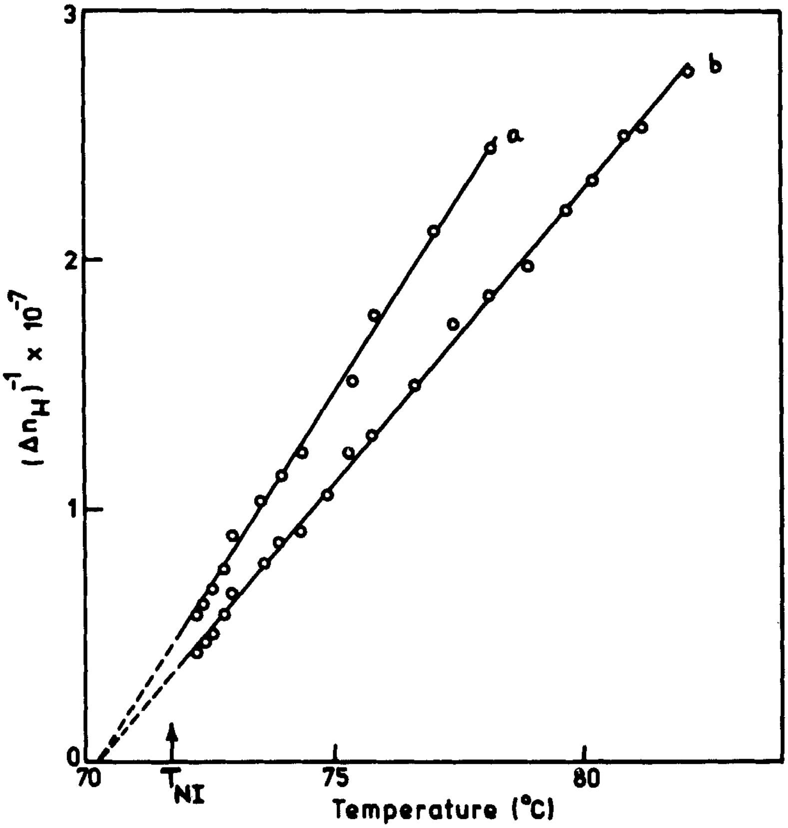

FIGURE 3 Inverse of Δn_H versus temperature for (a) H = 5600 and (b) 6520 Gauss.

Two optically flat glass plates were fixed to the two ends of the tube using an epoxy (Epo–Tek H77) which could stand temperatures up to 150°C, and which did not react with the sample. The cell used for Δn_E measurements consisted of an optical cell of 1 cm path length into which non-magnetic stainless steel electrodes, whose separation (0.255 cm) was fixed by teflon spacers, were inserted. The cells were enclosed in electrically heated copper chambers provided with glass windows. The sample temperatures were measured using chromel-alumel thermocouples. The temperatures could be maintained and measured to an accuracy of 0.025°C. Before the start of a measurement the copper chamber was flushed with dry nitrogen to prevent oxidation of the sample. The transition temperatures of the sample, determined using a hot stage microscope were the same before and after the experiments. The cells were previously calibrated by measuring the Cotton–

Mouton constant and the Kerr constant of freshly distilled nitrobenzene. The agreement between the measured and standard values of the constants was better than 2% which is therefore reckoned to be the absolute accuracy of our data. However, changes in the relative value of the birefringence as small as 10^{-9} could be detected.

RESULTS AND DISCUSSION

In Figures 1 and 2 we have plotted the measured angle of rotation, which is proportional to the birefringence, versus H^2 and E^2 respectively for 8OMCPC at different temperatures. All the plots are straight lines passing through the origin. These results are in agreement with the results of Coles.[7,8]

Both Δn_H and Δn_E were measured at temperature as close as 0.1°C to T_{NI}. In Figure 3 we have shown the variation of the inverse of Δn_H with temperature for the two field strengths used. The plots are straight lines in conformity with the phenomenological model. The lines on extrapolation meet on the temperature axis giving the same value of $T^*(T_{NI} - T^* = 1.4°C$; $T^* = 70.3°C)$.

The inverse of Δn_E as a function of temperature is shown in Figure 4. The variation is linear for both the field strengths, establishing the $(T - T^*)^{-1}$ dependence of Δn_E also. On extrapolation the two lines meet at the same T^*, the value of T^* being 70.3°C.

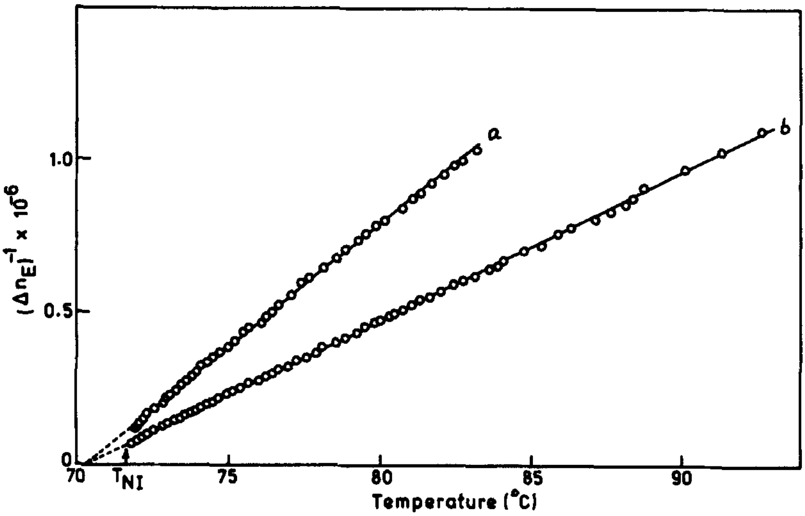

FIGURE 4 Inverse of Δn_E versus temperature for (a) $E = 2.98$ and (b) 3.92 kV/cm.

Thus both Δn_H and Δn_E in the isotropic phase of 8 OMCPC behave similarly giving the same value of T^*, confirming that the pretransitional effect in the isotropic phase can be satisfactorily accounted for in terms of the Landau–de Gennes model.

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