

Experimental studies of short range order in nematogens of strong positive dielectric anisotropy

B R RATNA, M S VIJAYA, R SHASHIDHAR and
B K SADASHIVA

Raman Research Institute, Bangalore 560006, India.

Abstract. The magnetic and electric birefringence in the isotropic phase of 4'-*n*-hexyl-4-cyanobiphenyl, a nematogen of high positive dielectric anisotropy, have been measured as functions of temperature. Both show a $(T-T^*)^{-1}$ dependence in the range of temperatures studied. We also report the dielectric constants of 4'-*n*-octyloxy-4-cyanobiphenyl measured in the nematic and isotropic phases. The mean dielectric constant shows a slight increase on passing from the nematic to the isotropic phase. These results are in conformity with the model of antiferroelectric short range order proposed by Madhusudana and Chandrasekhar.

Introduction

It has been experimentally established that the magnetic birefringence^{1,2,3} in the isotropic phase of a nematogen can be described in terms of de Gennes' model according to which the temperature dependence is given by $(T-T^*)^{-1}$ where T^* is the hypothetical second order transition point. On the other hand, the electric birefringence of the few compounds that have been studied^{2,4} does not follow this type of behaviour. For example, in *p*-azoxyanisole (PAA) there is a reversal of sign of electric birefringence a few degrees above the nematic-isotropic transition point T_0 ². Madhusudana and Chandrasekhar⁵ have shown that this reversal in PAA can be explained on the basis of the phenomenological model when proper allowance is made for the contributions of the polarizability and the permanent dipole moment. From their theory it follows that compounds with dipole moments parallel to the long molecular axis should show a temperature dependence similar to that of magnetic birefringence, viz., as $(T-T^*)^{-1}$. Schadt and Helfrich⁴ have measured the Kerr constant (in the isotropic phase) of some compounds with strong positive dielectric anisotropy and have reported that the temperature dependence of the electric birefringence is expressible as $(T-T_0)^{-\gamma}$ where γ ranges between 0.5-0.7. They have remarked that it would be of interest to see if the magnetic birefringence of such compounds also exhibit a slower temperature variation.

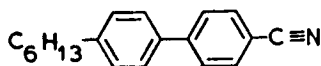
Madhusudana and Chandrasekhar⁶ have recently proposed a model of antiferroelectric short range order in materials which have strong positive dielectric anisotropy. Two important consequences of their theory are

(i) the mean dielectric constant should increase slightly on going over from the nematic to the isotropic phase, (ii) the electric and magnetic birefringence should show essentially the same type of behaviour, *viz.*, $(T - T^*)^{-1}$. However, if the dipolar or $P_1 \cos \theta_{11}$ interactions are extremely strong, much greater than $P_2 \cos \theta_{11}$ interactions, then the electric birefringence may exhibit a slower variation at temperatures well above T_* , whereas the magnetic birefringence should still vary as $(T - T^*)^{-1}$. The present experimental study was undertaken to verify these predictions.

So far no extensive studies of both magnetic (Δn_M) and electric birefringence (Δn_E) of a strongly positive material have been reported. We have carried out precise measurements of Δn_M and Δn_E , using highly purified 4'-*n*-hexyl-4-cyanobiphenyl (HCB), over a wide range of temperatures. It is established that the temperature variation of both Δn_M and Δn_E is well represented by $(T - T^*)^{-1}$ throughout the range, in agreement with the prediction of Madhusudana and Chandrasekhar. We have also measured the principal dielectric constants in the nematic and isotropic phases of 4'-*n*-octyloxy-4-cyanobiphenyl (OOCB). The value of ϵ obtained by extrapolating the isotropic dielectric constant ϵ_{is} into the nematic phase is found to be significantly higher than the mean dielectric constant $\bar{\epsilon}$ in the nematic phase confirming an earlier observation by Schadt⁷. This result is again in agreement with the theory of antiparallel correlation.

Experimental

(1) *Electric and magnetic birefringence:* HCB⁸ used in the experiments



was synthesized in the laboratory. The nematic-isotropic transition temperature was 29.1° C. The conductivity of the sample was of the order of 10^{-10} ohm⁻¹ cm⁻¹.

The schematic diagram of the experimental set up used for the magnetic and electric birefringence measurements is shown in figure 1. Light from He-Ne gas laser was linearly polarized at an angle of 45° to the field direction. The emergent light from the sample was allowed to fall on a $\lambda/4$ plate whose principal axes were inclined at 45° to the field (electric or magnetic) direction, so that the phase retardation could be measured as a rotation of the plane of polarization. The angle of rotation was measured by means of a graduated analyzer (Winkel-Zeiss No. 103071) reading to an accuracy of 0.02°. The position of the minimum intensity was located using a photomultiplier tube (Philips PW 4111) in conjunction with a

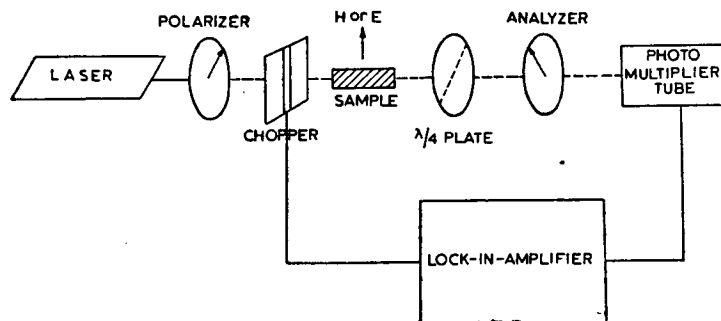


Figure 1 Schematic diagram showing the experimental set up used for the electric and magnetic birefringence measurements.

lock-in-amplifier (Unipan-Selective Nanovoltmeter, type 227, Homodyne Rectifier Voltmeter, type 202B). For magnetic birefringence measurements the incident light was modulated using an electronic chopper (American Time Products, type TNC-L8C) of frequency 400 Hz. For electric birefringence measurements the AC field itself served as the modulation.

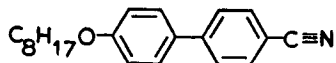
An optical cell of 1 cm path length was used for the electric birefringence measurements. Electrodes made of non-magnetic stainless steel were inserted in the cell with teflon spacers. The separation between the electrodes was 0.32 cm. A 500 Hz AC field of 3.12 kV/cm was used. As the sample had very low conductivity, there was no electrohydrodynamic instability at this field. The glass cell was enclosed in a copper chamber with suitably provided optically flat glass windows. This chamber was electrically heated. The temperature of the sample was measured by Chromel-Alumel thermocouple to an accuracy of 0.025° C.

HCB being a strongly positive compound its electric birefringence is expected to be an order of magnitude greater than the magnetic birefringence with the fields normally available in the laboratory. In order that the Δn_M could be measured to the same accuracy as Δn_E it was necessary to increase the path length, and a separate cell was designed for this purpose. The sample was contained in a narrow teflon tube of length 10 cm sealed at both ends using optical windows. The sample tube was inserted in a copper jacket to ensure good thermal capacity and the entire assembly was placed inside a heater whose temperature could be controlled accurately. By keeping temperature probes at different positions of the sample tube it was ascertained that there were no temperature gradients within the sample. A magnetic field of 6.9 kgauss was used.

The chambers containing the sample cells were filled with nitrogen to prevent oxidation of the sample. The cell constants were evaluated by measuring the Kerr constant and Cotton-Mouton constant of nitrobenzene.

The absolute accuracy of the measurement for electric birefringence was found to be about 1% and that for magnetic birefringence 1.5%.

(2) *Dielectric constants*: The substance studied was OOCB⁸ which has



a nematic range of 67–80.5°C. Below 67°C it exhibits a smectic phase which however has not been identified.

The dielectric constants were measured at 1 kHz using a General Radio impedance bridge (Type 1656) with a digital readout and capable of measuring the capacitance to an accuracy of 0.1 pf. The dielectric cells consisted of two tin-oxide coated glass plates. The separation between the electrodes was fixed by 25–50 μ thick mylar spacers. The cell was kept inside an electrically heated copper chamber provided with glass windows for checking the alignment of the sample visually during the measurements. This chamber was evacuated and filled with nitrogen. Homeotropic alignment was obtained by treating the glass plates with a surface agent. A 17 kgauss magnetic field was used to align the sample homogeneously. The dielectric constant was determined by measuring the capacitance of the cell without and with the sample. The bridge voltage across the capacitor plates was very low (300 mV) and did not have any disturbing influence on the alignment of the sample. The values of ϵ_{is} obtained from the independent measurements in the two geometries matched to within $\pm 0.2\%$. Thus the relative values of $\epsilon_{||}$ and ϵ_{\perp} are reckoned to be accurate to within these limits, but absolute values are estimated to be accurate to only $\pm 3\%$.

Results

The plot of the reciprocal of the electric and magnetic birefringence versus temperature is shown in figure 2. The magnetic birefringence measured upto 12°C above the transition temperature (T_c), shows $(T - T^*)^{-1}$ behaviour throughout. Measurement above this temperature was not possible owing to the fact that the variation of Δn_M became comparable to the accuracy of the instrument. However, the electric birefringence could be measured upto 25°C above T_c and it also shows a similar temperature dependence throughout the range. Both measurements give the same value of T^* ($T^* = 28^\circ\text{C}$, $T_c - T^* = 1.1^\circ\text{C}$).

Figure 3 shows the variation of the principal dielectric constants of OOCB with temperature. It exhibits large anisotropy ($\epsilon_{||} > 2\epsilon_{\perp}$) evidently

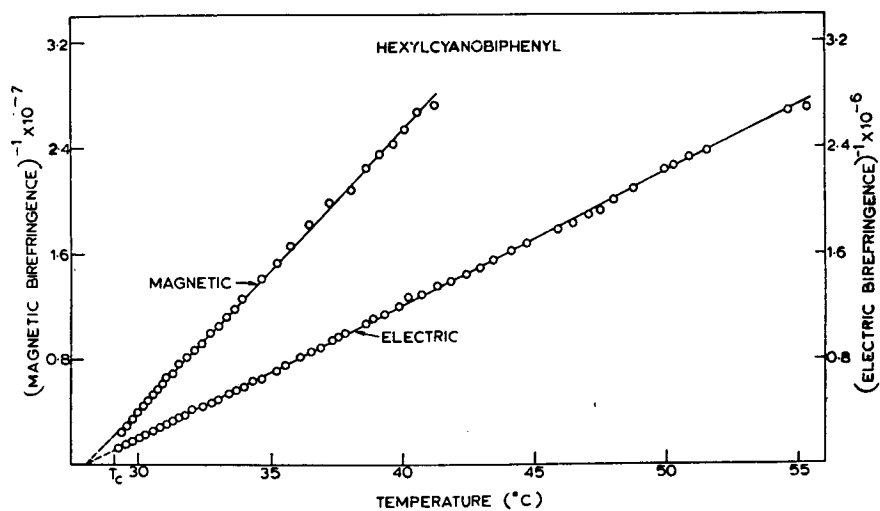


Figure 2 Plot of the reciprocal of the magnetic and electric birefringence versus temperature in HCB. (Both give the same T^* , $T^* = 28^\circ\text{C}$, $T_c - T^* = 1.1^\circ\text{C}$).

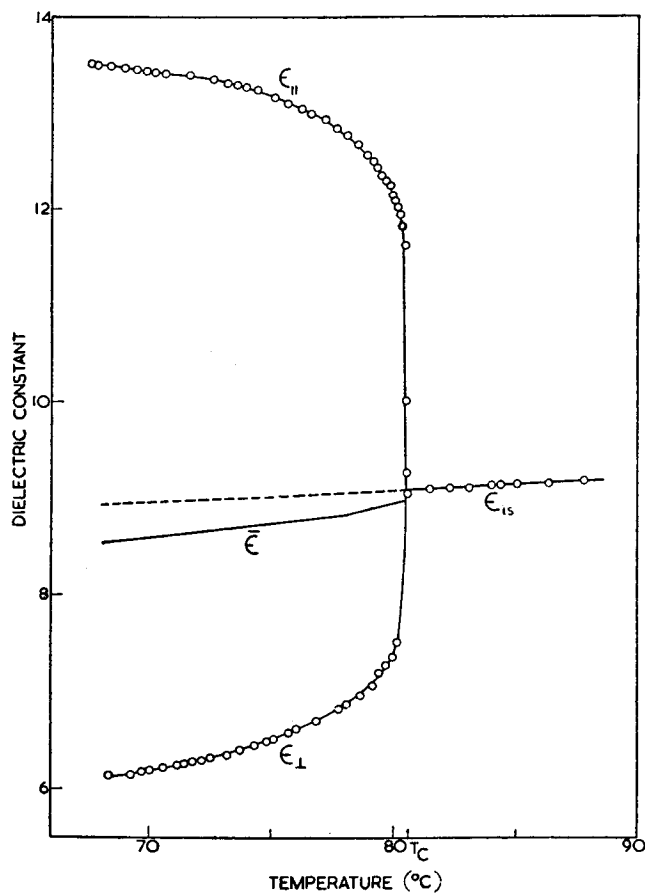


Figure 3 Principal dielectric constants of OOCB. ($\bar{\epsilon}$ is the mean dielectric constant evaluated from the experimental values of ϵ_{\parallel} and ϵ_{\perp} . The broken line denotes the extrapolated value of ϵ_{1s}).

because of the strong dipole moment along the molecular axis. The mean dielectric constant, $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ is also shown in the figure. It can be seen that it is 2-3% lower than the extrapolated value of ϵ_{is} denoted by the dashed line. This is in accordance with the theory of antiferroelectric short range order in nematic liquid crystals of positive dielectric anisotropy.

Acknowledgements

We wish to thank Professor S Chandrasekhar for his continued interest and advice and Dr N V Madhusudana for valuable suggestions and help in setting up the apparatus.

References

- 1 ZADOC-KAHN J *Ann. Phys. (Paris)* **11** 455 (1936)
- 2 TSVETKOV V N and RYUMTSEV E I *Sov. Phys. Crystallogr.* **13** 225 (1968)
- 3 STINSON T W and LITSTER J D *Phys. Rev. Lett.* **25** 503 (1970)
- 4 SCHADT M and HELFRICH W *Mol. Cryst. Liquid Cryst.* **17** 355 (1972)
- 5 MADHUSUDANA N V and CHANDRASEKHAR S *Liquid Crystals and Ordered Fluids* Vol. 2, ed JOHNSON J F and PORTER R S (*Plenum, New York*) p. 657 (1973)
- 6 MADHUSUDANA N V and CHANDRASEKHAR S, This conference (1973)
- 7 SCHADT M J. *Chem. Phys.* **56** 1494 (1972)
- 8 GRAY G W, HARRISON K J and NASH J A *Ele. Lett.* **9**(6) 130 (1973)