

Dielectric properties of 4'-n-alkyl-4-cyanobiphenyls in their nematic phases

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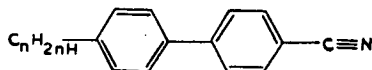
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Abstract. The principal dielectric constants of the pentyl to octyl derivatives of 4'-n-alkyl-4-cyanobiphenyl have been measured as functions of temperature in their nematic and isotropic phases. All the compounds exhibit a strong positive dielectric anisotropy due to the presence of a large dipole moment along the major molecular axis. The principal dielectric constants ϵ_{\parallel} and ϵ_{\perp} as well as the anisotropy $\Delta\epsilon$ decrease with increasing alkyl chain length. The experimental value of $\bar{\epsilon} = \frac{1}{3}(\epsilon_{\parallel} + 2\epsilon_{\perp})$ decreases with decreasing temperature, and is throughout less than the extrapolated isotropic value, in conformity with the model of antiferroelectric short range order proposed by Madhusudana and Chandrasekhar.

Keywords. Nematic liquid crystals; dielectric anisotropy; cyanobiphenyl.

1. Introduction

Nematic liquid crystals with strong positive dielectric anisotropy are of considerable interest because of their use in electrooptical devices. There have been only a few studies on the dielectric properties of such compounds (Schadt 1972, Ratna *et al* 1973, Titov *et al* 1975). Gray *et al* (1973) have recently synthesized 4'-n-alkyl-4-cyanobiphenyls which have the following structural formula :



Because of the cyano end group these compounds possess a large dipole moment $\sim 4D$ (Minkin *et al* 1970) along the long axis of the molecule. This leads to a large value of ϵ_{\parallel} and consequently to a large positive dielectric anisotropy. Also, these compounds are characterized by low melting points, are colourless, chemically and photochemically stable. The first three members of this series are non-mesomorphic. The fourth member shows only a monotropic nematic phase whereas the fifth member onwards they are enantiotropic. We have taken up a systematic experimental study of the dielectric properties of four of these compounds; *viz.*, pentyl (5CB), hexyl (6CB), heptyl (7CB) and octyl (8CB) cyanobiphenyls. Of these 5CB, 6CB and 7CB are room temperature nematics whereas 8CB is a room temperature smectic with the nematic phase above $32.5^{\circ}C$.

2. Experimental

All the compounds studied except 8CB were synthesized in our chemistry laboratory. 8CB was supplied by BDH, England. They show the nematic phase in the temperature ranges of 22.5–35°C, 13.5–29°C, 28.5–42°C and 32.5–40.4°C respectively. 8CB also exhibits a smectic phase below 32.5°C which has been recently identified as smectic A (Luckhurst and Poupko 1975, Gray 1975). However, we have not made any measurements in the smectic phase of this compound owing to difficulty in aligning the sample in this phase. The resistivities of the samples were of the order of 10^{10} ohm cm. The experimental set up has already been briefly described (Ratna *et al* 1973). The capacitances were measured at a frequency of 1 KHz using a GR 1656 impedance bridge reading to an accuracy of 0.1%. The dielectric cells consisted of two indium oxide coated glass plates supplied by Vari Light Corporation, USA. The separation between the plates was fixed by mylar spacers of 25–50 μ thickness. The cell was mounted in a copper frame and the entire unit introduced into an electrically powered copper chamber of large thermal capacity whose temperature could be accurately controlled. A chromel-alumel thermocouple was used to measure the sample temperature to an accuracy of 0.025°C. By keeping probes at different locations of the heater it was ascertained that the cell did not experience any temperature gradients. Windows were provided both in the frame as well as in the heater for visually checking the alignment of the sample during the course of the experiment. The electrical contacts with the glass plates were made through spring mounted screws. Leads from the electrodes were fixed rigidly and the lead capacitance was subtracted from the measured value to get the true capacitance of the cell. All the measurements were carried out after evacuating the copper chamber and then filling it with nitrogen ensuring that the chamber is sealed at the points where thermocouple and contact leads are taken out. 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.

All the cyanobiphenyls studied have a natural tendency to align homeotropically (Gray *et al* 1973). As a result, homeotropic alignment was easily achieved provided the surfaces of the glass plates were extremely clean. To facilitate this alignment a new set of plates was used every time. Homogeneous alignment was obtained by a 17 KGauss magnetic field. The relative variation of ϵ_{\parallel} or ϵ_{\perp} could be determined to an accuracy of $\pm 0.1\%$ which is the accuracy of the instrument itself. The value in the isotropic phase obtained independently from the two different geometries matched to within 1%. Also the cells were calibrated using freshly distilled toluene and chlorobenzene and the values obtained agreed within 2% of the standard values which is therefore reckoned to be the absolute accuracy.

3. Results and discussions

The curves showing the variation of the principal dielectric constants with temperature for 5CB, 6CB, 7CB and 8CB are given in figures 1–4 respectively. Figure 5 gives a plot of their dielectric anisotropy ($\Delta\epsilon$) as a function of $T - T_{NI}$, where T_{NI} is the nematic-isotropic transition temperature. All the compounds exhibit a

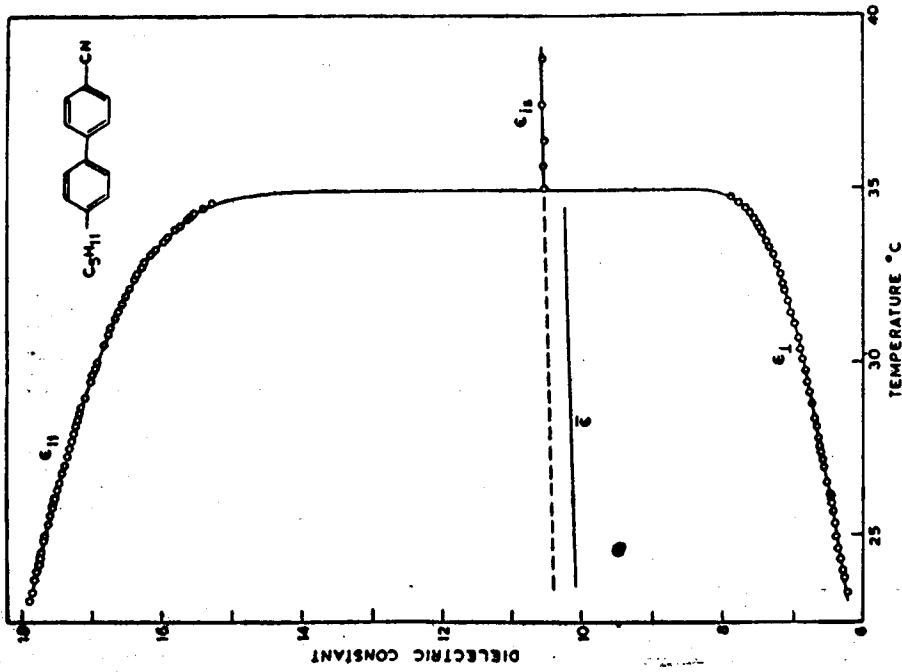


Figure 1. Principal dielectric constants of 5CB. $\bar{\epsilon}$ is the mean dielectric constant evaluated from the measured values of ϵ_{11} and ϵ_1 . The broken line indicates the extrapolated value of ϵ_{1a} in the nematic phase ($T_N = 35.0^\circ\text{C}$).

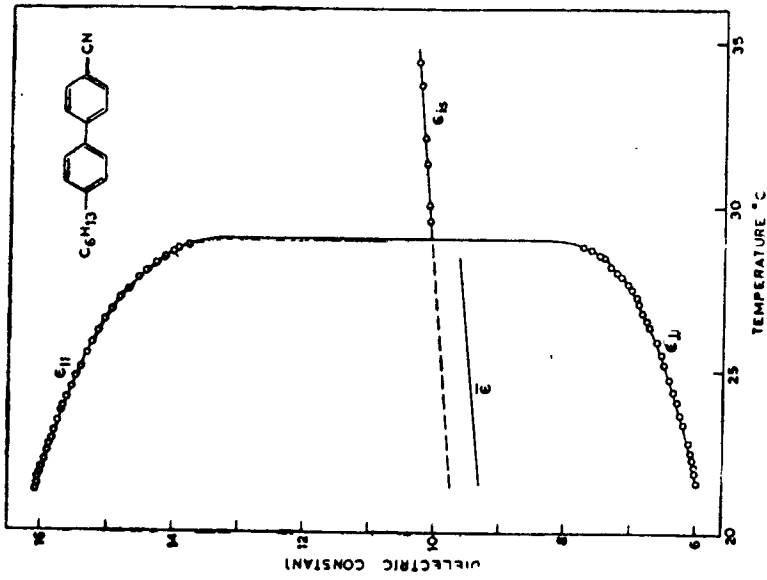


Figure 2. Principal dielectric constants of 6CB ($T_N = 29.0^\circ\text{C}$).

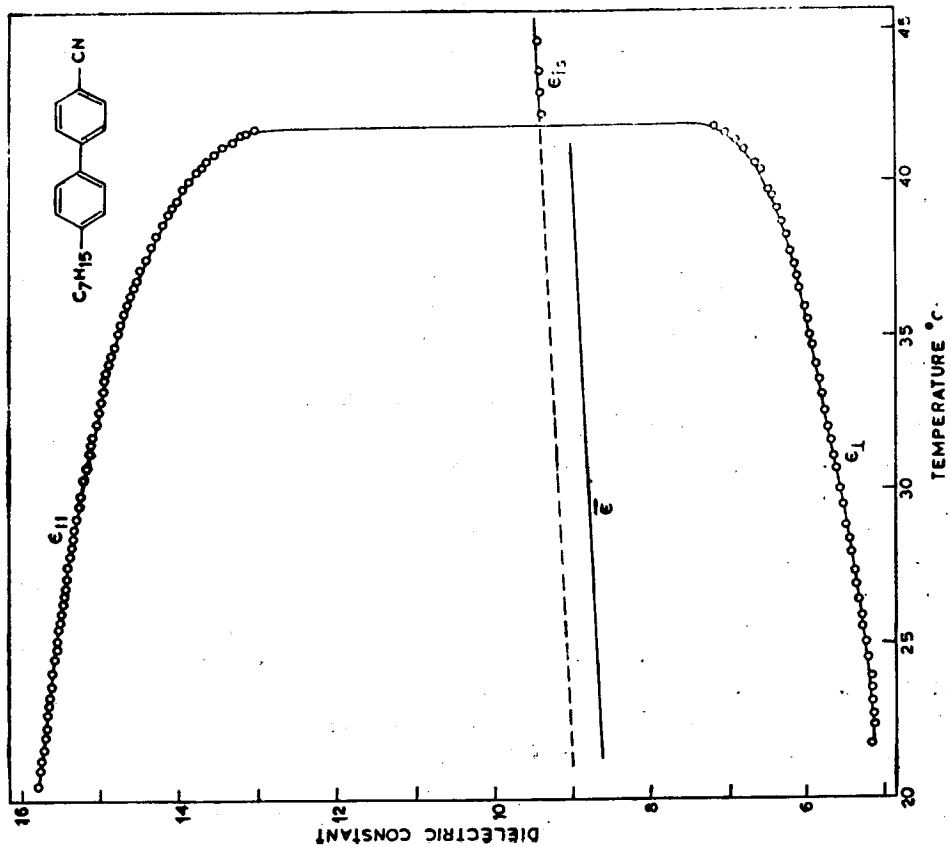


Figure 3. Principal dielectric constants of 7CB ($T_{NI} = 42.0^\circ\text{C}$).

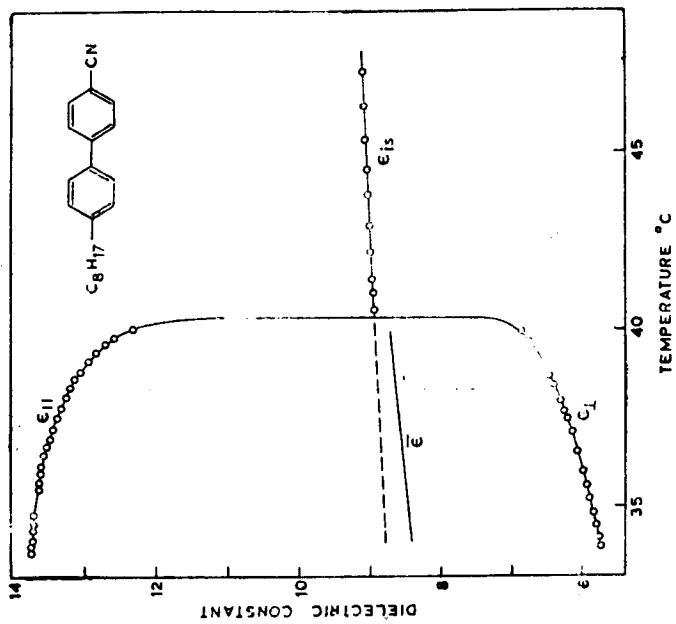


Figure 4. Principal dielectric constants of 8CB ($T_{NI} = 40.4^\circ\text{C}$).

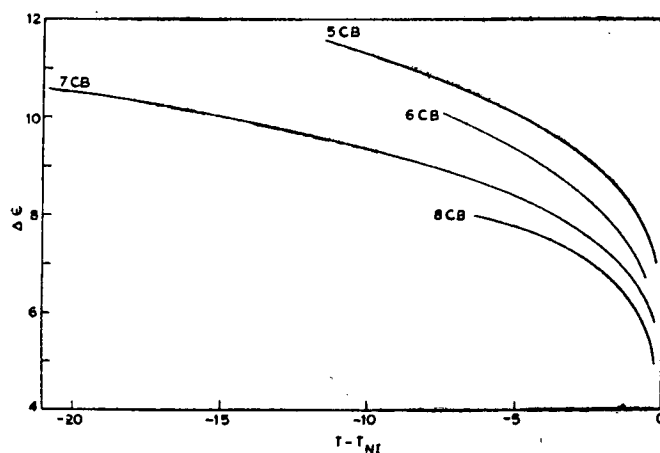


Figure 5. Dielectric anisotropy $\Delta\epsilon$ as a function of $T - T_{NI}$.

Table 1. Dielectric constants of 5CB, 6CB, 7CB and 8CB at a temperature of $(T_{NI} - 1)^\circ\text{C}$

Compound	T_{NI}	ϵ_{\parallel}	ϵ_{\perp}	$\Delta\epsilon$
5CB	35.0	15.70	7.50	8.20
6CB	29.0	14.45	7.18	7.27
7CB	42.0	13.55	6.80	6.75
8CB	40.4	12.80	6.65	6.15

large positive dielectric anisotropy, the dielectric constant along the preferred molecular direction (ϵ_{\parallel}) being about twice that in the transverse direction (ϵ_{\perp}). Table 1 gives the ϵ_{\parallel} , ϵ_{\perp} and $\Delta\epsilon$ values taken at a common relative temperature of $(T_{NI} - 1)^\circ\text{C}$.

We see from table 1 that both ϵ_{\parallel} and ϵ_{\perp} are highest for 5CB and show a continuous decrease as we go to higher members of the series. It is interesting to note that although T_{NI} as well as the order parameters are known to show an alternation for the same compounds (Karat and Madhusudana) as the homologous series is ascended, $\Delta\epsilon$ does not show such an alternation (figure 5). The reason for this is still not clear to us.

The other interesting result is that in all these compounds, the average dielectric constant ($\bar{\epsilon}$), calculated from the measured values of ϵ_{\parallel} and ϵ_{\perp} using the relation $\bar{\epsilon} = 1/3 (\epsilon_{\parallel} + 2\epsilon_{\perp})$, is less than the extrapolated value of ϵ_{it} by about 4%. This is in contrast to the behaviour of non-polar molecules wherein it has been shown experimentally that $\bar{\epsilon}$ and ϵ_{it} coincide at T_{NI} (de Jeu and Lathouwers 1974). A similar difference between $\bar{\epsilon}$ and ϵ_{it} has also been observed by Schadt (1972) in the case of some other nitrile compounds. Derzhanski and Petrov (1971) have suggested that this difference may be due to a second order flexoelectric effect.

A more straightforward explanation is given by Madhusudana and Chandrasekhar (1973) in terms of a statistical model of antiferroelectric short range order in nematic liquid crystals of strong positive dielectric anisotropy. According to these authors, the mean dielectric constant should show an *increase* on going over from the nematic to the isotropic phase; the increase being due to a decrease in the antiferroelectric short range order at T_{NI} . Further, we see from the figures 1-4 that $\bar{\epsilon}$ decreases with the decrease of temperature. This again can be attributed to an increased antiferroelectric short range order correlation at lower temperatures. Such a behaviour has also been predicted theoretically.

4. Conclusion

These dielectric studies therefore indicate that the molecules in the strongly positive 4'-n-alkyl-4-cyanobiphenyls are arranged in an antiparallel configuration. From their x-ray studies in the nematic phases of 5CB and 7CB, Leadbetter *et al* (1975) have also come to the same conclusion. A similar antiparallel arrangement of molecules has been proposed for the smectic phase of 8CB by Lydon and Coakley (1975) on the basis of their x-ray investigations.

Further experiments are in progress to study the dielectric properties of other positive compounds.

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