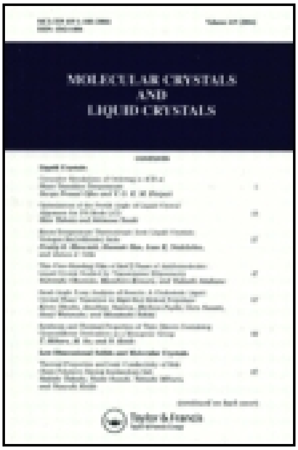

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Dielectric Studies on Liquid Crystals of Strong Positive Dielectric Anisotropy

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Dielectric Studies on Liquid Crystals of Strong Positive Dielectric Anisotropy

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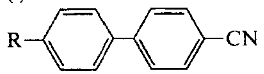
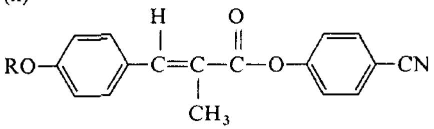
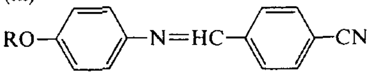
The static dielectric constants of the following compounds have been measured as functions of temperature in their nematic and isotropic phases: (i) 4′-*n*-alkyl-4-cyanobiphenyls, (ii) *trans*-*p*-*n*-alkoxy-α-methyl *p*′-cyanophenyl cinnamates and (iii) CBOOA. All these exhibit a very large positive dielectric anisotropy because of the C≡N end group. For all the compounds the average dielectric constant $\bar{\varepsilon}$ evaluated from the measured values of $\varepsilon_\parallel$ and $\varepsilon_\perp$ is, throughout the nematic phase, less than the extrapolated isotropic value. Further, $\bar{\varepsilon}$ decreases with decreasing temperature, the effect being greater in compounds whose nematic phase is preceded by a smectic phase. These facts are in conformity with the model of antiferroelectric short range order proposed by Madhusudana and Chandrasekhar. For the two homologous series (i) and (ii), the dielectric anisotropy does not show an alternation with increasing chain length, but decreases continuously.

INTRODUCTION

The importance of liquid crystals with strong positive dielectric anisotropy was brought to focus by the observation of the twisted nematic effect by Schadt and Helfrich[1] which resulted in the development of a new type of electro-optic device.[2,3] There have been a few studies on the dielectric properties of such compounds,[4–6] but a systematic investigation of different members of a homologous series has not yet been reported. In this paper we present the results of our experimental studies on the dielectric properties of (i) 4′-*n*-alkyl-4-cyanobiphenyls, (ii) *trans*-*p*-*n*-alkoxy-α-methyl *p*′-cyanophenyl cinnamates, and (iii) *p*-cyanobenzylidene *p*′-octyloxyaniline, all of them exhibiting large positive dielectric anisotropy. The results on cyanobiphenyls have already been published[7] but are included here for the sake

TABLE I

Transition temperatures of the compounds studied.

Chemical structure	R	Compound abbreviation	Temperature of transition to		
			Smectic (°C)	Nematic (°C)	Isotropic (°C)
(i) 	C_5H_{11}	5CB	—	22.5	35.0
	C_6H_{13}	6CB	—	13.5	29.0
	C_7H_{15}	7CB	—	28.5	42.0
	C_8H_{17}	8CB	21.0	32.5	40.4
(ii) 	C_2H_5	2 OMCPC	—	80.0	89.5
	C_4H_9	4 OMCPC	—	63.0	73.8
	C_8H_{17}	8 OMCPC	—	58.0	72.0
	C_9H_{19}	9 OMCPC	—	56.0	70.3
	$C_{10}H_{21}$	10 OMCPC	(57.1)	62.8	73.5
	$C_{11}H_{23}$	11 OMCPC	(70.0)	70.0	73.2
(iii) 	C_8H_{17}	CBOOA	73.0	82.6	107.0

Transition temperatures in parentheses indicate monotropic transitions.

of completeness and comparison. The compounds studied and their transition temperatures are listed in Table I. The dielectric constants were measured only in the nematic and isotropic phases of these compounds even though four of them exhibit a smectic phase below the nematic phase.

The 4'-*n*-alkyl-4-cyanobiphenyls, first synthesized by Gray *et al.*,[8] are characterized by low melting points and are colourless, chemically and photochemically stable. The 5CB, 6CB and 7CB used in the measurements were synthesized in our Chemistry Laboratory and 8CB was obtained from BDH, England. The *trans*-*p*-*n*-alkoxy-α-methyl *p*'-cyanophenyl cinnamates have been very recently synthesized by Sadashiva.[9] These are colourless, fairly low melting and chemically stable materials. We have measured the dielectric constants of only those members which exhibit an enantiotropic nematic phase. The other compound studied, viz., CBOOA was given to us by Dr. P. Cladis. All the compounds were recrystallized several times until the nematic–isotropic transition temperature (T_{NI}) was constant. For biphenyls, the transition temperatures agreed with those reported by Gray *et al.*[8]; in fact for 6CB, our value of T_{NI} was 2°C higher. In the case of CBOOA, the maximum of T_{NI} we could get was 107°C compared to 109°C obtained by Cladis.[10] However, some preliminary experiments clearly showed that such differences in T_{NI} do not affect the variation of the dielectric constant with temperature.

EXPERIMENTAL

The capacitances were measured at a frequency of 1 KHz using a GR-1656 Bridge reading to an accuracy of 0.1 %. The dielectric cells consisted of two tinoxide coated glass plates separated by 25–50 μ thick mylar spacers. The cells were calibrated using freshly distilled toluene and chlorobenzene and the values obtained agreed within 2 % of the standard values. A detailed description of the experimental set up is given elsewhere.[7] The measurements were made in an atmosphere of nitrogen to avoid deterioration of the sample by oxidation. The resistivities of the samples used were of the order of 10^9–10^{10} ohm-cm. Also the birdge voltage across the sample was very low ($\sim$300 mV) and did not have any disturbing influence on the sample. The biphenyls have a natural tendency to align homeotropically when the surfaces of the plates are very clean.[8] Planar alignment was achieved by using a 17 Kgauss magnetic field. In case of cinnamic acid esters and CBOOA, both the alignments were achieved by the magnetic field. The isotropic values obtained in the two independent measurements of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ matched to within 2 %. The relative variation of both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ could be measured to an accuracy of 0.1 % whereas the absolute accuracy is reckoned to be $\sim$2 %, increasing to a somewhat larger value very near the nematic–isotropic transition.

RESULTS

The principal dielectric constants of (i) 4′-*n*-alkyl-4-cyanobiphenyls, (ii) *trans-p-n*-alkoxy-α-methyl *p*′-cyanophenyl cinnamates, and (iii) CBOOA measured as functions of temperature are given in Figures 1–4, Figures 6–11 and Figure 13 respectively. The average value of the dielectric constant $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp}/3)$ in the nematic phase, calculated from the measured values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, is also shown in the figures. The dielectric anisotropy $\Delta\varepsilon$ is plotted as a function of $(T - T_{NI})$ for the various members of the two series in Figures 5 and 12. Tables II and III give the principal dielectric constants and the dielectric anisotropy of these compounds evaluated at a common relative temperature of $(T_{NI} - 1)$.

DISCUSSION

1) It is seen from Tables II and III that for all the compounds the dielectric constant along the preferred direction $(\varepsilon_{\parallel})$ is about twice that in the transverse

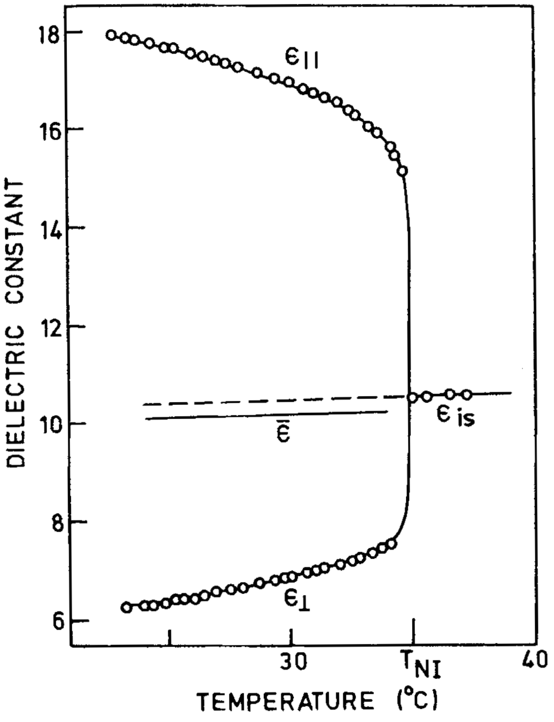


FIGURE 1 Principal dielectric constants of 5CB. $\bar{\varepsilon}$ is the mean dielectric constant evaluated from the measured values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The broken line indicates the extrapolated value of ε_{is} the nematic phase ($T_{NI} = 35°C$).

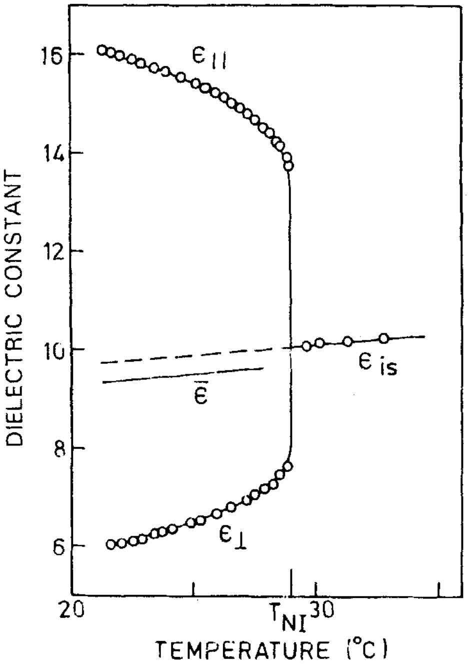


FIGURE 2 Principal dielectric constants of 6CB (T_{NI} = 29.0°C).

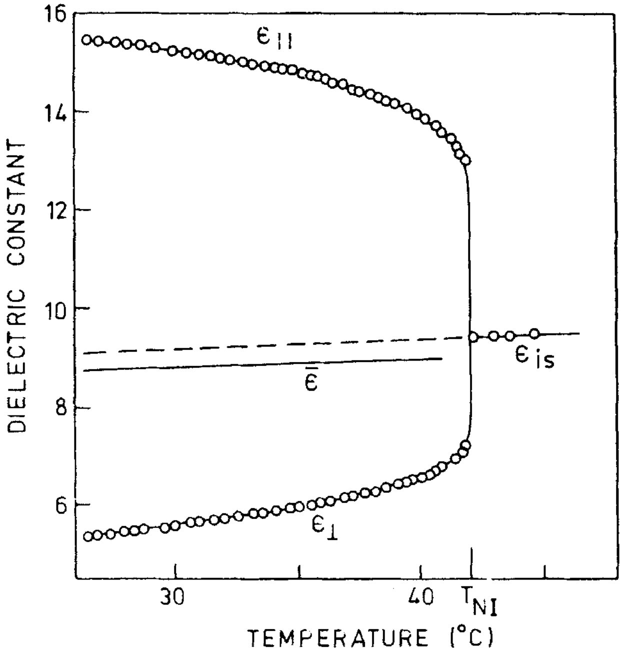


FIGURE 3 Principal dielectric constants of 7CB (T_{NI} = 42°C).

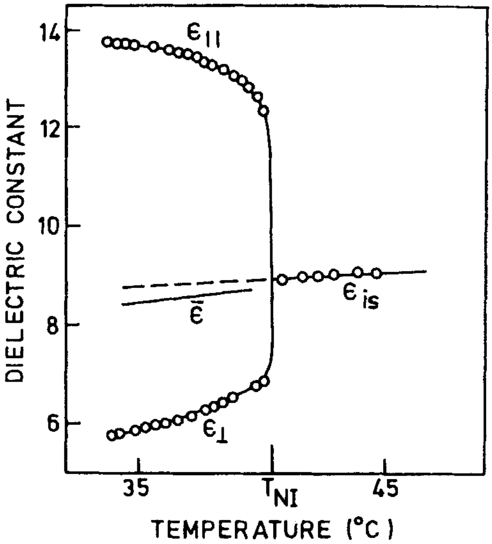


FIGURE 4 Principal dielectric constants of 8CB (T_{NI} = 40.4°C).

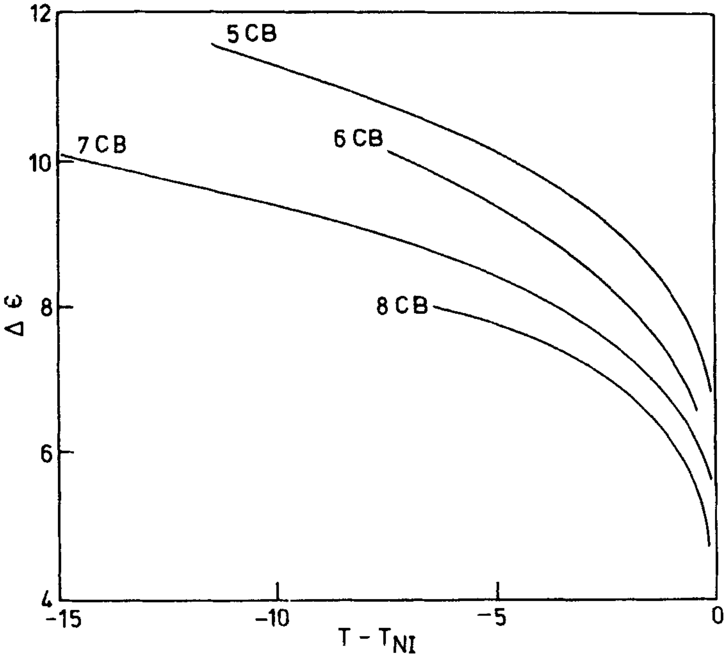


FIGURE 5 Dielectric anisotropy $\Delta\varepsilon$ of 4′-*n*-alkyl-4-cyanobiphenyls as a function of $T - T_{NI}$.

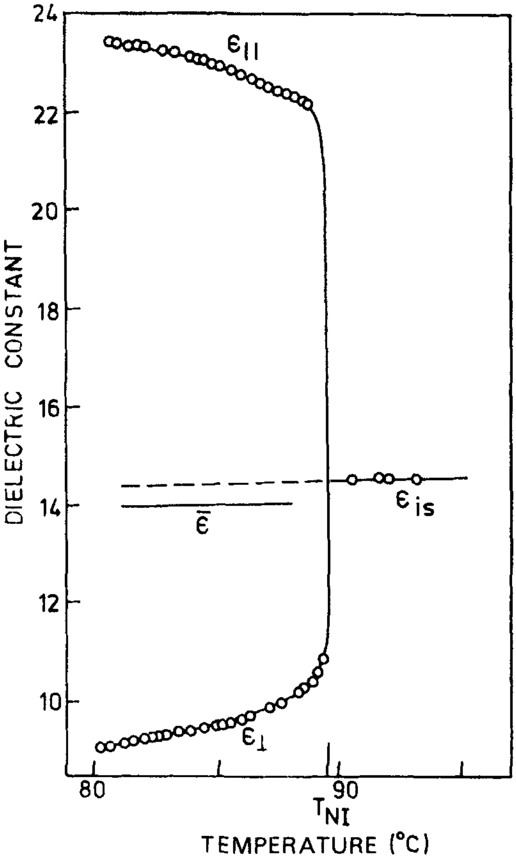


FIGURE 6 Principal dielectric constants of 2 OMCPC (T_{NI} = 89.5°C).

TABLE II

Dielectric constants of 5CB, 6CB, 7CB and 8CB at (T_{NI} − 1)°C

Compound	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
5CB	15.70	7.50	8.20
6CB	14.45	7.18	7.27
7CB	13.55	6.80	6.75
8CB	12.80	6.65	6.15

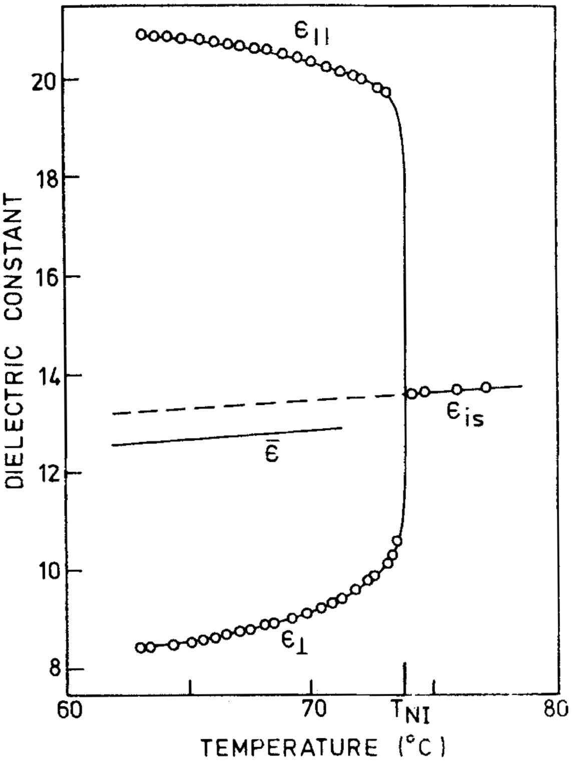


FIGURE 7 Principal dielectric constants of 4 OMCPC (T_{NI} = 73.8°C).

TABLE III

Dielectric constants of *trans-p-n*-alkoxy-α-methyl *p'*-cyanophenyl cinnamates at (T_{NI} − 1)°C

Compound	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
2 OMCPC	22.22	10.27	11.95
4 OMCPC	19.80	10.00	9.80
8 OMCPC	16.88	9.11	7.77
9 OMCPC	14.79	8.04	6.75
10 OMCPC	14.16	7.95	6.21
11 OMCPC	13.97	8.05	5.92

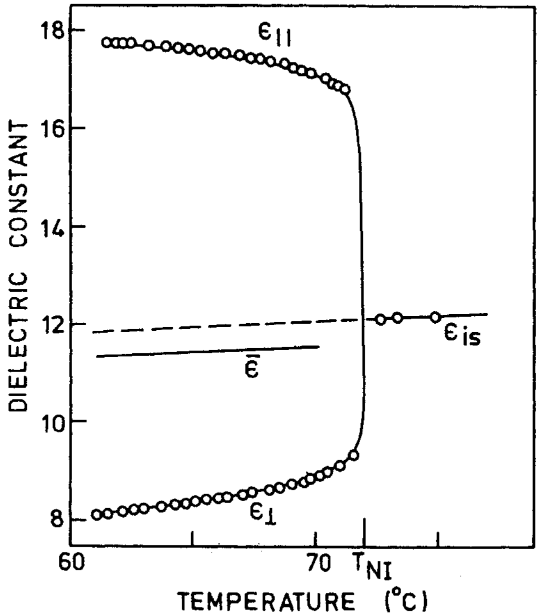


FIGURE 8 Principal dielectric constants of 8 OMCPC (T_{NI} = 72.0°C).

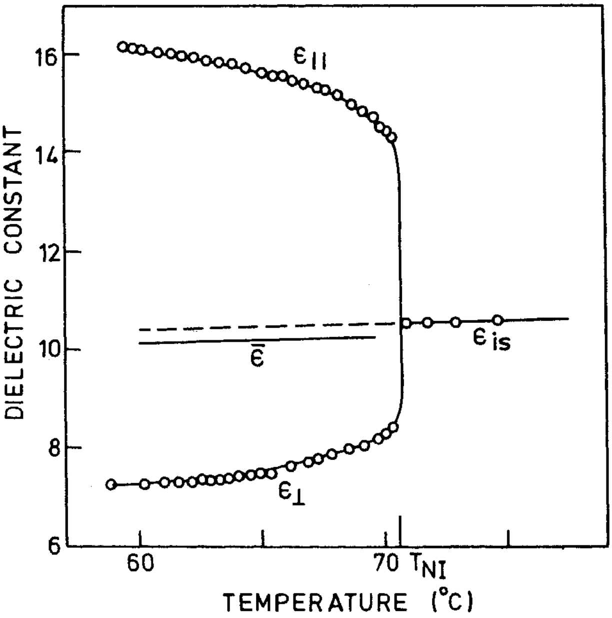


FIGURE 9 Principal dielectric constants of 9 OMCPC (T_{NI} = 70.3°C).

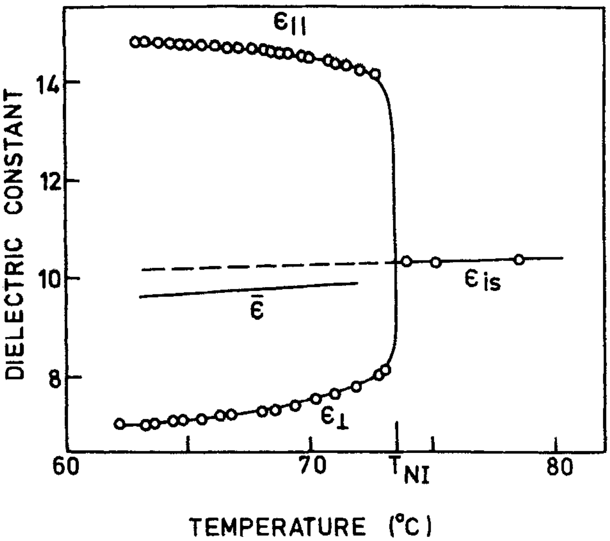


FIGURE 10 Principal dielectric constants of 10 OMCPC (T_{NI} = 73.5°C).

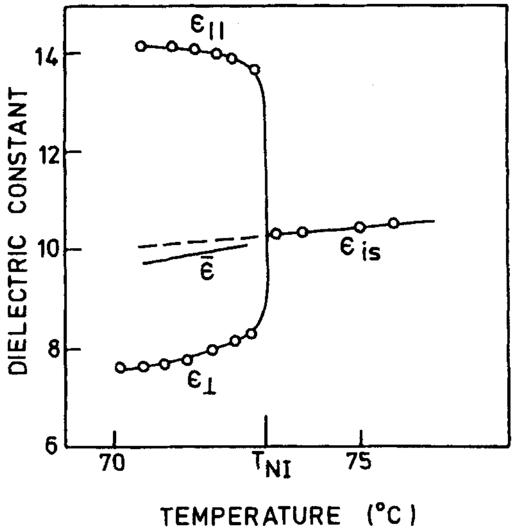


FIGURE 11 Principal dielectric constants of 11 OMCPC (T_{NI} = 73.2°C).

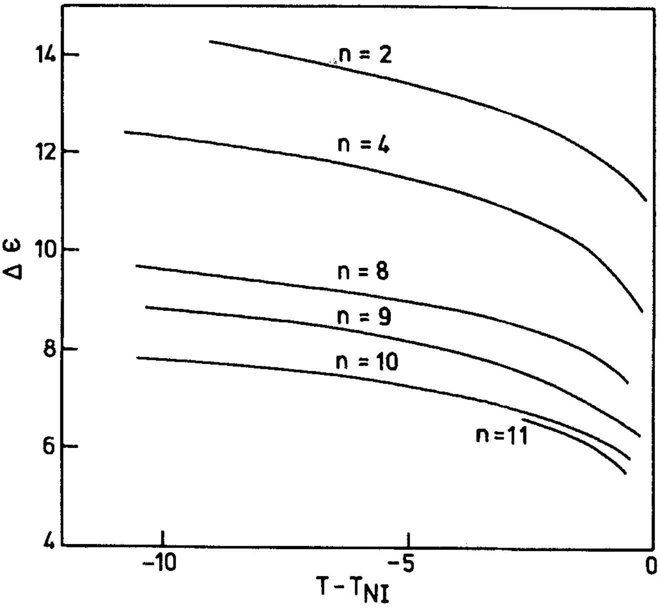


FIGURE 12 Dielectric anisotropy $\Delta\varepsilon$ of *trans-p-n*-alkoxy-α-methyl *p*′-cyanophenyl cinnamates as a function of $T - T_{NI}$.

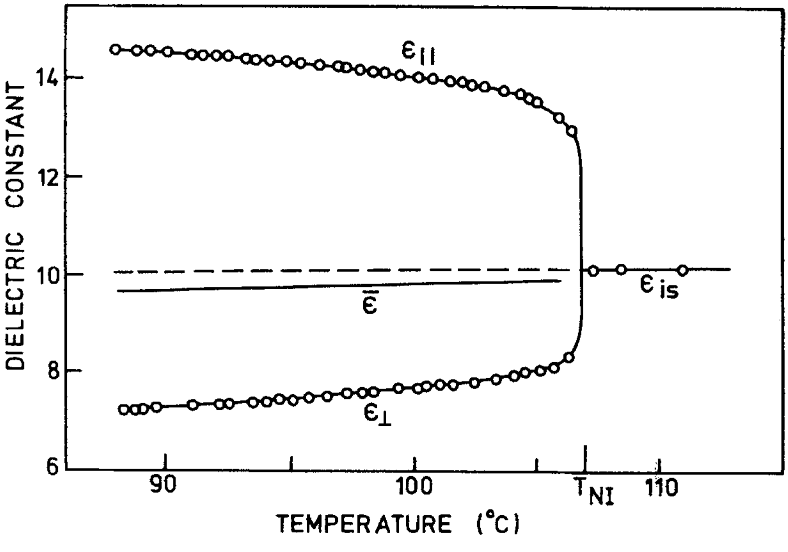


FIGURE 13 Principal dielectric constants of CBOOA (T_{NI} = 107.0°C).

direction ($\varepsilon_\perp$). This large dielectric anisotropy is due to the presence of C≡N as the end group which has a dipole moment of 4.05 D.[11] We also notice that in all cases $\bar{\varepsilon}$ is, throughout the nematic phase, less than the extrapolated isotropic value ε_{is}. A similar difference has also been observed by Schadt[4] in the case of some nitrile compounds. (This is in contrast to the behaviour of non-polar molecules wherein it has been experimentally observed that $\bar{\varepsilon}$ and ε_{is} coincide at T_{NI}.[12]) Also, it is seen that $\bar{\varepsilon}$ decreases with decrease of temperature, the effect being greater in compounds whose nematic phase is preceded by a smectic phase. These facts are in conformity with the predictions of the statistical model of antiferroelectric short range order in nematic liquid crystals composed of polar molecules proposed by Madhusudana and Chandrasekhar.[13,14] According to this theory $\bar{\varepsilon}$ should increase on going over from the nematic to the isotropic phase owing to a decrease in the antiparallel correlation at the transition. Some recent X-ray studies[15–17] have provided direct evidence of the existence of such antiparallel ordering of strongly polar molecules.

2) The nematic–isotropic transition temperature and a number of other physical properties show a pronounced alternation as the homologous series is ascended. For example, in the case of 4′-*n*-alkyl-4-cyanobiphenyls the even-numbered carbon atom makes a large angle with the long axis of the molecule while the odd-numbered carbon atom is along the long axis. Thus the polarizability anisotropy, T_{NI} and the order parameter are lowered in even-members of the series while they are enhanced in the odd-members. Such an alternation in the order parameter,[18] though not very pronounced, is observed in 5CB, 6CB and 7CB but the *s*-value increases between 7CB and 8CB. This increase of *s* in 8CB is attributed to an increased antiparallel correlation and the presence of smectic A phase at lower temperatures.

The dielectric anisotropy has contributions from the polarizability anisotropy ($\Delta\alpha$) and the permanent dipole moment.[19] For a molecule with zero dipole moment $\Delta\varepsilon$ is directly proportional to $\Delta\alpha$. Since $\Delta\alpha$ alternates we expect $\Delta\varepsilon$ also to show an alternation. Such an alternation is indeed observed in di-alkyl-azobenzenes.[12] But the strongly polar 4′-*n*-alkyl 4-cyanobiphenyls show only a continuous decrease in $\Delta\varepsilon$ with increasing chain length (see Table II). A similar trend is observed in *trans*-*p*-*n*-alkoxy-α-methyl p′-cyanophenyl cinnamates also. This may be partly due to the fact that the increase in the order parameter increases the effect of antiparallel correlation which as discussed earlier results in a diminution of the dielectric anisotropy.

3) The total anisotropy of the molecule in series (ii) is higher than that of series (i) because of the presence of an additional bridging group between the two phenyl rings. In addition to the nitrile group there are three other dipolar groups in (ii) which contribute to $\Delta\varepsilon$: (a) the alkoxy group which

contributes mainly to $\varepsilon_\perp$ (b) the methyl group in the α-position which also contributes to $\varepsilon_\perp$ and (c) the carbonyl group which contributes both to $\varepsilon_\parallel$ and $\varepsilon_\perp$. Thus we expect a higher value of $\varepsilon_\parallel$, $\varepsilon_\perp$ as well as $\Delta\varepsilon$ for series (ii) as compared to series (i) which is indeed found to be the case experimentally (see Tables II and III).

In CBOOA the benzylidene group contributes strongly to $\varepsilon_\perp$ with a dipole moment ($\mu_\perp$) of 1.51 D while its parallel component of about 0.4 D, directed antiparallel to the direction of the nitrile group, reduces the value of $\varepsilon_\parallel$. If the terminal substituents, namely, the alkoxy and the nitrile groups are reversed then the $\mu_\parallel$ of CH=N will be directed similar to that of the nitrile group increasing the value of $\varepsilon_\parallel$. The dielectric constants of such compounds have been measured by Schadt[4] whose value of $\varepsilon_\parallel$ is indeed higher than that of CBOOA.

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