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Dielectric Properties of Some Nematics of Positive Dielectric Anisotropy

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Dielectric Properties of Some Nematics of Positive Dielectric Anisotropy

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The static dielectric constants of biphenyl-4-*p*-*n*-alkoxybenzoates have been measured as functions of temperature. The dielectric anisotropy ($\Delta\varepsilon$) for the successive homologues (hexyl to undecyl) shows an alternation similar to that exhibited by the nematic–isotropic transition temperature (T_{NI}). The dispersion of $\varepsilon_{\parallel}$ in the frequency range of 0.1–15 MHz has been studied for four successive members of biphenyl-4-*p*-*n*-alkoxybenzoates (heptyl to decyl derivatives) as well as of *trans*-*p*-*n*-alkoxy-α-methyl-*p'*-cyanophenyl cinnamates (eighth to eleventh members). For both series the relaxation frequency (f_R) and the frequency of dielectric isotropy (f_0) evaluated at a common relative temperature show an alternation similar to T_{NI}. For any given compound the Arrhenius plots for f_R and f_0 give the same value of the activation energy (W). In the case of the biphenyl esters the vaue of W is the same for the seventh and eighth members, but increases for the higher members which exhibit a smectic phase at lower temperatures. On the contrary for cinnamic acid esters W is found to be the same for all homologues irrespective of whether the nematic phase is preceded by a smectic phase or not.

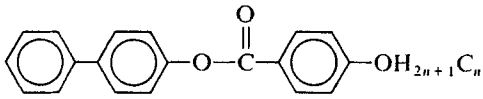
INTRODUCTION

In our earlier papers we presented the static[1] as well as the dynamic[2] behavior of the principal dielectric constants of 4'-*n*-alkyl-4-cyanobiphenyls. As is well known, these compounds show very strong positive dielectric anisotropy owing to the presence of the C≡N end group. Two interesting results emerged from these studies: (a) Although the order parameter and T_{NI} show an alternation with increasing alkyl chain length, the dielectric anisotropy $\Delta\varepsilon$ decreases continuously as the homologous series is ascended. This is in contrast to the behavior of compounds of weak positive dielectric anisotropy which exhibit an alternation of $\Delta\varepsilon$ with increasing alkyl chain length. The continuous decrease of $\Delta\varepsilon$ in strongly positive materials may be attributed to the fact that an increase in the order parameter increases the effect of antiparallel correlation between neighbouring molecules and

therefore reduces the dielectric anisotropy. (b) The relaxation frequency f_R shows an alternation similar to T_{NI} and order parameter s.

In this paper we report dielectric studies on two new homologous series:

i) Biphenyl-4-*p*-*n*-alkyoxybenzoates (Bn OB)



These compounds, synthesized by Sadashiva and Subba Rao,[3] have a low positive dielectric anisotropy. The first five members of the homologous series exhibit a monotropic nematic phase. A monotropic smectic A phase appears at the nonyl derivative. The static dielectric constants of the six successive homologues $n = 6$ to 11 and the dielectric dispersion for four successive homologues $n = 7$ to 10 have been measured. Their transition temperatures are given in Table I.

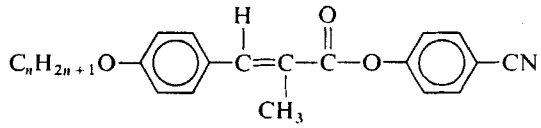
TABLE I

Transition temperatures of biphenyl-4-*p*-*n*-alkoxybenzoates

Compound	Temperature of transition to		
	Smectic (°C)	Nematic (°C)	Isotropic (°C)
B6 OB	—	132.5	135.5
B7 OB	—	128.0	130.0
B8 OB	—	120.0	131.0
B9 OB	(101.0)	119.5	127.5
B10 OB	(106.0)	111.0	126.5
B11 OB	100.5	109.5	124.5

Transition temperatures in parentheses indicate monotropic transition.

ii) trans-*p*-*n*-Alkoxy-α-methyl-*p*'-cyanophenyl cinnamates (*n* OMCPC)



These compounds, synthesized by Sadashiva,[4] are colourless, fairly low melting and chemically stable materials. They exhibit a very large dielectric anisotropy again owing to the presence of the C≡N end group. The static dielectric constants in the nematic and isotropic phases of several members

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TABLE II

Transition temperatures of
trans-p-n-alkoxy-α-methyl-*p'*-cyanophenyl cinnamates

Compound	Temperature of transition to		
	Smectic (°C)	Nematic (°C)	Isotropic (°C)
8 OMCPC	—	58.0	72.0
9 OMCPC	—	56.0	70.3
10 OMCPC	(57.1)	62.8	73.5
11 OMCPC	(70.0)	70.0	73.2

of this homologous series have already been reported.[1] Now we present the results on the dielectric dispersion of $\varepsilon_{\parallel}$ in the radio-frequency range for four successive members $n = 8$ to 11. Their transition temperatures are given in Table II.

There are marked differences in the dielectric properties of series (i) and (ii) as we shall see presently.

The experimental set up used for both the static and dynamic measurements has been described previously[1,2] and will not be repeated here.

RESULTS AND DISCUSSION

a) Principal dielectric constants of biphenyl-4-*p*-*n*-alkoxybenzoates

The principal dielectric constants in the nematic ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) and isotropic (ε_{is}) phases of biphenyl-4-*p*-*n*-alkoxybenzoates are given in Figures 1 and 2 as functions of temperature. The values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decrease with increasing alkyl chain length. The dielectric anisotropy ($\Delta\varepsilon$) is small and positive for all compounds. The value of $\Delta\varepsilon$ evaluated at a common relative temperature of $(T_{NI} - 2)$°C when plotted as a function of the number of carbon atoms in the alkyl chain shows an alternation similar to that exhibited by T_{NI} (see Figure 3). Such an alternation in $\Delta\varepsilon$ has also been observed in other homologous series[5,6] of compounds with small positive dielectric anisotropy. On the other hand in the case of strongly positive compounds, we have shown previously[1] that $\Delta\varepsilon$ shows only a continuous decrease with increasing alkyl chain length.

For nonpolar molecules, e.g., di-alkyl azobenzenes,[6] the average value of the dielectric constant $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ is equal to the extrapolated isotropic values ε_{is}. However if the molecule has a component of the dipole moment along the major molecular axis, ε_{is} is greater than $\bar{\varepsilon}$. The difference between ε_{is} and $\bar{\varepsilon}$ is less than 0.5% for biphenyl-4-*p*-*n*-alkoxybenzoates. However for the strongly positive compounds[1,7] the difference may be as

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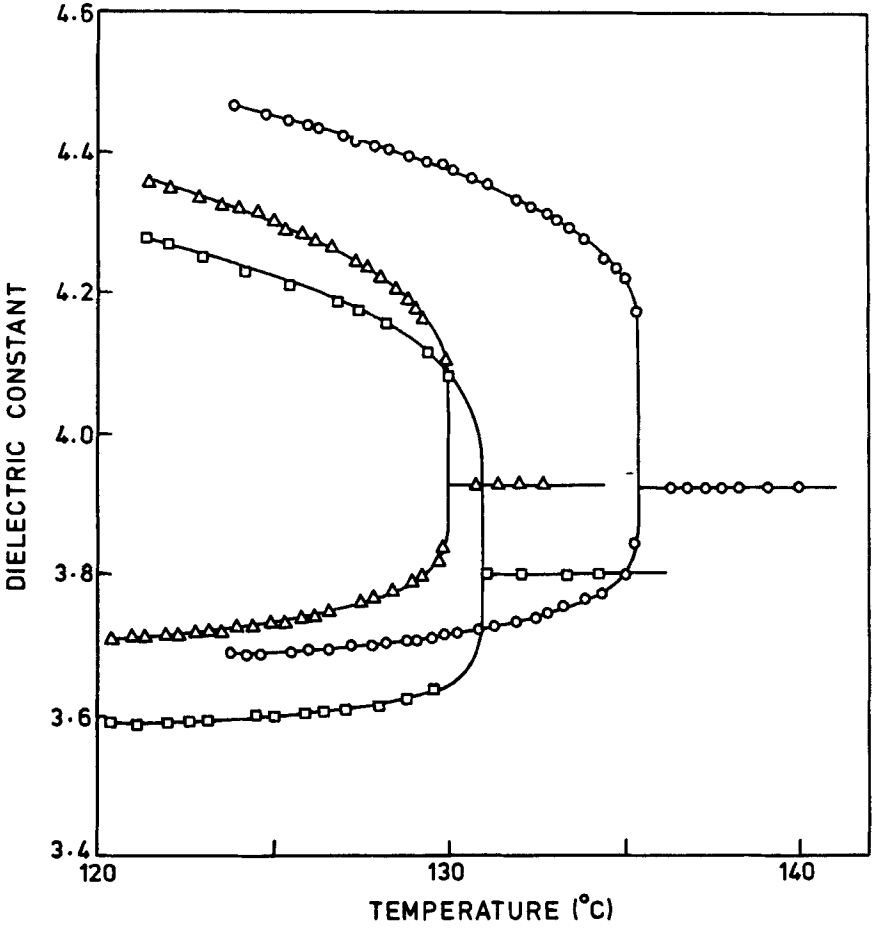

FIGURE 1 The principal dielectric constants of B6 OB (○), B7 OB (△) and B8 OB (□).

much as 4–5%. This difference is attributed to the presence of antiferroelectric short range order[8,9] in the nematic phase. Some recent X-ray studies [10–12] have given direct evidence of the existence of such antiparallel correlation.

The dielectric constants of hexyl and heptyl derivatives are measured down to 12°C below T_{NI} by supercooling the sample. In the temperature range measured, all the compounds except the undecyl derivative show the normal behavior of increasing $\varepsilon_{\parallel}$ with decreasing temperature. An anomalous behavior is observed for the undecyl compound below $(T_{NI} - 6)$°C (Figure 2). Similar anomaly was observed for the dodecyl derivative also though the

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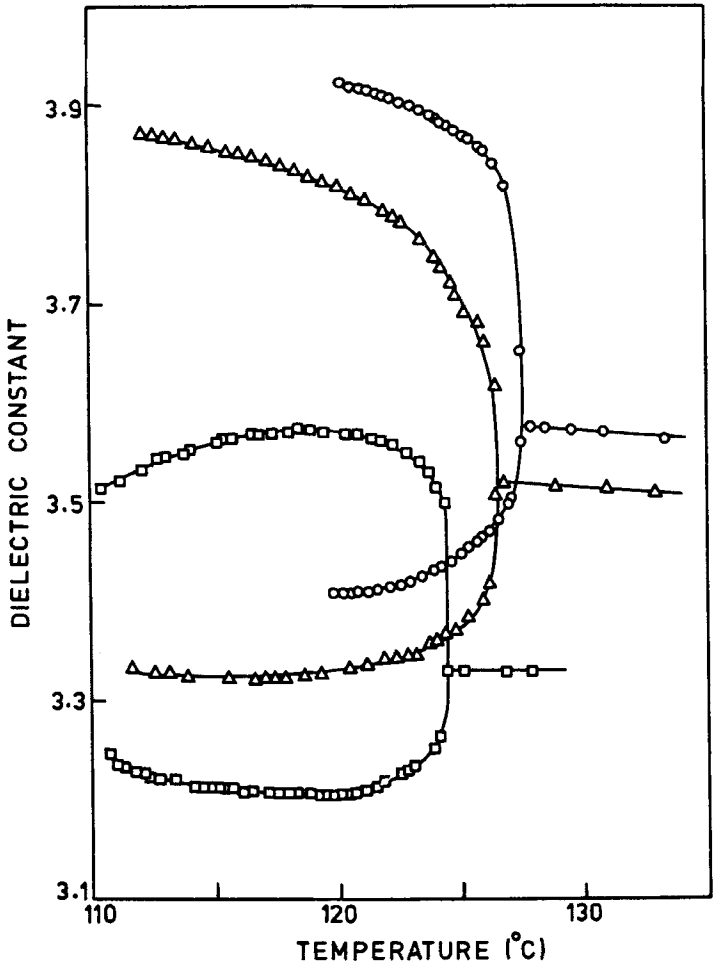

FIGURE 2 The principal dielectric constants of B9 OB (○), B10 OB (△) and B11 OB (□).

data are not presented here. The same type of anomaly leading to a change in the sign of $\Delta\varepsilon$ has been observed in other weakly positive compounds, viz., hexyl to octyl azoxybenzenes, by de Jeu *et al.*,[13,14]

b) Dielectric dispersion of biphenyl-4-*p*-*n*-alkoxybenzoates

The dielectric constant $\varepsilon_\perp$ for measuring field perpendicular to the optic axis is characterized by a single relaxation comparable to the Debye relaxation in normal liquids. On the other hand $\varepsilon_\parallel$ exhibits an additional dispersion in the radio-frequency region. This arises because of the strong hindering

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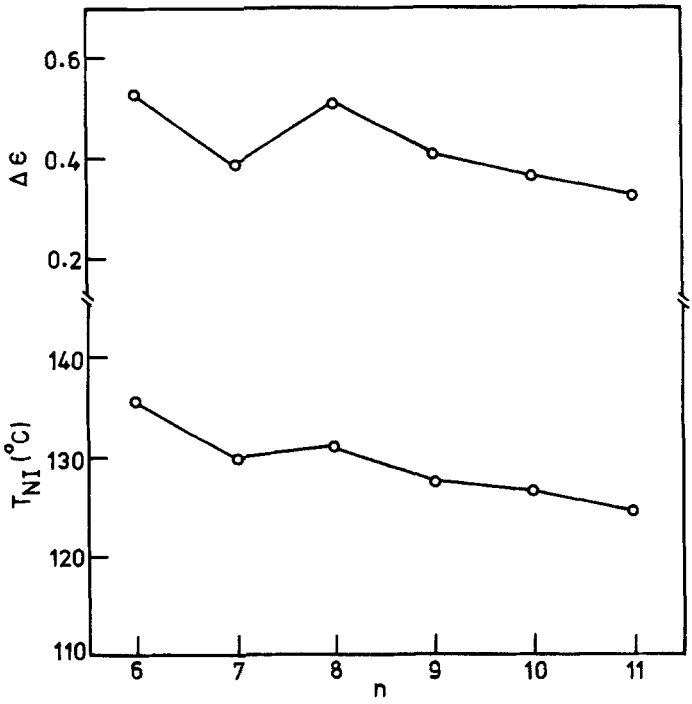

FIGURE 3 The dielectric anisotropy ($\Delta\varepsilon$) at a relative temperature of (T_{NI} − 2)°C and T_{NI} as functions of the number of carbon atoms in the alkyl chain of Bn OB.

of the rotation of the longitudinal component of the dipole moment about a transverse axis. We have measured only the low-frequency dispersion of $\varepsilon_{\parallel}$.

For each compound the dispersion was measured in the frequency range of 0.4–15 MHz at four temperatures. In Figure 4 we have plotted $\varepsilon''_{\parallel}$ versus frequency for B7 OB. The relaxation frequency (f_R) given by the maximum of $\varepsilon''_{\parallel}$ shifts to higher values with increasing temperatures. Therefore f_R could be determined only for temperatures in the supercooled region of the nematic phase. Figure 5 is a Cole–Cole plot for the same compound at different temperatures. It is a semi-circle with the centre lying on the $\varepsilon'_{\parallel}$-axis characterizing a single relaxation time. Similar curves were obtained for the other three homologues also.

Meier and Saupe[15] and Martin *et al.*,[16] have extended the Debye theory[17] of dielectric relaxation of liquids to nematics and showed that the relaxation time τ_R is larger than the ordinary Debye relaxation time τ_D by a factor

$$g \simeq \frac{kT}{q} \exp\left(\frac{q}{kT}\right)$$

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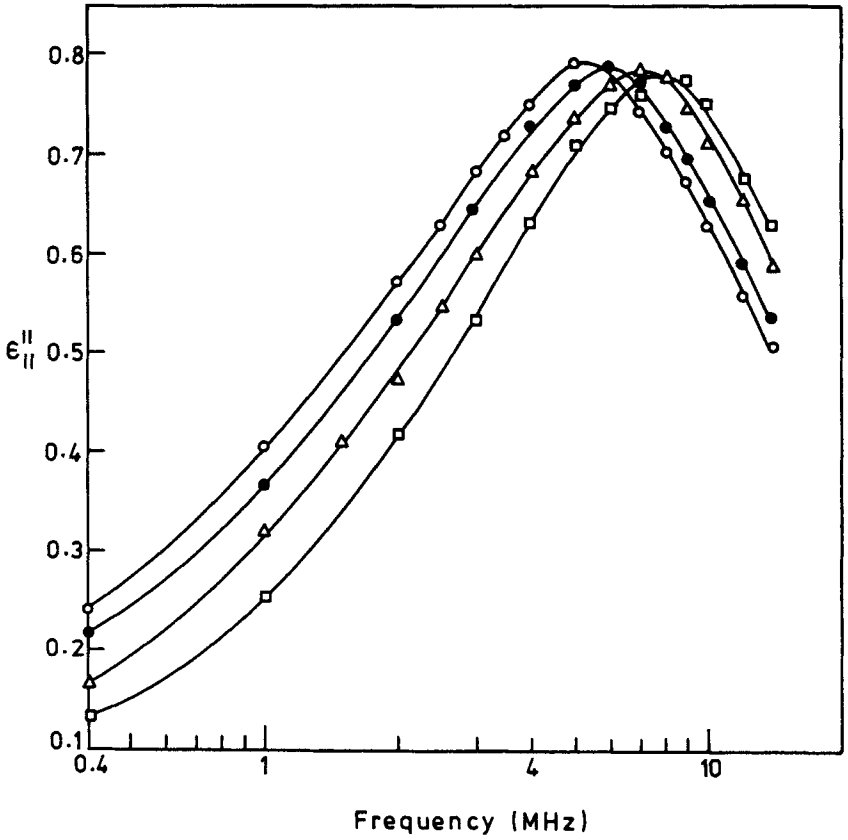

FIGURE 4 $\varepsilon''_{\parallel}$ as a function of frequency for B7 OB at 112.95°C (○), 115.1°C (●), 117.6°C (△) and 121.3°C (□).

called the retardation factor. It can be easily shown[18] that $\tau_R (= 1/2\pi f_R)$ is proportional to $\exp(W/kT)$, where $W = q + W_\eta$, q being the nematic potential and W_η the activation energy due to viscosity effects. Therefore a plot of log f_R versus $1/T$ yields only the total activation energy W.

In Figure 6 we have plotted log f_R and log f_0 (where f_0 is the frequency of dielectric isotropy) as functions of $1/T$ for Bn OB. For any given compound both f_R and f_0 give the same value of W within the experimental error (see Table III). Both f_R and f_0 taken at a common relative temperature of $(T_{NI} - 2)$°C alternate with increasing chain length similar to T_{NI} (Figure 7). Unfortunately, as we do not have the order parameter data for these compounds, a comparison of the behaviors of f_R and s with increasing chain length is not possible here.

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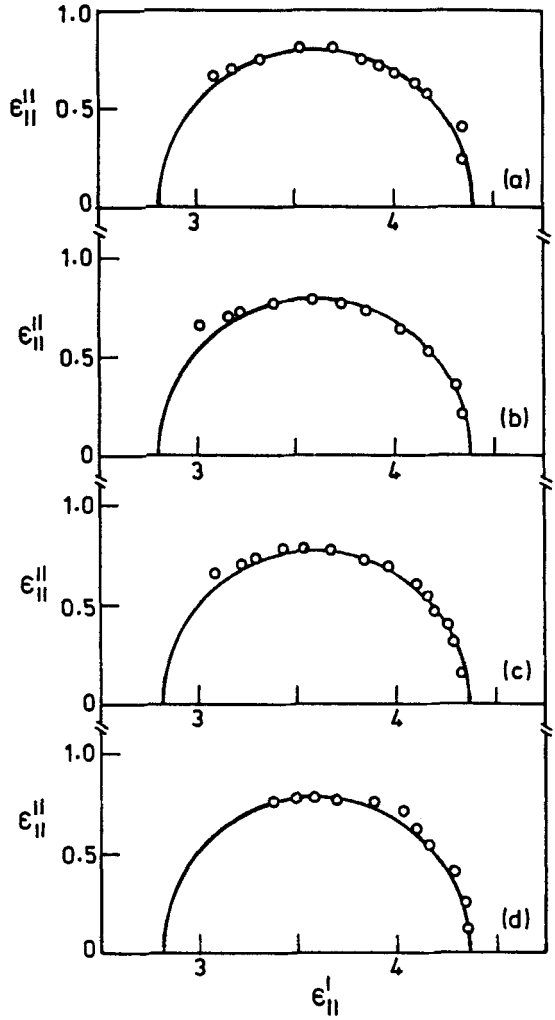

FIGURE 5 The Cole–Cole plot for B7 OB at (a) 112.95°C, (b) 115.1°C, (c) 117.6°C and (d) 121.3°C.

The value of W is the same for $n = 7$ and $n = 8$. But there is an increase in the value of W for the nonyl and the decyl derivatives whose nematic phase is preceded by a smectic phase; compared to the value of $n = 8$, the increase is $\sim 13\%$ for the nonyl derivative and $\sim 25\%$ for the decyl derivative. A similar increase in W has been observed in 4,4′-di-*n*-alkoxy azoxy benzenes by Mircea-Roussel and Rondelez.[19] They attribute this partly to the presence of the smectic like short range order in the nematic phase. However the

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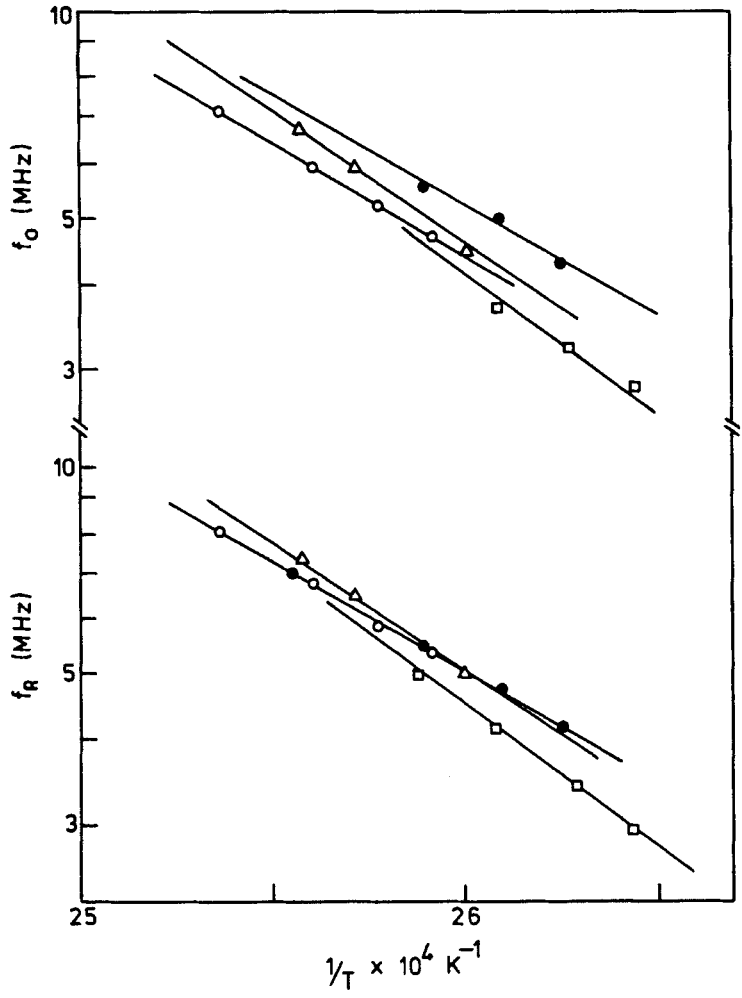

FIGURE 6 Logf_R and logf_0 as functions of $1/T$ for Bn OB; $n = 7$ (○), $n = 8$ (●), $n = 9$ (△) and $n = 10$ (□).

absence of any viscosity data for the Bn OB prevents us from drawing any definite conclusions on the nature of this effect.

c) Dielectric dispersion of trans-*p*-*n*-Alkoxy-α-methyl-*p*'-cyanophenyl cinnamates

The dispersion of $\varepsilon_{\parallel}$ for four successive members of this series was measured in the frequency range of 0.1–10 MHz at various temperatures in the nematic

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TABLE III

The values of f_R, f_0 and W for biphenyl-4-*p*-*n*-alkoxybenzoates

Compound	Temperature (°C)	f_R (MHz)	f_0 (MHz)	W_{f_R} (eV)	W_{f_0} (eV)
B7 OB	112.95	5.4	4.7	0.621	0.608
	115.1	5.9	5.2		
	117.6	6.8	5.9		
	121.3	8.0	7.1		
B8 OB	107.9	4.2	4.3	0.621	0.628
	110.25	4.8	5.0		
	113.3	5.5	5.5		
	118.5	7.0	—		
B9 OB	111.6	5.0	4.5	0.718	0.736
	116.0	6.5	5.9		
	118.1	7.4	6.7		
B10 OB	105.2	3.0	2.85	0.806	0.806
	107.6	3.5	3.25		
	110.4	4.2	3.70		
	113.6	5.0	4.10		

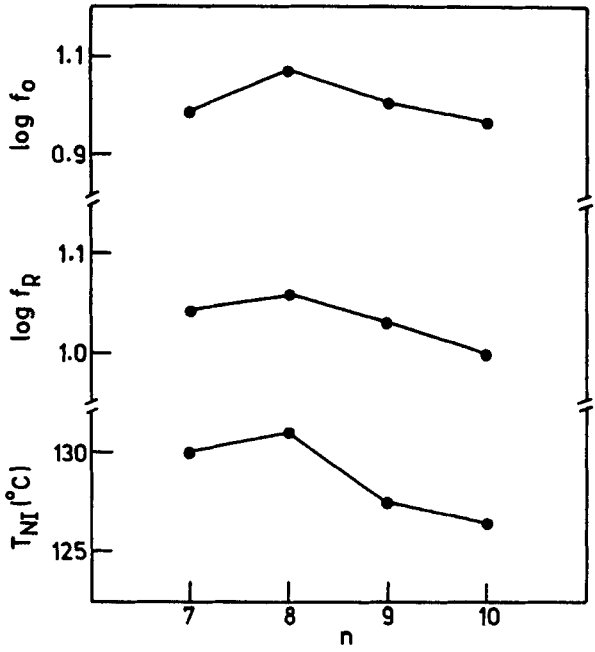

FIGURE 7 Log f_0 and log f_R at a relative temperature of $(T_{NI} - 2)$°C and T_{NI} as functions of the number of carbon atoms in the alkyl chain of Bn OB.

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phase. The values of f_R and f_0 obtained for these compounds are much lower than the corresponding values for Bn OB. Probably this is partly due to the greater length of the molecule. Because of the lower frequencies involved all the parameters could be determined to a better accuracy than for Bn OB.

Figure 8 is a plot of the variation of $\varepsilon''_{\parallel}$ with frequency for 9 OMCPC at different temperatures. The decrease in the maximum value of $\varepsilon''_{\parallel}$ with increasing temperature is more prominent here than in B7 OB (see Figure 4). The Cole–Cole plot for the same compound is given in Figure 9. Similar curves were obtained for the other compounds also. The dielectric relaxation of 9 OMCPC has been measured previously using the Freedericksz transition technique.[20] Our results for this compound agree with the earlier data.

The values of f_R and f_0 at different temperatures are listed in Table IV along with the values of W calculated from them. For any given compound both f_R and f_0 give the same value of W. Since the nematic range of 11 OMCPC is only 3°C, the relaxation frequency for this compound was measured at a

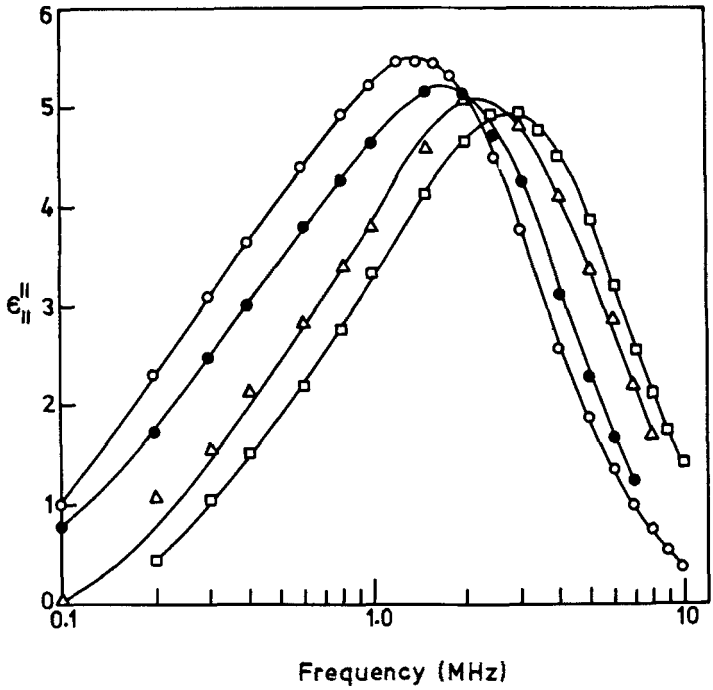

FIGURE 8 $\varepsilon''_{\parallel}$ as a function of frequency for 9 OMCPC at 59.8°C (○), 62°C (●), 65°C (△) and 67.5°C (□).

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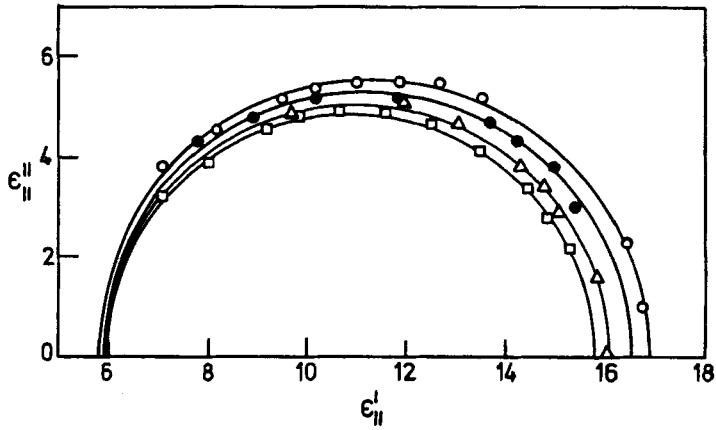

FIGURE 9 The Cole–Cole plot for 9 OMCPC at different temperatures (see Figure 8).

single temperature, viz., $(T_{NI} - 2)$°C. Both f_R and f_0 show an alternation similar to T_{NI} and s[21] (Figure 10) just as in 4′-*n*-alkyl-4-cyanobiphenyls[2] (n CB).

The value of W for *n* OMCPC are high compared to that of Bn OB. Further we notice that unlike Bn OB the value of W is the same for all compounds irrespective of whether it has a smectic phase or not. A similar behavior was observed for n CB[2] also.

Since the dielectric properties of n OMCPC are very similar to that of n CB we can assume the molecular associations to be the same in both of them.

TABLE IV

The values of f_R, f_0 and W for *trans*-*p*-*n*-alkoxy-α-methyl-*p*′-cyanophenyl cinnamates

Compound	Temperature (°C)	f_R (MHz)	f_0 (MHz)	W_{f_R} (eV)	W_{f_0} (eV)
8 OMCPC	59.4	1.4	2.4	0.917	0.917
	64.4	2.25	3.7		
	65.5	2.55	4.2		
	69.0	3.35	5.4		
9 OMCPC	59.8	1.4	2.9	0.917	0.917
	62.0	1.7	3.4		
	65.0	2.25	4.6		
	67.5	2.8	5.5		
10 OMCPC	62.9	1.75	3.7	0.903	0.906
	65.75	2.3	4.1		
	67.8	2.7	4.8		
	69.6	3.25	5.6		
11 OMCPC	71.2	3.6	6.5	—	—

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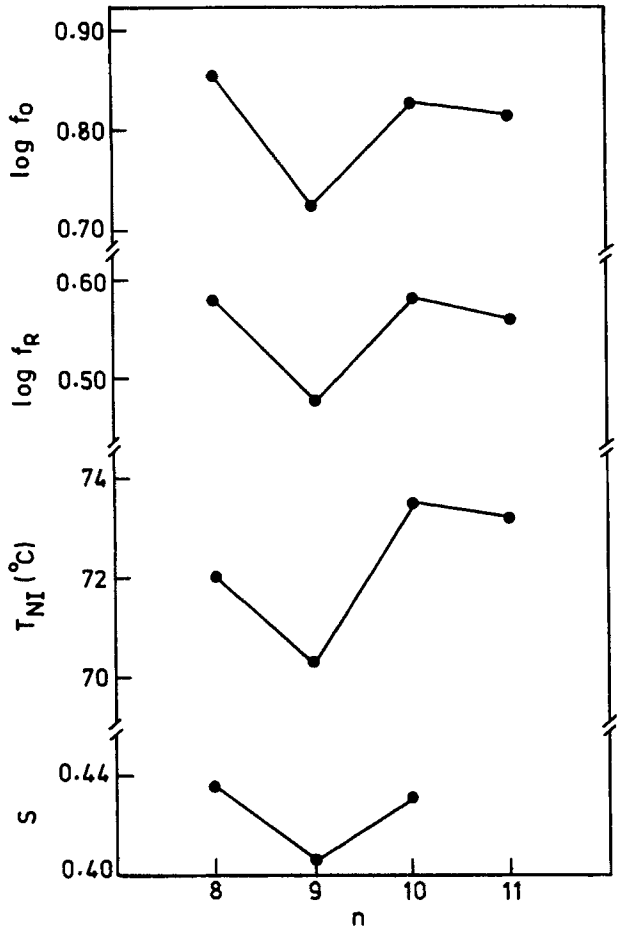

FIGURE 10 Log f_0, log f_R and s at a relative temperature of $(T_{NI} - 2)$°C and T_{NI} as functions of the number of carbon atoms in the alkyl chain of n OMCPC.

X-ray studies on 5 CB and 7 CB by Leadbetter *et al.*[10] have revealed that the short range order in the nematic phase has a strong layer character wherein each layer is made up of two molecules with their polar ends interdigitated. They find the layer thickness to be about 1.4 times the molecular length. Mircea-Roussel *et al.*[22] have measured the electrical conductivity of such compounds and found their behavior to be markedly different from that of compounds whose layer thickness is equal to the molecular length. It seems therefore likely that the difference in the dielectric properties of the two series studied in this paper might also be due to this difference in the molecular associations.

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