CHAPTER IV

DIELECTRIC PROPERTIES OF TRANS-p-n-ALKOXY-α-METHYL p'-CYANOPHENYL CINNAMATES

Intma ———

In this chapter W present our measurements on the dielectric properties of some more strongly positive compounds belonging to a new homologous series, viz., trans-p-n-alkoxy-α-methyl p'-cyanophenyl cinnamates. We shall abbreviate them as n CMOPC for the sake of convenience. These compounds synthesized by Sadashiva[1] are colourless, fairly low melting and chemically stable. Out of the twelve members synthesized we have measured the dielectric constants of only those which exhibit an enantiotropic nematic phase. The transition temperatures of the compounds studied are given in table 4.1. The tenth and eleventh members exhibit a monotropic smectic phase in addition to the

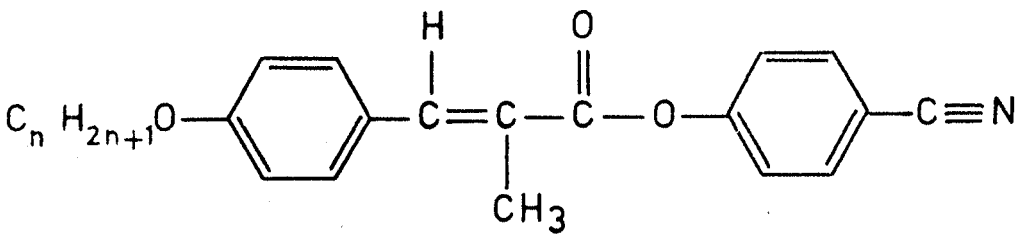
Table 4.1: Transition temperatures of n OMCPC (n = 2,4,8-11)

Compound	Temperature of transition to		
	Smectic (°C)	Nematic (°C)	Isotropic (°C)
2 OMCPC	-	80.0	89.5
4 OMCPC	-	63.0	73.8
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

Transition temperatures in parentheses indicate monotropic transitions.

nematic phase. The smectic phase shows a simple fan shaped texture and is therefore believed to be smectic A. Also the twist and bend elastic constants[2] diverge near the smectic-nematic transition temperature confirming that the lower temperature phase is smectic A.

In figure 4.1 we have given the chemical structure of a OMCPC. In the odd-members of the series the final C-C bond of the alkoxy group on the average makes a large angle with the long molecular axis. This reduces the molecular anisotropy. On the other hand, in the even-members the final segment is nearly parallel to the long molecular axis enhancing the anisotropy of the molecule. As a result in this cinnamic acid ester series the odd-members have a lower T_{NI} than the even members whereas the opposite was true in the 4'-n-alkyl 4-cyanobiphenyls (see chapter III).



n = 2, 4, 8—11

Figure 4.1

Structural formula of trans-p-n-alkoxy-α-methyl p'-cyanophenyl cinnamates (n OMCPC, n = 2,4,8-11).

The experimental details concerning the methods of alignment and measurement have already been given in chapter III. Therefore we shall only present the results in this chapter.

Results and Discussion

A Static dielectric constants

The variation of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and with temperature are plotted in figures 4.2-4.7 for 2 OMCPC, 4 OMCPC, and 8 OMCPC-11 OMCPC respectively. Measurements were done only in the nematic and isotropic phases although the decyloxy and undecyloxy derivatives exhibit a monotropic smectic A phase at lower temperatures. The dielectric anisotropy ($\Delta\varepsilon$), for all the compounds, is plotted as a function of $(T - T_{NI})$ La figure 4.8. We have tabulated the values of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\Delta\varepsilon$ for all the compounds taken at a common relative temperature of $(T_{NI} - 1)°C$ (see table 4.2). The following observations are made:

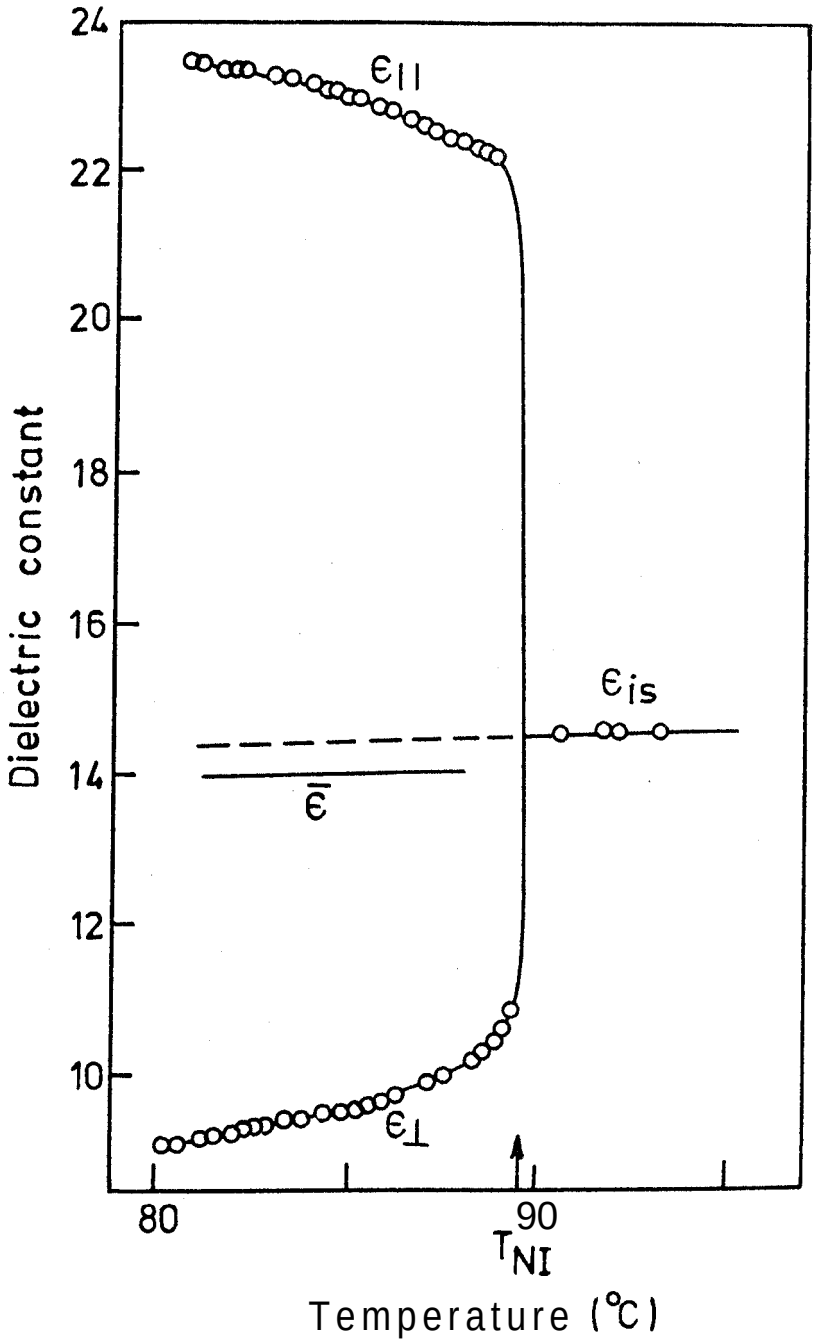


Figure 4.2

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

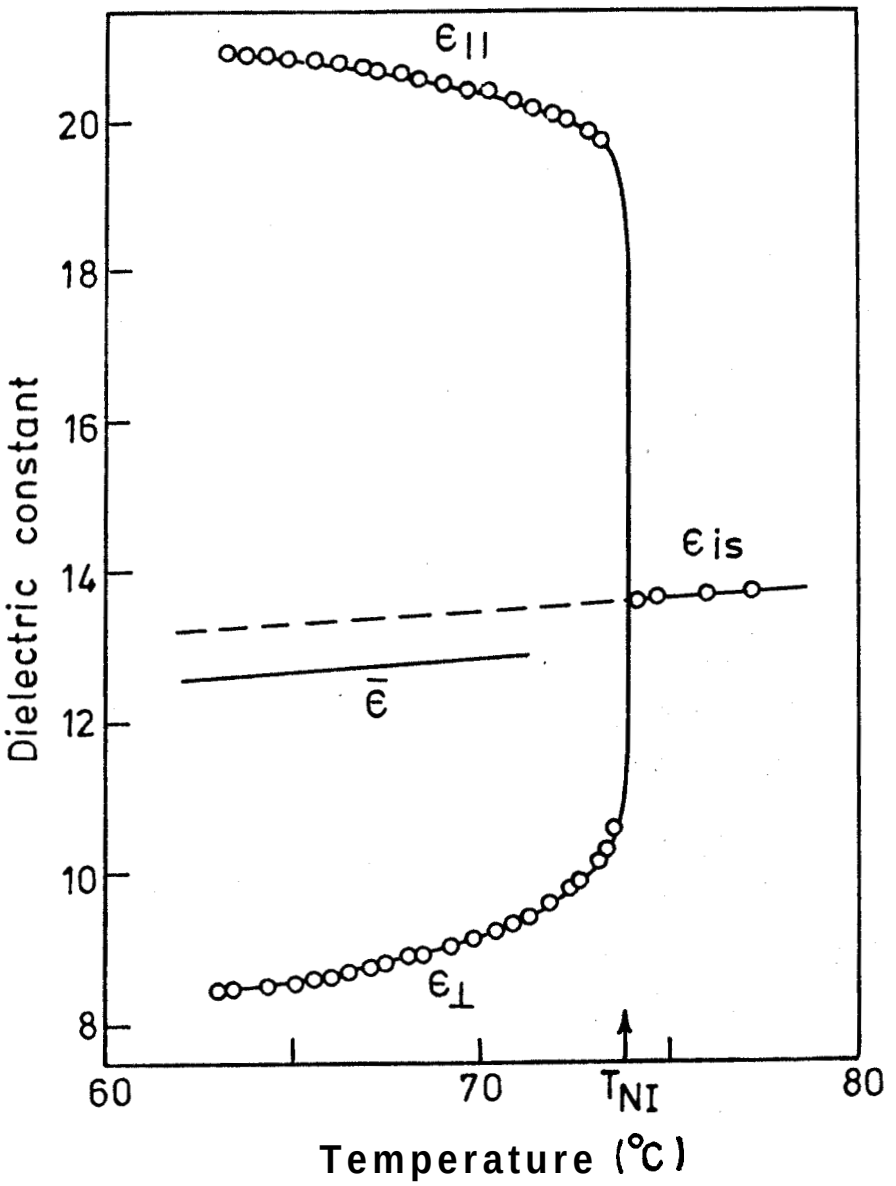


Figure 4.3

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

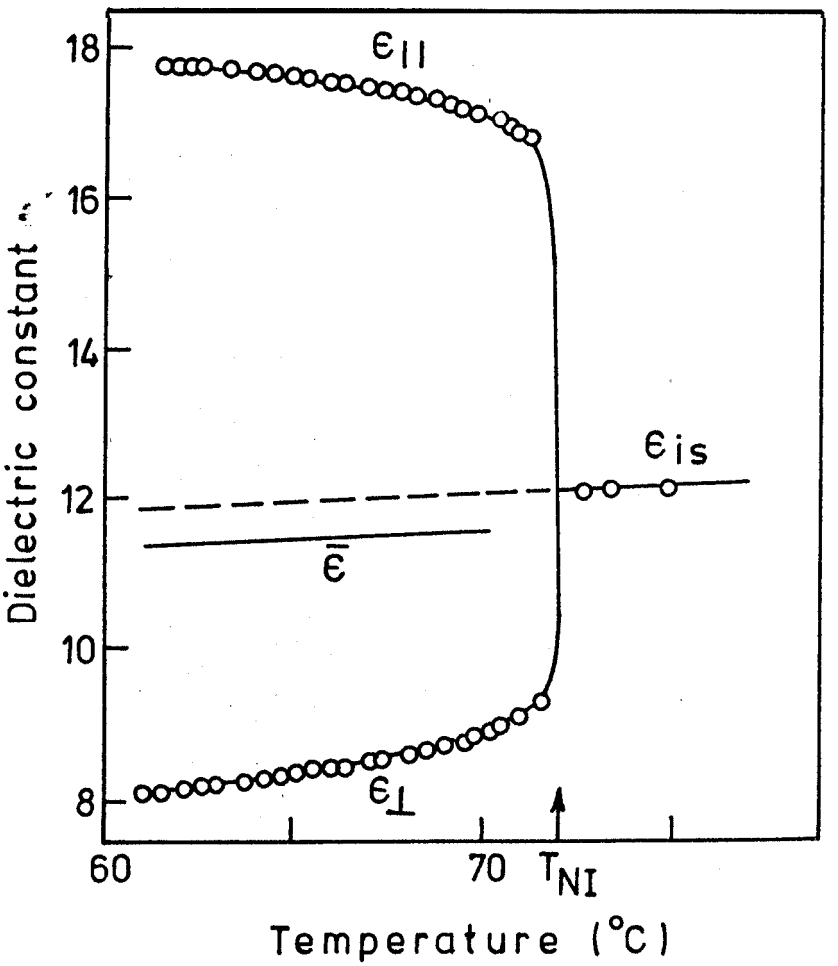


Figure 4.4

Principal dielectric constants of 8 OMCPC (T_{NI} = 72 °C)

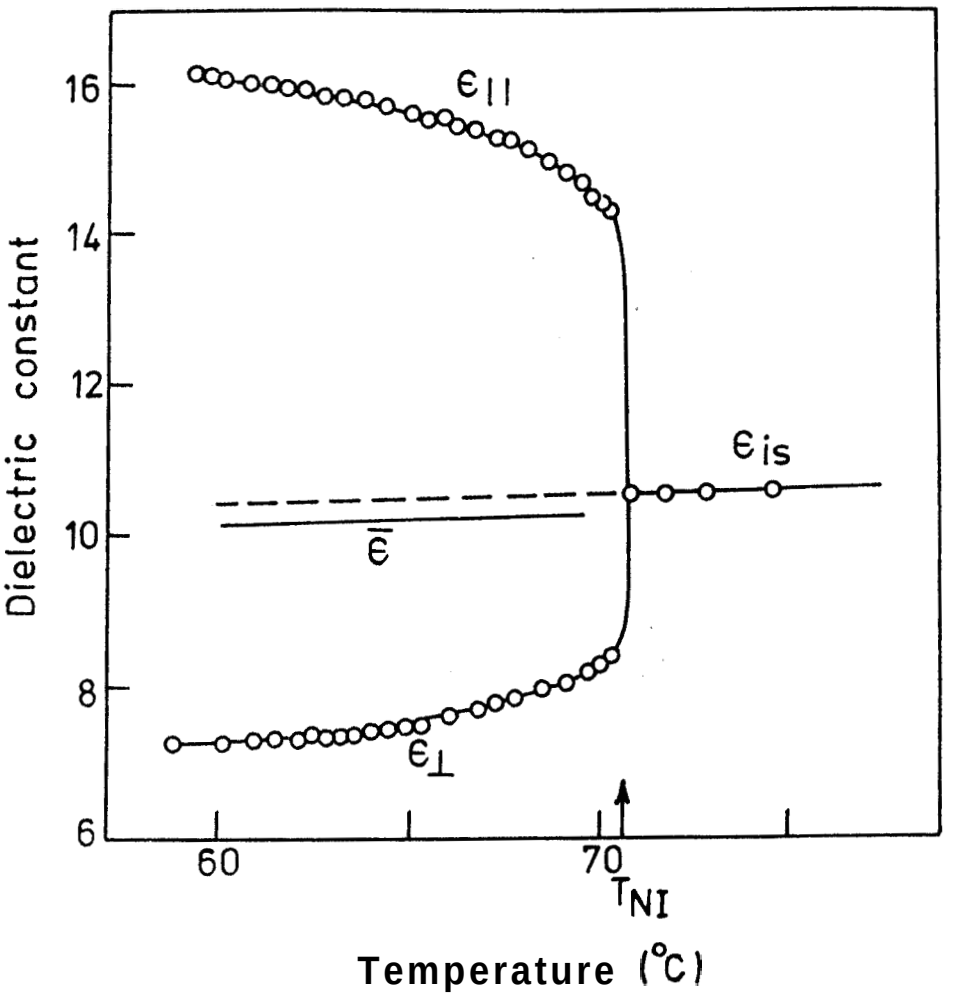


Figure 4.5

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

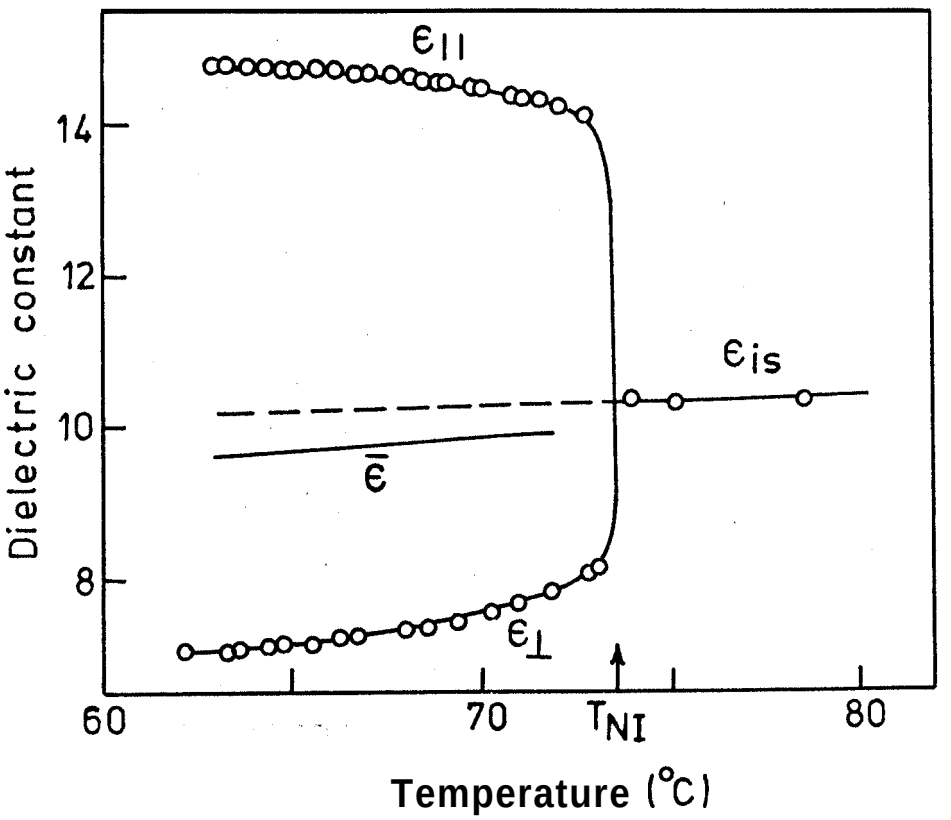


Figure 4.6

Principal dielectric constants of 10 OMCPC

(T_{NI} = 73.5 °C)

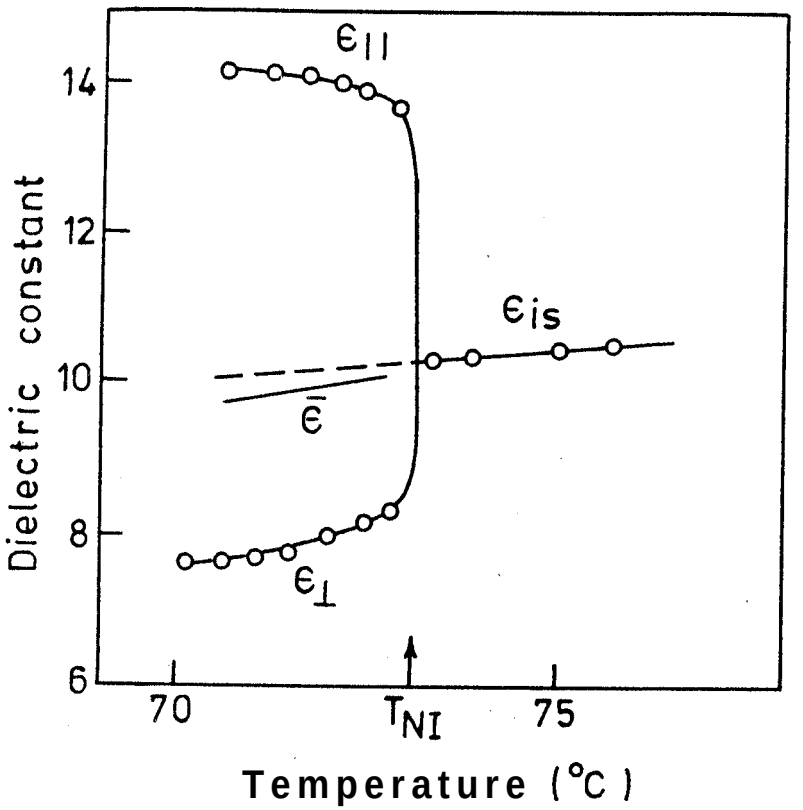


Figure 4.7: **Principal dielectric constants of 11 OMCPC (T_{NI} = 73.2 °C)**

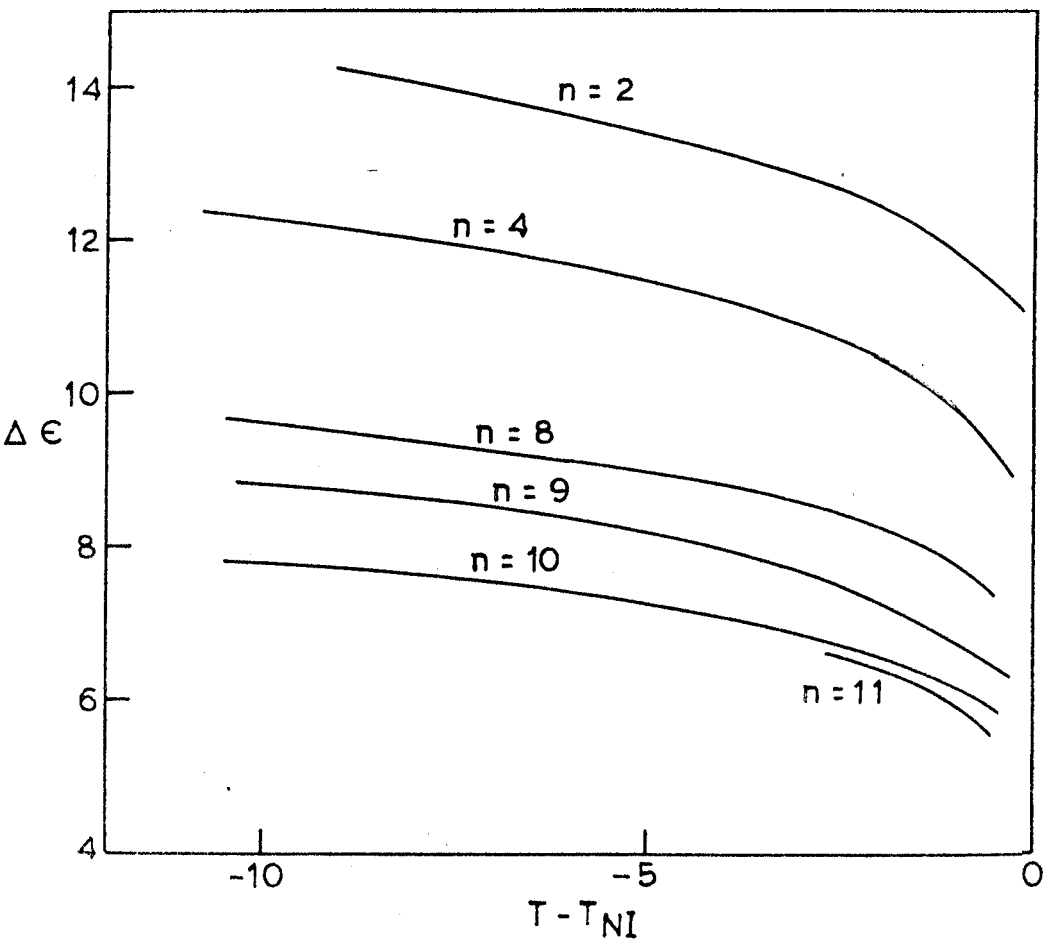


Figure 4.8

Dielectric anisotropy ($\Delta\varepsilon$) of n OMCPC as a function of $T - T_{NI}$

Table 4.2: Principal dielectric constants and dielectric anisotropy of n OMCPC 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

1. From table 4.2 it is observed that for all the compounds $\varepsilon_{\parallel}$ is about twice $\varepsilon_{\perp}$. In fact $\varepsilon_{\parallel}$ is slightly greater than $2\varepsilon_{\perp}$ for 2 OMCPC and the difference decreases as we go up the homologous series. For homologues above 8 OMCPC $\varepsilon_{\parallel}$ is less than $2\varepsilon_{\perp}$. The large dielectric anisotropy is mainly due to the presence of C≡N as the end group.

2. In addition to the cyano group there are three other dipolar groups 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 (of the carbonyl group which contributes to both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. Also the polarizability anisotropy ($\Delta\alpha$) of a molecule of n OMCPC is higher than that of nCB because of the presence of the bridging group between the two phenyl rings in n OMCPC (see figure 4.1). Thus we expect a higher value of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ as well as $\Delta\varepsilon$ for n OMCPC as compared to nCB which is indeed found to be the case.

3. Both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decrease continuously with increasing length of the alkoxy chain. The percentage of decrease between successive members decreases as the homologous series is ascended. For e.g., the decrease from 8 OMCPC to 9 OMCPC is $\sim$ 12% while that between 10 OMCPC and 11 OMCPC is only $\sim$ 2%. This decrease cannot be due only to the changes in density[2] which is only $\sim$ 0.5% between successive members.

4. The isotropic value of the dielectric constant shows a positive slope for all the compounds. The mean value $\bar{\varepsilon}$ is throughout the nematic phase less (by about 3%) than the extrapolated isotropic value. Further $\bar{\varepsilon}$ decreases with decrease of temperature the effect being greater in 10 OMCPC and 11 OMCPC whose nematic phase is preceded by a smectic A phase. These facts are in conformity with the predictions of the statistical model of antiferroelectric short range order in nematics composed of polar molecules, discussed in chapter II.

5. The order parameter of n OMCPC determined from IR measurements[3] exhibits an odd-even effect. However no such alternation is found in the dielectric anisotropy which decreases continuously with increasing alkoxy chain length (figure 4.8).

6. Even though 10 OMCPC and 11 OMCPC exhibit a smectic A phase we were unable to make measurements in this phase because of the difficulty in getting a good alignment, either homogeneous or homeotropic. However no reversal in the trend of either $\varepsilon_{\parallel}$ or $\varepsilon_{\perp}$ is observed in the nematic phase.

Comparison with 4'-n-alkyl 4-cyanobiphenyls

Thus we find that the static dielectric behaviour of n OMCPC is very similar to that of nCB. The theoretical prediction that in strongly polar materials the near neighbours have a tendency to align antiparallel to each other has been supported by X-ray studies[4,5]

in the case of nCB. Unfortunately no X-ray data on n OMCPC are available. However the similarity in the static behaviour of the dielectric constants of the two series leads us to infer that even in n OMCPC we may have double molecular layers with strong antiparallel correlations between neighbouring molecules. Soon we shall see that the dynamic behaviours of n OMCPC and nCB are again alike further corroborating our conclusions.

Effect of the bridging group

have also measured the static dielectric constants of p-cyanobenzylidene p'-octyloxyaniline (CBOOA) in its nematic and isotropic phases. values of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{is} are plotted as functions of temperature in figure 4.9. All the features noted in nCB and n OMCPC are visible in CBOOA also. was expected since it is also a strongly positive material with C≡N at one end of the molecule.

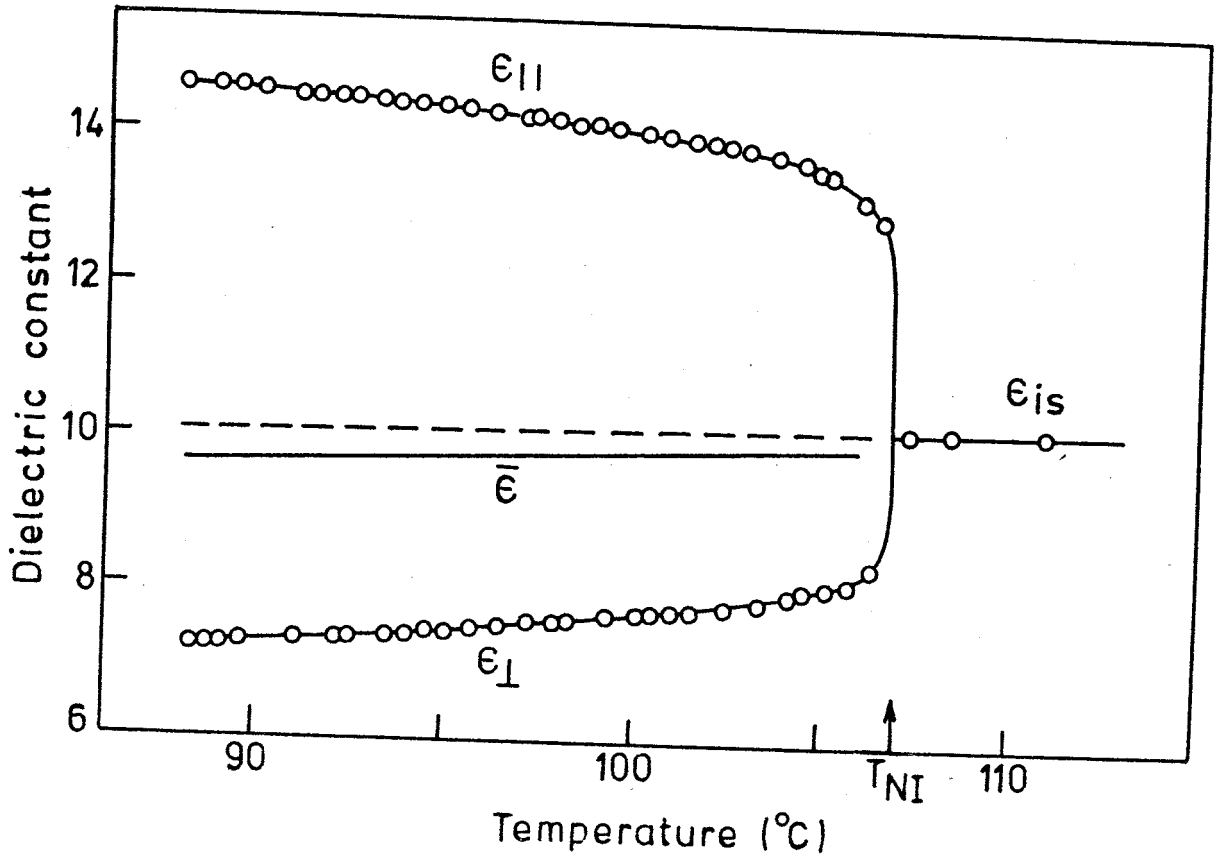


Figure 4.9

Principal dielectric constants of p-cyanobenzylidene p'-octyloxyaniline (CB00A) (T_{NI} = 107 °C).

We shall now compare CBOOA with 8 OCB and 8 OMCPC. Since the end groups of all the three are the same (see figure 4.10), we can ascribe the differences in the values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of these compounds to the different bridging groups. In figure 4.10 we have also shown the dipolar groups that contribute to the total dipole moment of the molecule along with the directions in which they will be acting. The measured values of the principal dielectric constants of these compounds taken at a relative temperature of $(T_{NI}-1)°C$ are listed in table 4.3 for the sake of comparison.

In the case of 8 OCB (figure 4.10a) there is no bridging group between the two phenyl rings and therefore the major contribution to $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ is from the cyano and alkoxy groups respectively. In comparison, CBOOA (figure 4.10b) has a benzylidene group bridging the phenyl rings. Since CH=N has a strong perpendicular component of the dipole moment

Figure 4.10

Structural formulae *of* (a) 4'-n-octyloxy-4-cyano-biphenyl (b) p-cyanobenzylidene p'-octyloxy aniline (c) trans-p-n-octyloxy-α-methyl p'-cyanophenyl cinnamate, and (d) p-alkoxy benzylidene p'-cyanoaniline. The parallel and perpendicular components of the dipole moment associated with each dipolar group is shown underneath the corresponding group.

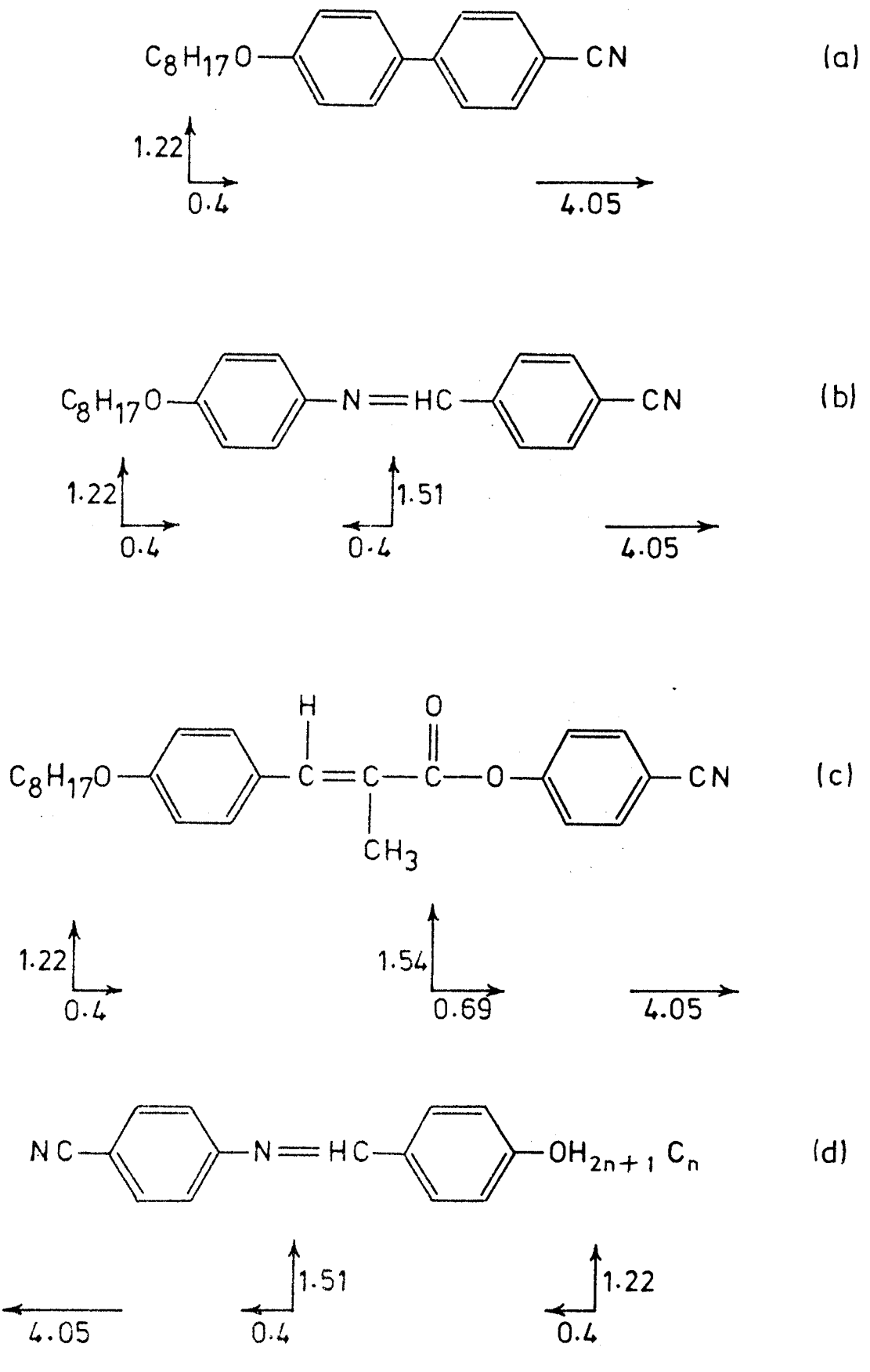

C8H17O
CN
(a)
1.22
0.4
4.05
C8H17O
N=HC
CN
(b)
1.22
0.4
1.51
0.4
4.05
C8H17O
H
O
C=C—C—O
CN
CH3
(c)
1.22
0.4
1.54
0.69
4.05
NC
N=HC
OH2n+1 Cn
(d)
4.05
1.51
0.4
1.22
0.4

Table 4.3: Principal dielectric constants and dielectric anisotropy of 8 OCB, CBOOA and 8 OMCPC at $(T_{NI} - 1)°C$

Compound	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
8 OCB	12.35	7.2	5.15
CBOOA	13.24	8.22	5.02
8 OMCPC	16.88	9.11	7.77

$\varepsilon_\perp$ increases. The increase in $\varepsilon_\parallel$ must be due to the increased polarizability anisotropy. On going over to 8 OMOPC (figure 4.10c) where the benzylidene group is replaced by a cinnamic acid group we notice that $\varepsilon_\parallel$ has increased by more than 20%. This is probably due to the contribution of about 0.7 Debye to $\mu_\parallel$ by the ester group whereas the increase in $\varepsilon_\perp$ is partly due to the methyl group in the α-position.

In CBOOA the parallel component of the CH=N group is directed antiparallel to the direction of the parallel component of the alkoxy group. This reduces the value of $\varepsilon_\parallel$ If the terminal substituents are interchanged (see figure 4.10d) then the $\mu_\parallel$ of CH=N will be directed similar to the $\mu_\parallel$ of $C_8H_{17}O$ as well as C≡N increasing the value of $\varepsilon_\parallel$. The dielectric constants of such compounds have been measured[6] whose value of $\varepsilon_\parallel$ is indeed found to be much higher than that of CBOOA.

B. Dielectric dispersion

The low frequency dispersion of $\varepsilon_{\parallel}$ was measured for the four successive members, viz., 8 OMCPC-11 OMCPC. For the three lower homologues the dispersion was measured at four different temperatures in the nematic phase. The relaxation frequency for 11 OMCPC was determined at only one temperature since it has a very narrow nematic range of 3°C. The frequency range covered was 0.1-10 MHz.

Figures 4.11-4.14 are the plots of the variation of $\varepsilon''_{\parallel}$ with frequency for 8 OMCPC-11 OMCPC at different temperatures. The maximum of $\varepsilon''_{\parallel}$ decreases with increasing temperature while the frequency at which the maximum occurs shifts to higher values. When the real and imaginary parts of the dielectric constant are plotted against each other, the experimental points lie on a semicircle with its centre on the $\varepsilon'_{\parallel}$-axis characterising a single relaxation time. These Cole-

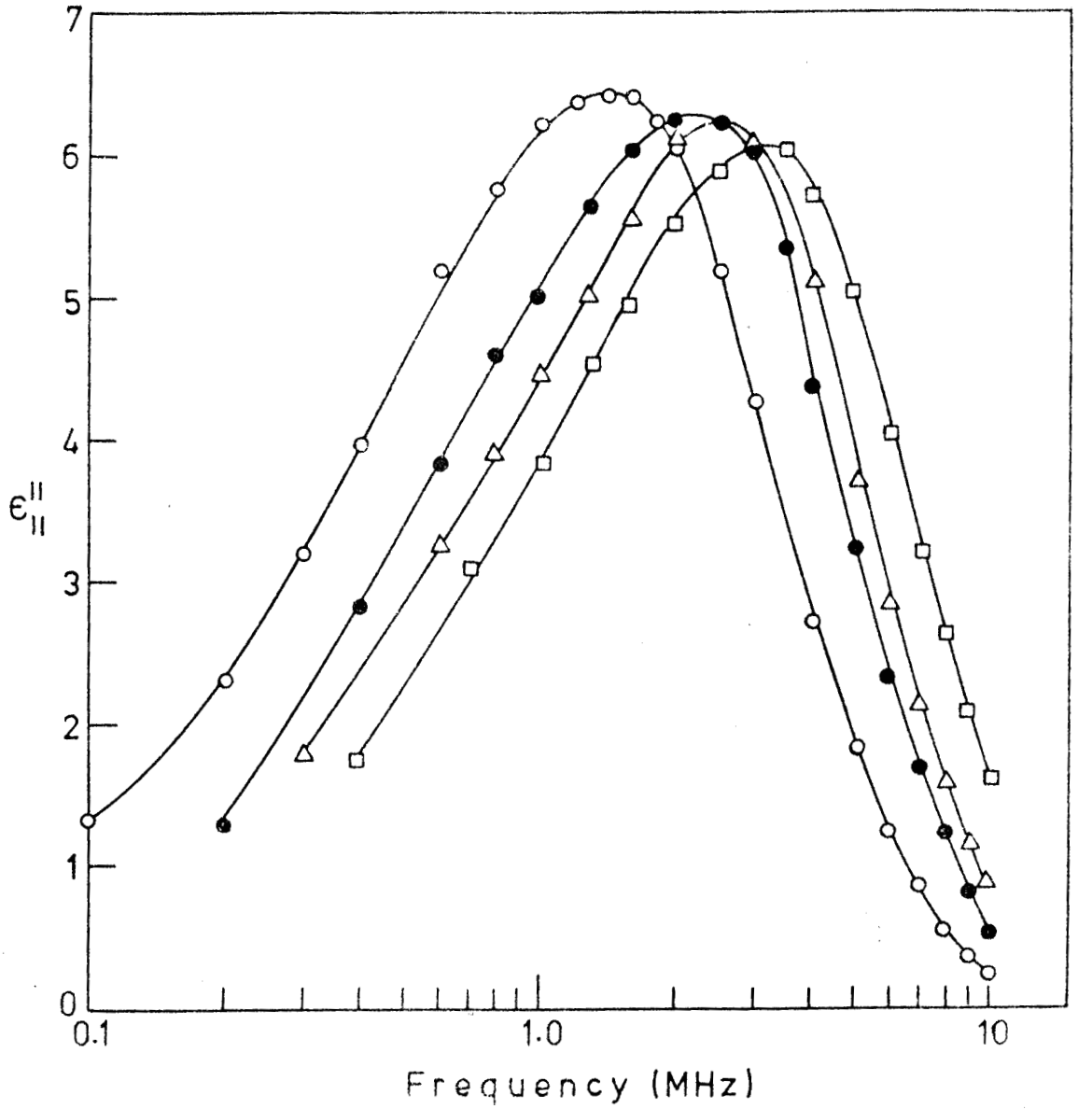


Figure 4.11

Dielectric loss ($\epsilon''_{\parallel}$) as a function of frequency for 8 QMCPC at 59.4 °C (○), 64.4 °C (●), 65.5 °C (△) and 69.0 °C (□).

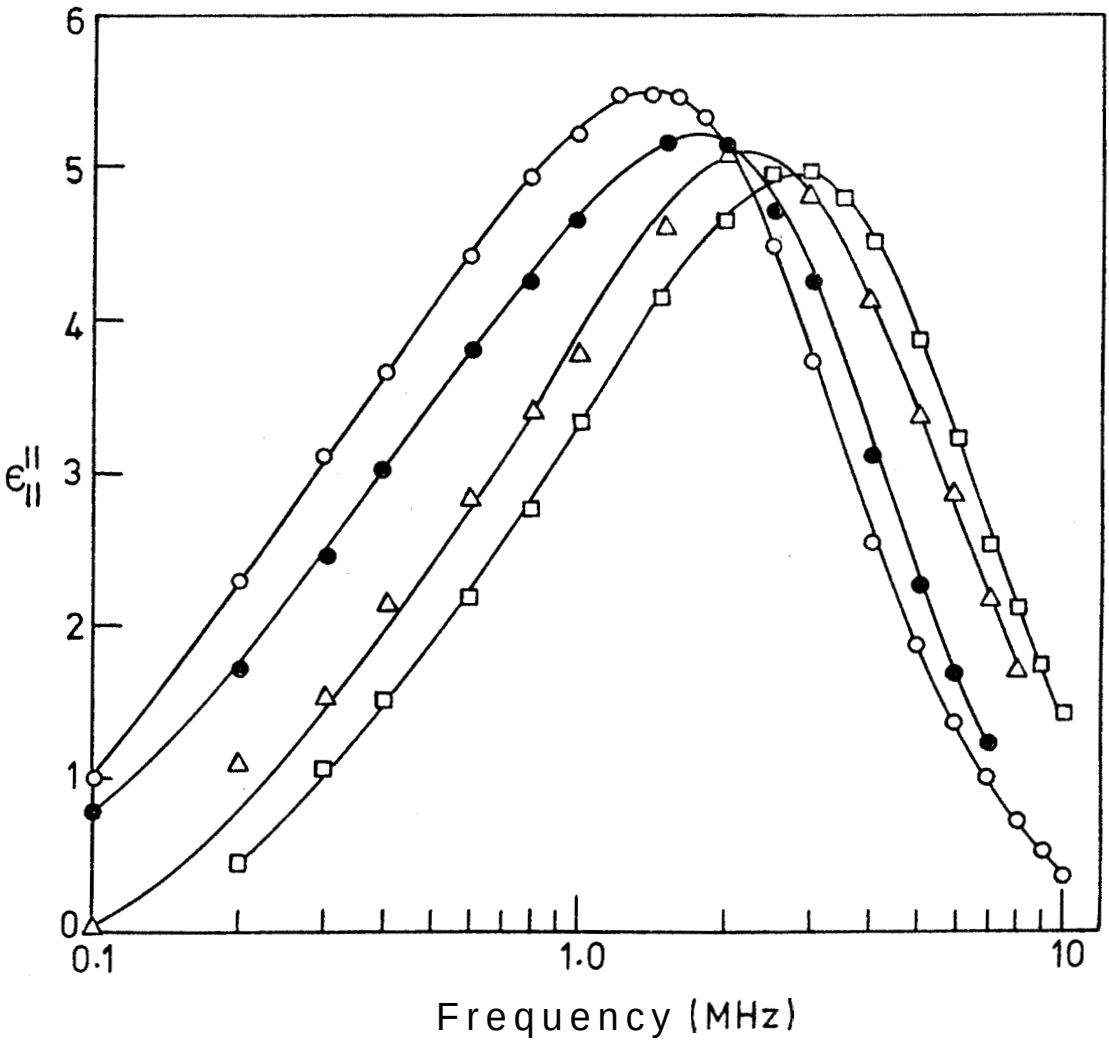


Figure 4.12

$\epsilon''_{\parallel}$ as a function of frequency for 9 OMCPC at 59.8 °C (○), 62.0 °C (●), 65.0 °C (a) and 67.5 °C (□)

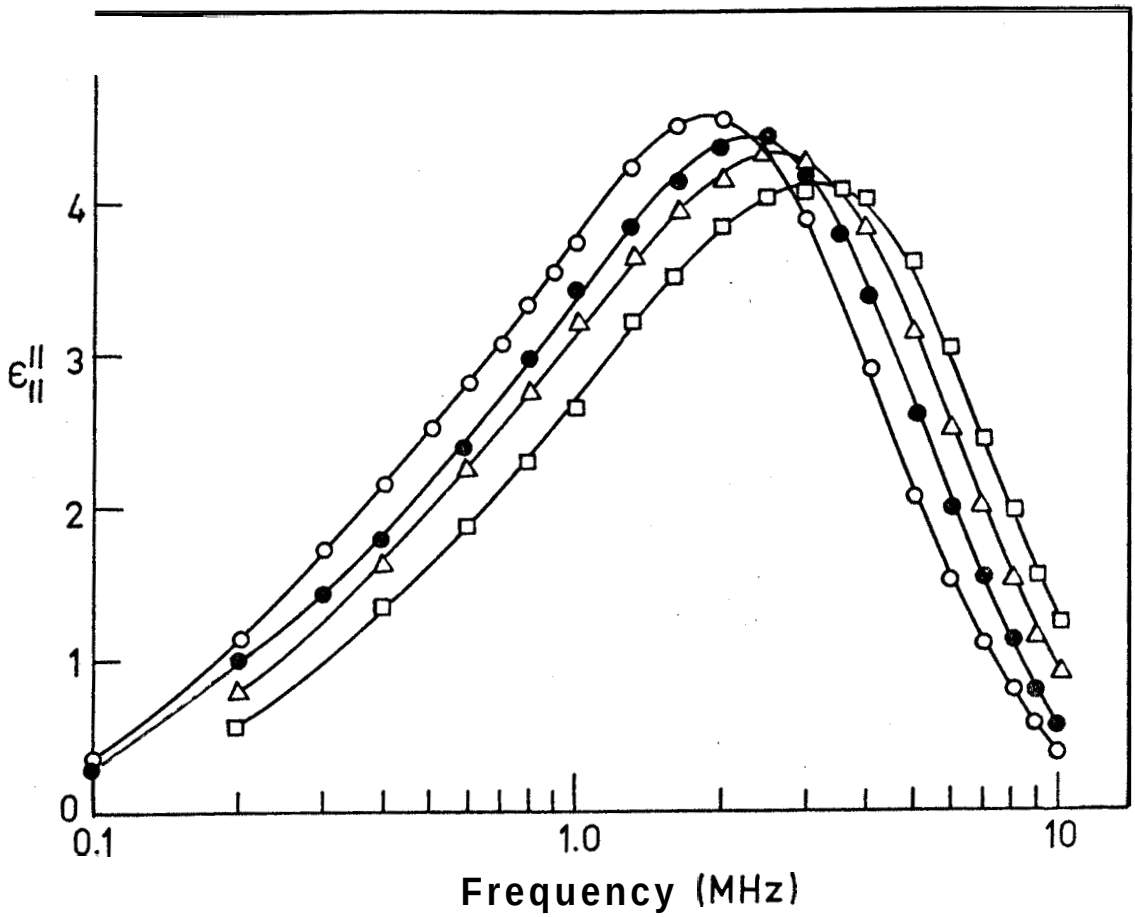


Figure 4.13

ε''_{II} as a function of frequency for 10 OMCPC at 62.9 °C (○), 65.75 °C (●), 67.8 °C (△) and 69.6 °C (□)

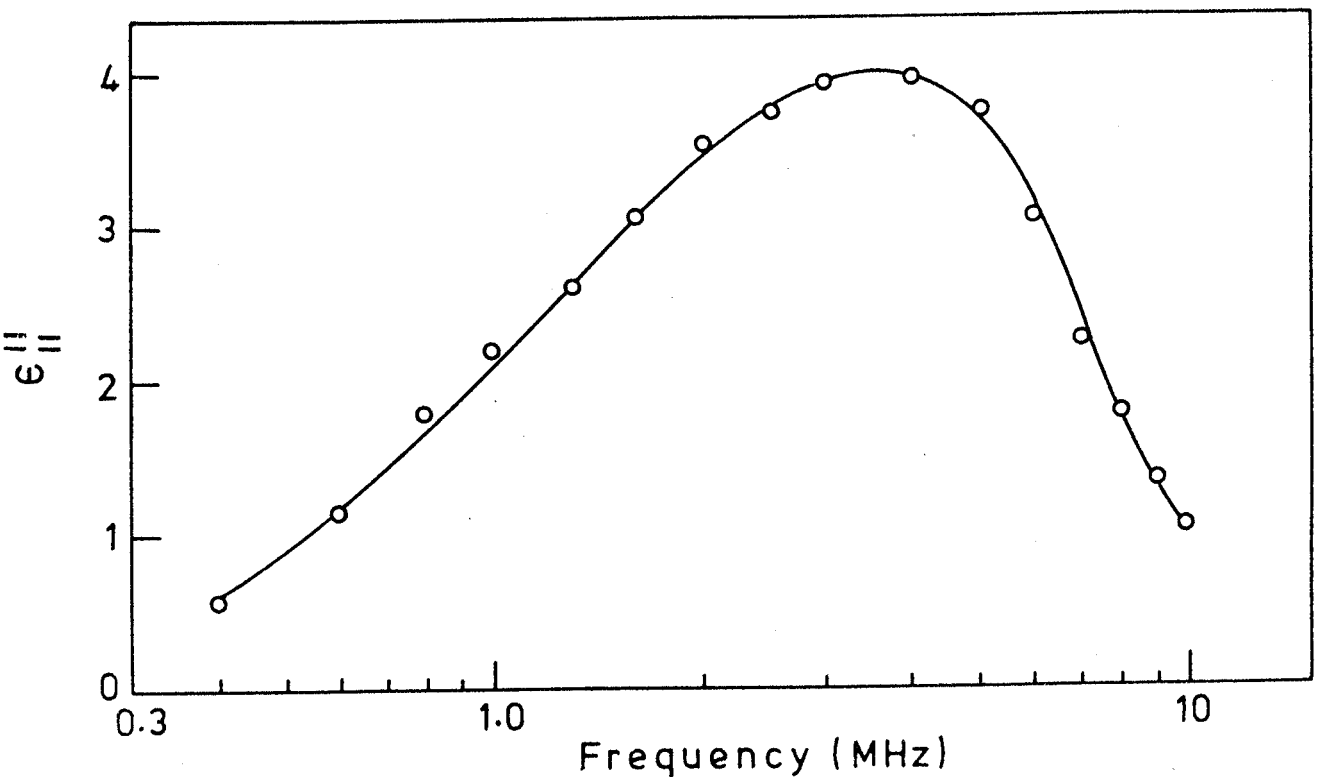


Figure 4.14

$\epsilon''_{\parallel}$ as a function of frequency for 11 OMCPC at 71.2 °C

Cole plots are shown in figures 4.15-4.18. The relaxation frequencies (f_R) were determined from the dielectric loss curves and the Cole-Cole diagrams. f_R measured at different temperatures are given in table 4.4.

On comparing the relaxation frequencies of n OMCPC with those of nCB at a relative temperature we find that the f_R of n OMCPC are lower than that of nCB. This was expected because of the longer length of the molecules of n OMCPC. While measuring the elastic constants of these compounds it was noticed[2] that the time taken by the deformed sample to relax back after the deforming field is removed is more than the time taken by nCB. This suggests that the viscosity of n OMCPC must be higher than that of nCB. This also contributes to lowering of f_R.

The relaxation frequencies of a OMCPC (n = 8-10) are plotted as functions of 1/T on a log-linear scale

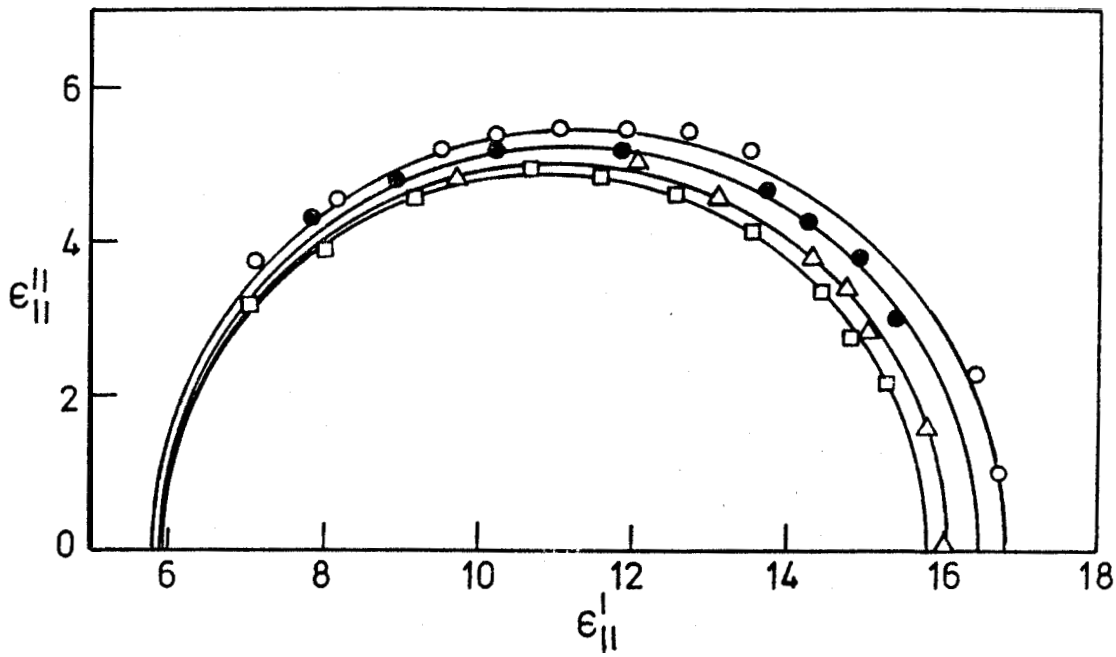


Figure 4.16

Cole-Cole plots for 9 OMCPC at 59.8 °C (○), 62.0°C (●), 65.0 °C (Δ) and 67.5 °C (□).

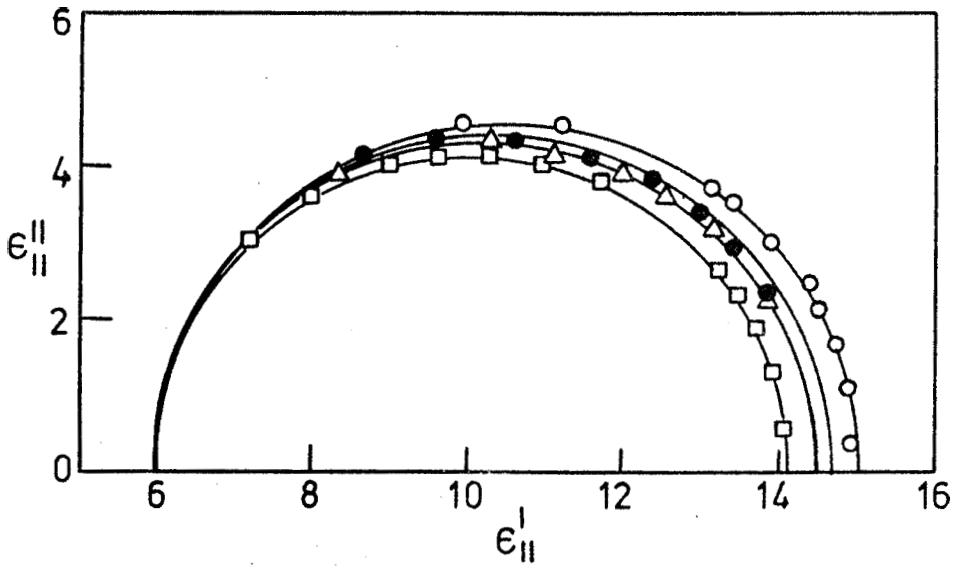


Figure 4.17

Ooze-Cole plots for 10 OMCPC at 62.9 °C (○), 65.75 °C (●), 67.8 °C (Δ) and 69.6 °C (□).

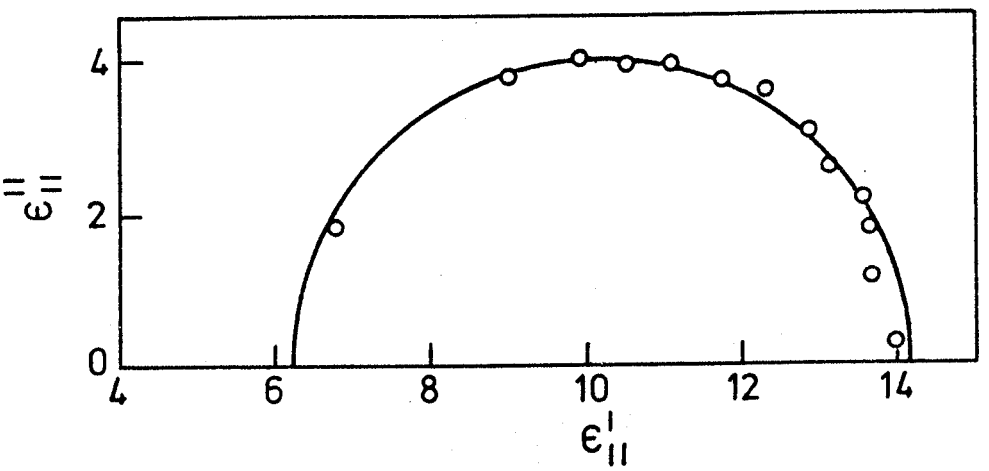


Figure 4.18

Cole-Cole plot for 11 OMCPC at 71.2 °C

Table 4.4: The relaxation frequency (f_R), frequency of dielectric isotropy (f_0) and activation energy (W) for n OMCPC (n = 8-11).

Compound	Temperature (°C)	f_R(MHz)	f_0(MHz)	W_{f_R}(eV)	W_{f_0}(eV)
8 OMCPC	59.4	1.40	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	1.40	2.9	0.917	0.917
	62.0	1.70	3.4		
	65.0	2.25	4.6		
	67.5	2.80	5.5		
10 OMCPC	62.9	1.75	3.7	0.903	0.903
	65.75	2.30	4.1		
	67.8	2.70	4.8		
	69.6	3.25	5.6		
11 OMCPC	71.2	3.60	6.5	-	-

(figure 4.19). They all show a linear relationship. The value of W_{f_R} (the subscript f_R denotes that W was determined from f_R) determined from the slope of the straight lines is the same for all compounds (see table 4.4). W_{f_R} for *It* OMCPC could not be determined since f_R *far* this compound was measured at only one temperature.

In all the compounds the relaxation of $_{\text{II}}$ leads to a change of sign of $\Delta\varepsilon$. We have determined the frequency of dielectric isotropy f_0 from the plot of ε_{II}' versus f. We find that f_0 is greater than f_R and its value increases with increase of temperature just like f_R. A plot of log f_0 versus 1/T is a straight line giving the same activation energy as f_R. The Arrhenius plots are shown in figure 4.20 and tha values of W calculated from them are given in table 4.4 under the heading W_{f_0} to distinguish it from W_{f_R}.

The value of W (0.91 ± 0.01 eV) for n OMCPC are

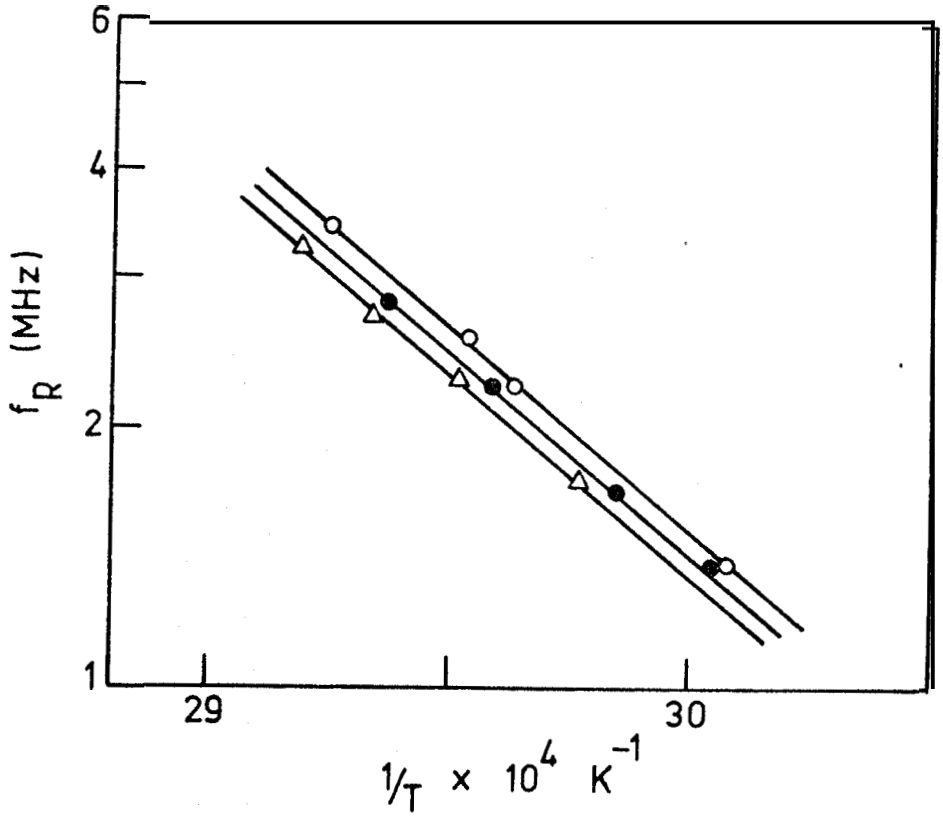


Figure 4.19

Relaxation frequency (f_R) versus 1/T for 8 OMCPC (○), 9 OMCPC (●), and 10 OMCPC (△).

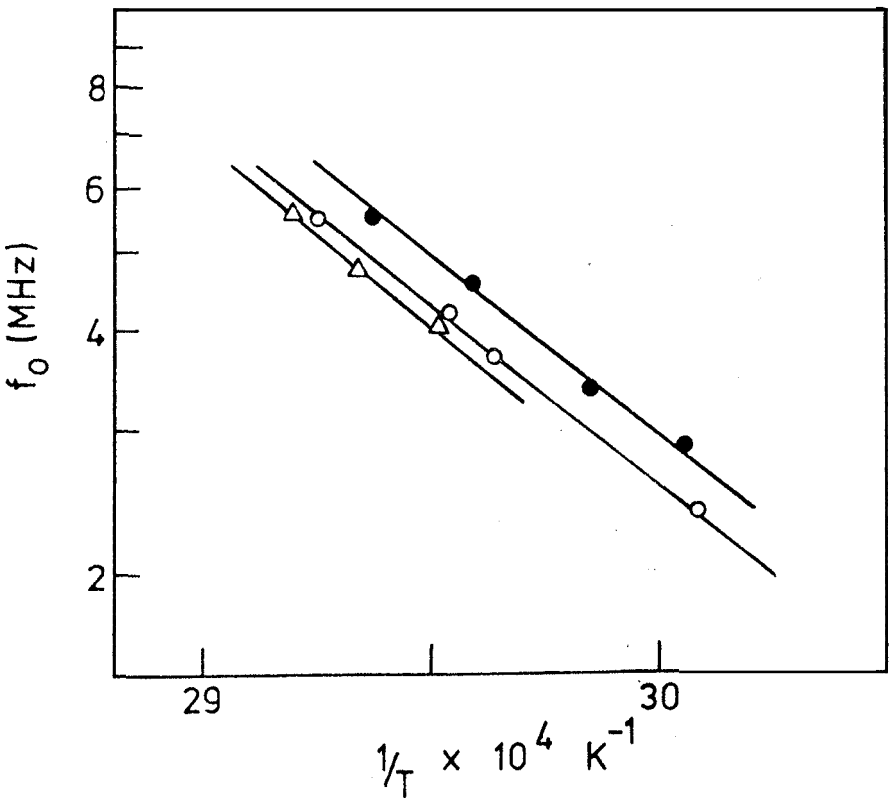


Figure 4.20

Frequency of dielectric isotropy (f_0) versus 1/T for 8 OMCPC (Θ), 9 OMCPC (●) and 10 OMCPC (▲)

high compared to that of nCB (0.56 ± 0.01) evidently due to the greater length of the molecule and the expected higher viscosity. However, we notice that W is the same for all homologues, just as in nCB.

In figure 4.21 we have plotted both $\log f_R$ and $\log f_0$ taken at a relative temperature of $(T_{NI} - 2)°C$ as functions of the number of carbon atoms *in* the alkoxy chain along with T_{NI} and s. All the four parameters alternate in a similar fashion between 8 OMOPC and 10 OMOPC. Between 10 OMOPC and 11 OMOPC the order parameter shows an increase while the other three show a decrease. The increase in s is probably due to the stronger influence of the smectic phase in 11 OMOPC since the temperature at which the value of s is taken is very close to T_{AN}.

The similarity in the static as well as dynamic behaviour of the permittivities of n OMOPC and nCB

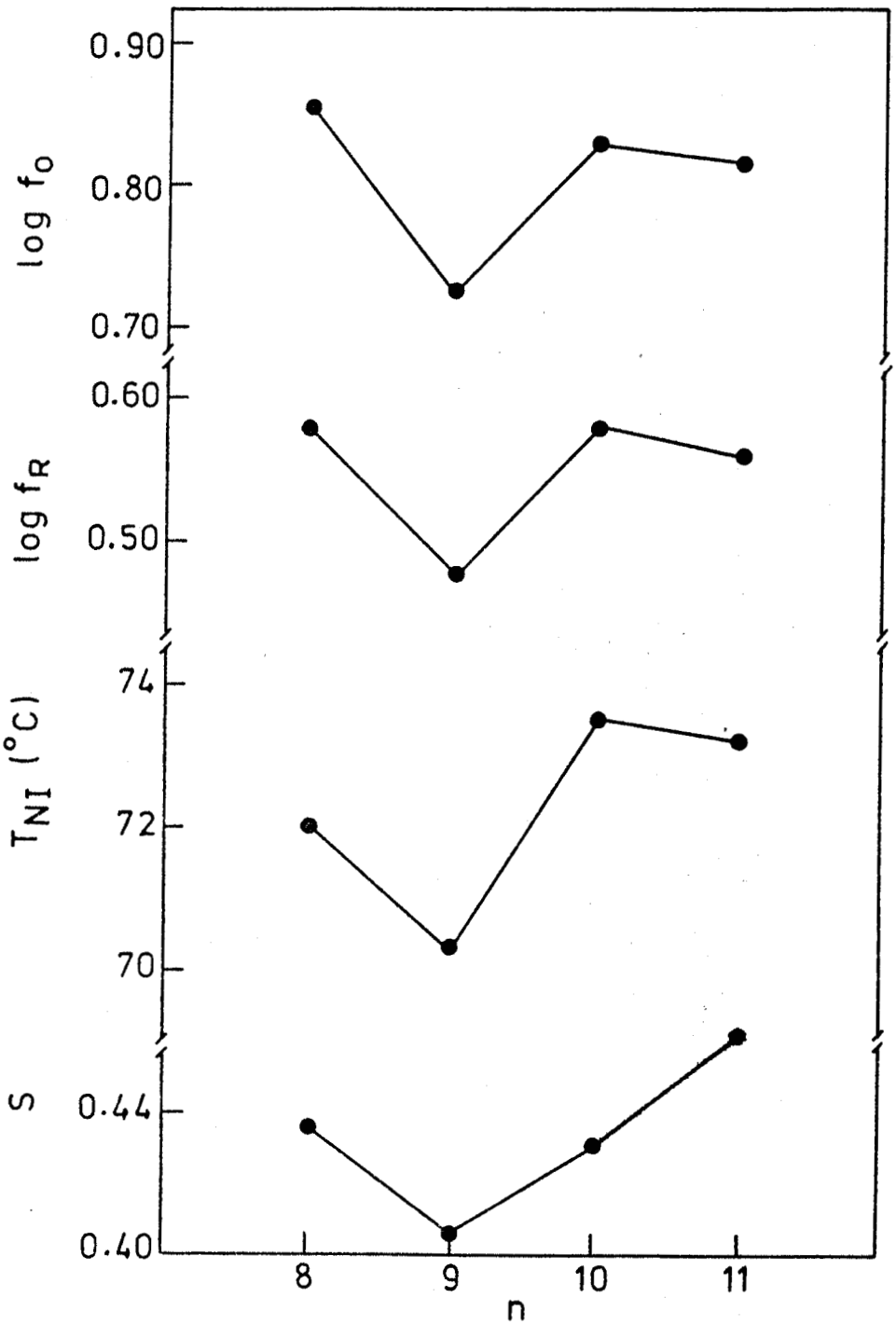


Figure 4.21 : Order parameter (S), log f_R and log f_O taken at a common relative temperature of $(T_{NI} - 2)$°C and T_{NI} as functions of the number of carbon atom (n) in the alkoxy chain of n OMCPC.

prompts us to assume the molecular associations to be similar in both of them. In the case of 8CB and 8 OCB which form bilayers the electrical conductivity behaviour[7] was markedly different from that of compounds whose layer thickness is equal to the molecular length. It will be therefore interesting to carry out electrical conductivity and X-ray studies on n OMCPC to confirm these conclusions.

References

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