CHAPTER V

DIELECTRIC PROPERTIES OF BIPHENYL-4-p-n-ALKOXYBENZOATES

Introduction

In the previous two chapters we presented the static as well as dynamic behaviour of the principal dielectric constants of members of two homologous series (nCB and n OMCPC) having a strong positive dielectric anisotropy. Three interesting results emerged from these studies: (a) Although s and T_{NI} show an alternation with increasing alkyl chain length, the dielectric anisotropy $\Delta\varepsilon$ decreases continuously as the homologous series is ascended. (b) The relaxation frequency f_R shows an alternation similar to T_{NI} and s. (c) The activation energy W is the same for all the homologues studied.

In this chapter we present our results of the dielectric studies on biphenyl-4-p-n-alkoxy bensoates (Bn OB) exhibiting a law positive dielectric anisotropy. In contrast to the strongly positive compounds the dielectric anisotropy of this homologous series exhibits a behaviour similar to that of T_{NI} and the value of $\bar{\epsilon}$ increases for the higher homologues. However f_R alternates similar to T_{NI} just as in nCB and n OMCPC.

Bn OB were synthesised by Sadashiva and Subba Rao.[1] The first five members of the homologous series exhibit a monotropic nematic phase. A monotropic smectic phase which appears at the octyloxy derivative is believed to be smectic A since it shows a simple fan-shaped texture. We have measured the static dielectric constants of the six successive homologues n = 6 to 11 and the dielectric dispersion of four successive homologues n = 7 to 10. Their transition temperatures are given in table 5.1 and their structural formula in figure 5.1.

Table 5.1: Transition temperatures of Bn OB (n = 6-11).

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	(97.4)	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.

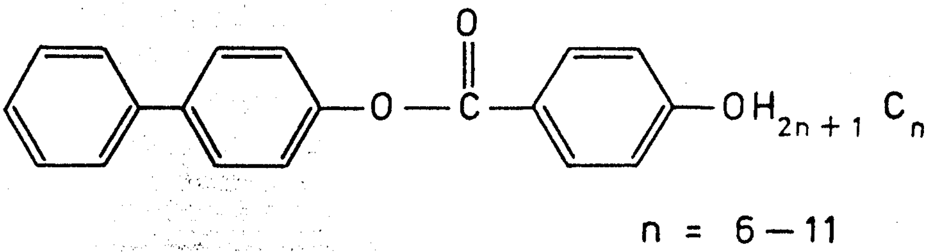

Figure 5.1

Structural formula of biphenyl 4-p-n-alkoxy benzoates (Bn OB, n = 6 - 11).

The experimental set up used for both the static and dynamic measurements has been described already in chapter III and will not be repeated here. We will only present the results and discuss them.

Results and Discussion

A. Static dielectric constants

The principal dielectric constants in the nematic ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) and isotropic (ε_{is}) phases of Bn OB (n = 6 to 11) are given in figures 5.2-5.7 as functions of temperature. The nematic range of the hexyloxy and heptyloxy derivatives is very small (2 and 3 °C respectively). However the dielectric constants of these two derivatives are measured down to 12 °C below T_{NI} by supercooling the sample.

Table 5.2 gives the values of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ as well as $\Delta\varepsilon$ for Bn OB (n = 6 to 11) at a common relative temperature of $(T_{NI} - 2)$°C. The values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decrease with increasing alkoxy chain length. The

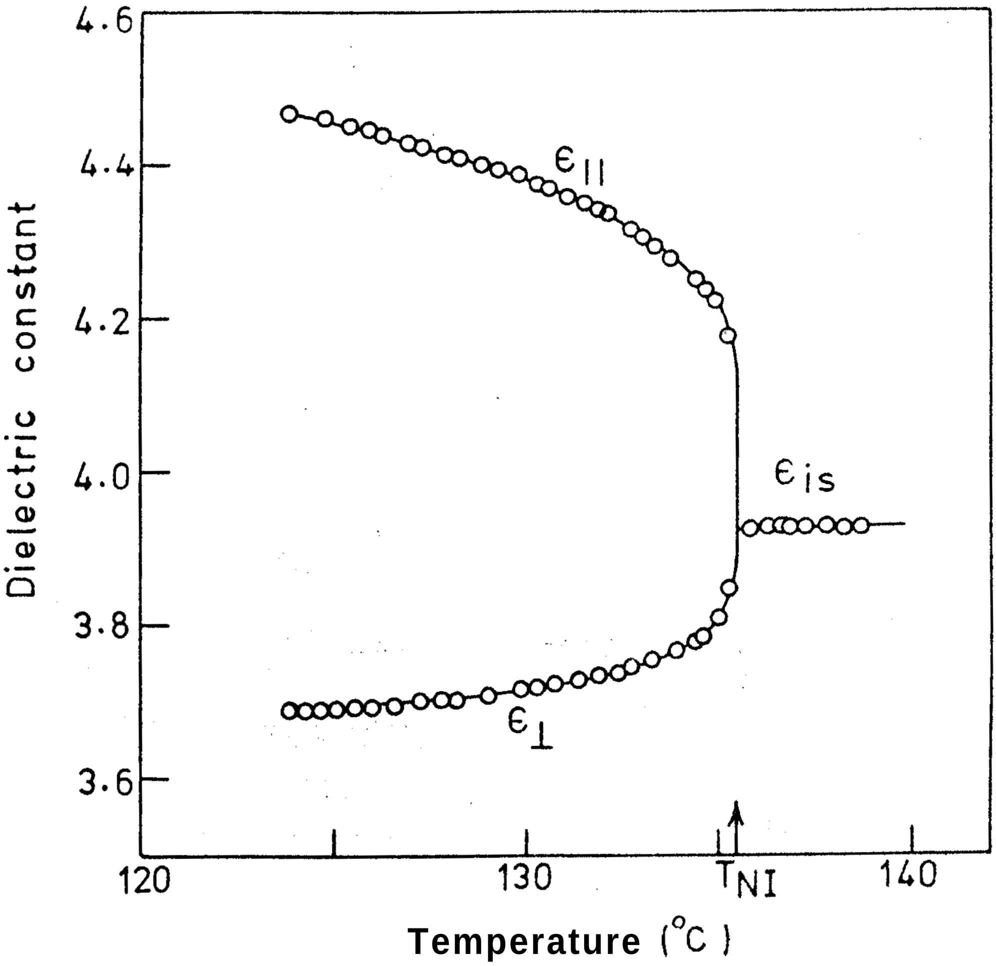

Figure 5.2

Principal dielectric constants of B6 OB

(T_{NI} = 135.5 °C)

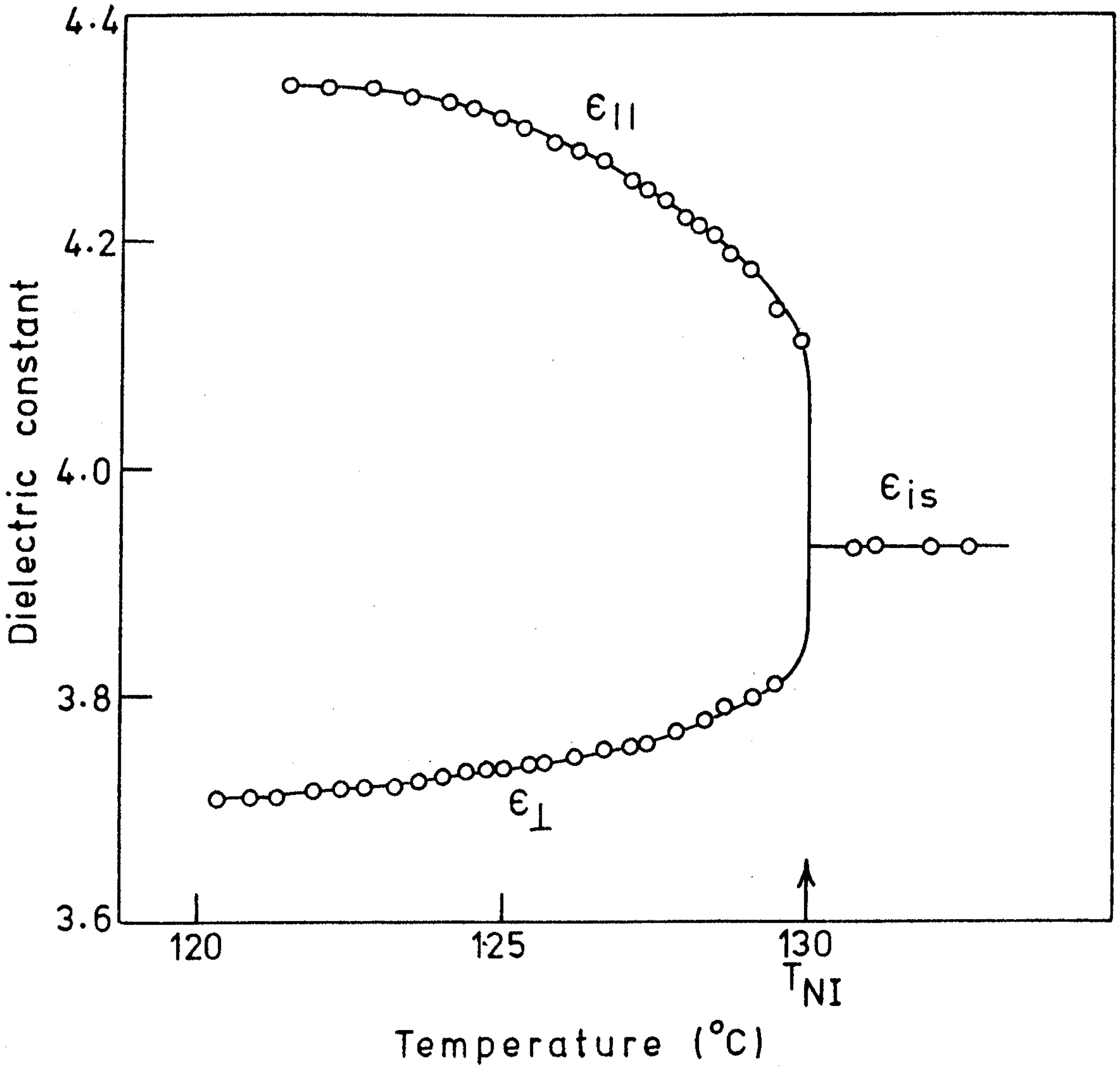

Figure 5.3

Principal dielectric constants of B7OB
(T_{NI} = 130.0 °C)

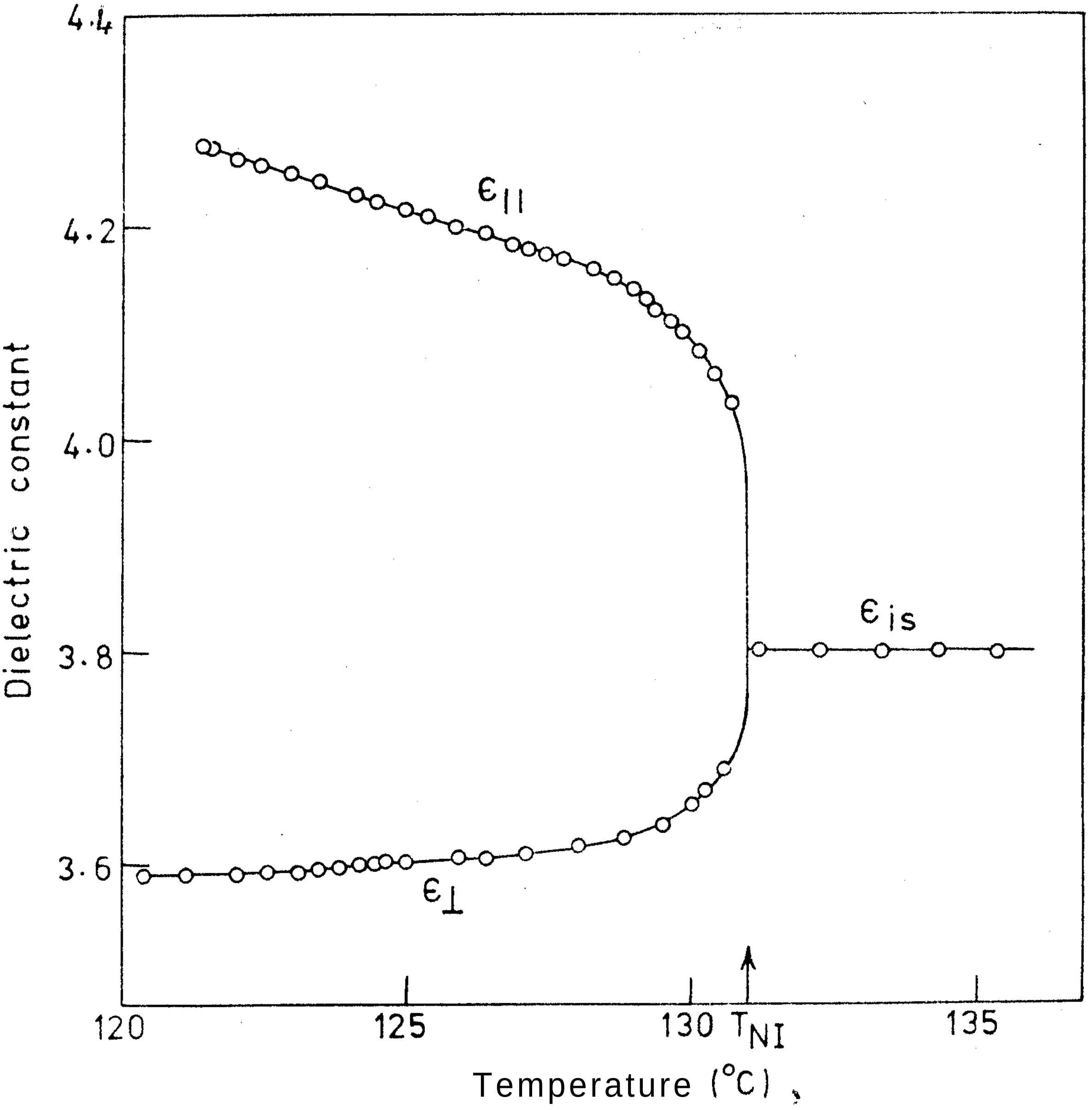

Figure 5.4

Principal dielectric constants of B8 OB (T_{NI} = 131.0 °C

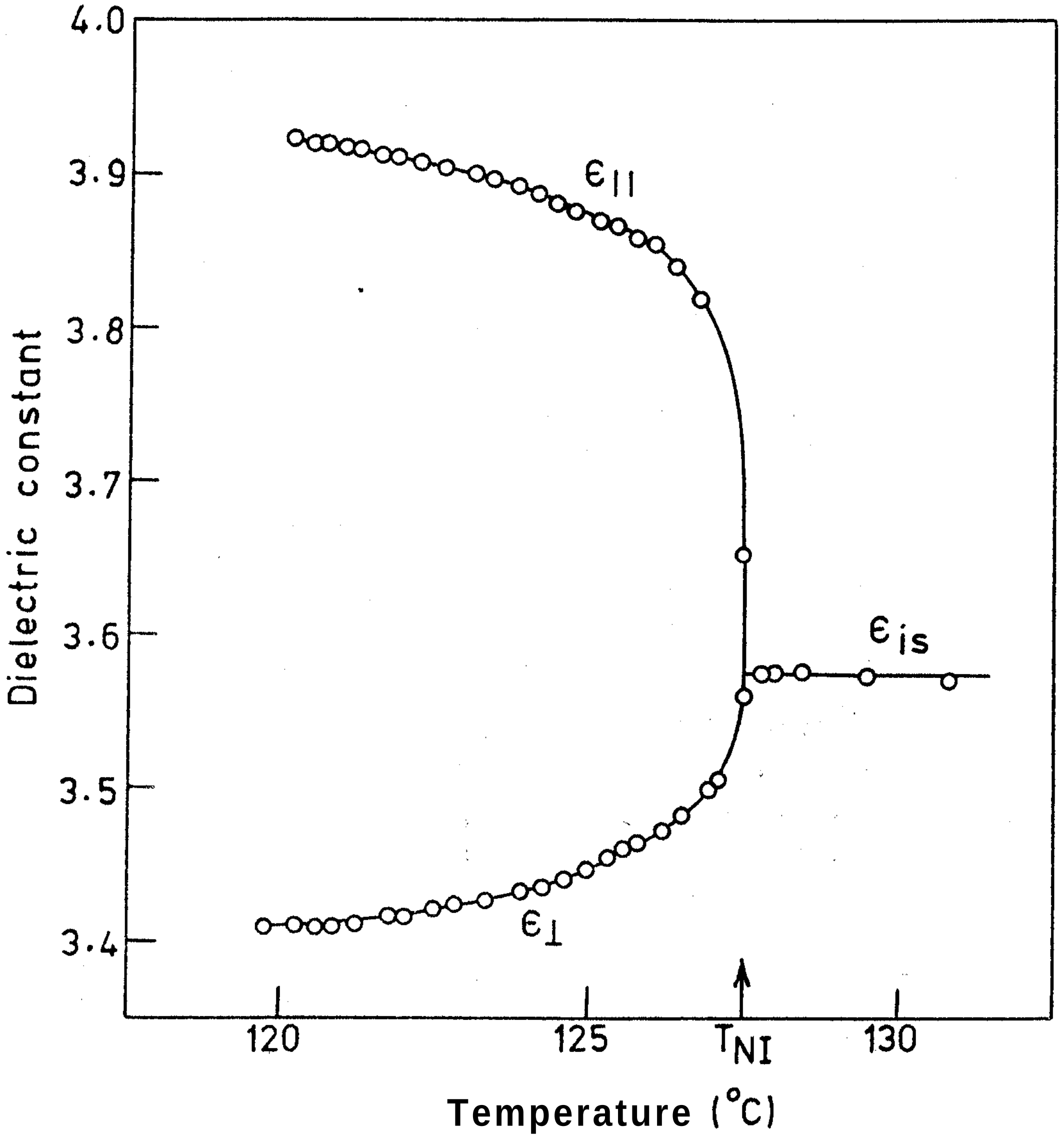

Figure 5.5

Principal dielectric constants of B9 OB (T_{NI} = 127.5°C)

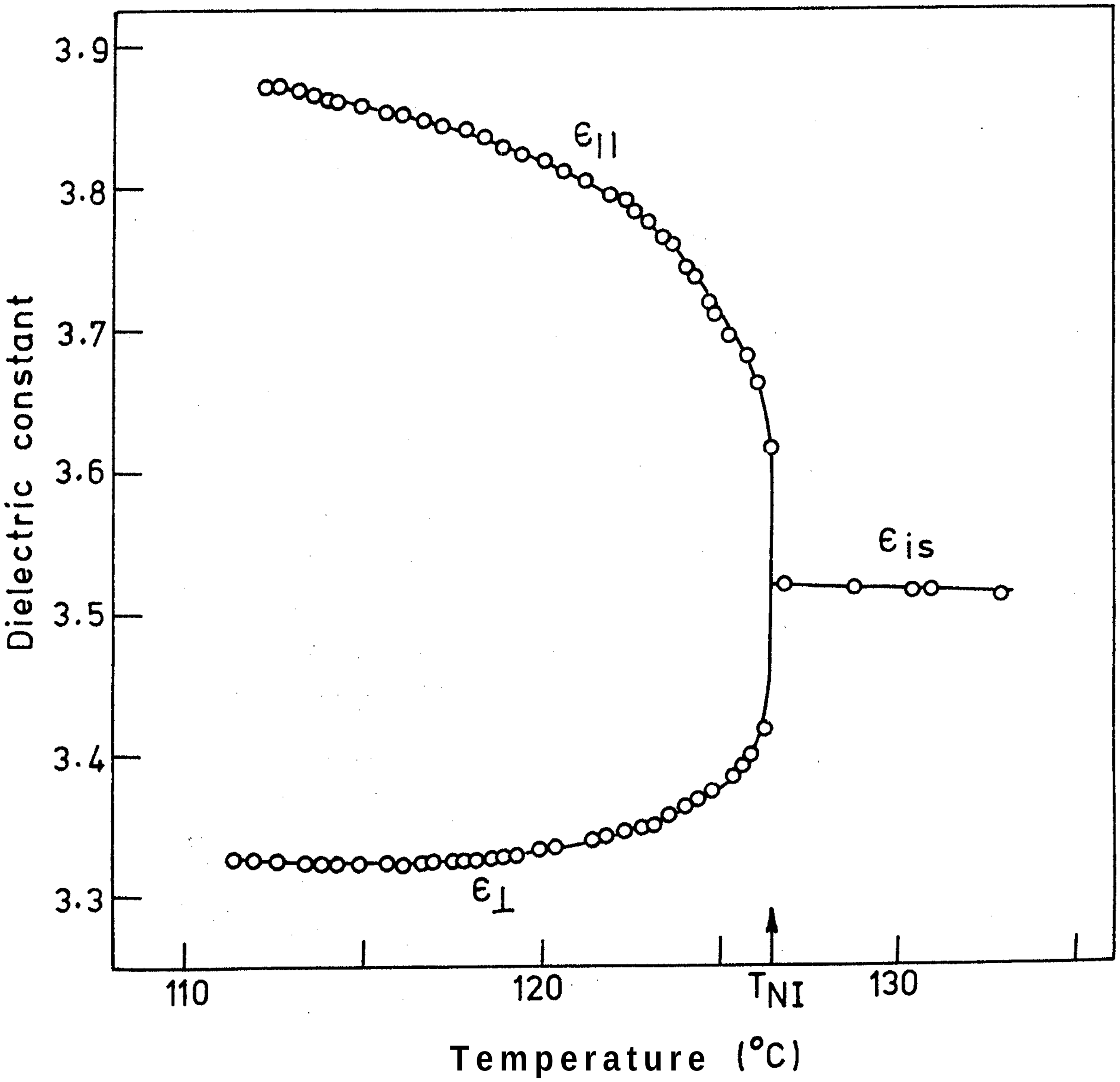

Figure 5.6

Principal dielectric constants of B10 OB (T_{NI} = 126.5 °C).

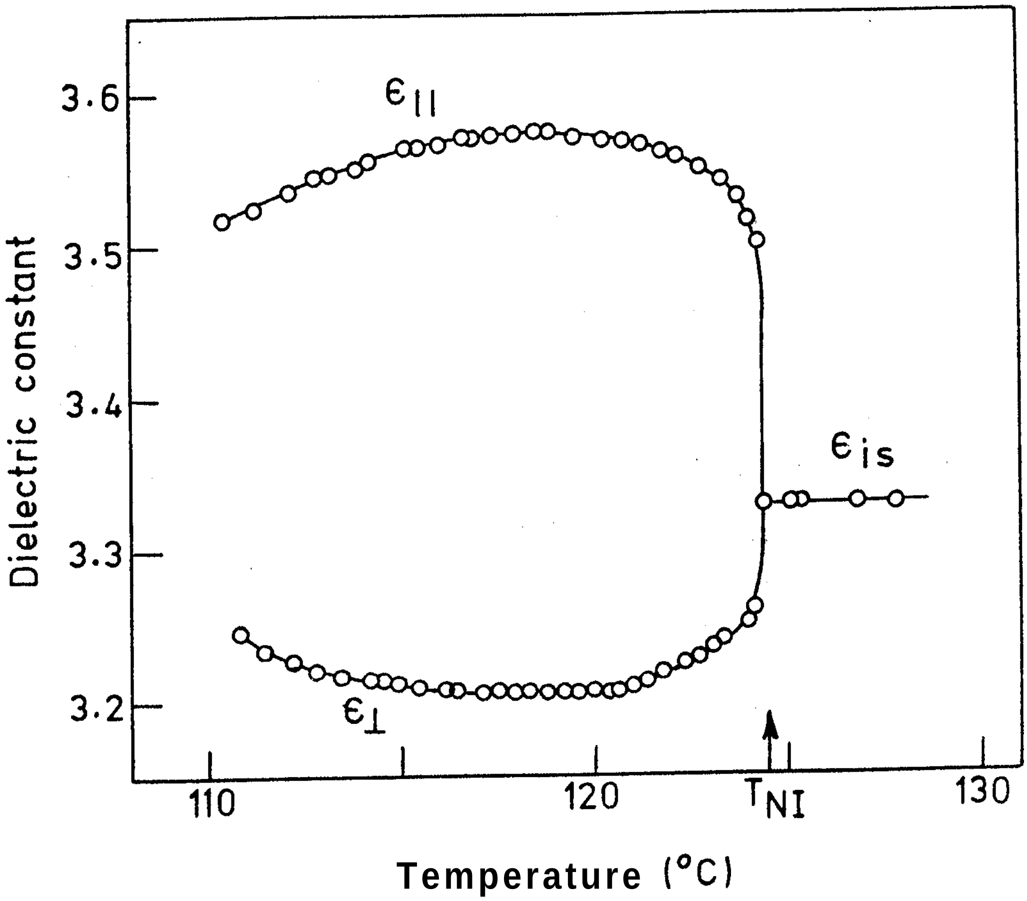

Figure 5.7

Principal dielectric constants of B11 OB (T_{NI} = 124.5 °C)

Table 5.2: Principal dielectric constants and dielectric anisotropy of Bn OB at $(T_{NI} - 2)$ °C

Compound	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
B6 OB	4.29	3.76	0.53
B7 OB	4.22	3.77	0.45
B8 OB	4.13	3.63	0.50
B9 OB	3.86	3.46	0.40
B10 OB	3.72	3.36	0.36
B11 OB	3.55	3.23	0.32

dielectric anisotropy is small and positive for all the compounds. As observed[2,3] in other homologous series of compounds with small positive dielectric anisotropy, the value of $\Delta\varepsilon$ when plotted as a function of the number of carbon atoms in the alkoxy chain shows an alternation similar to that exhibited by T_{NI} (see figure 5.8). In fact both T_{NI} and $\Delta\varepsilon$ alternate only between B6 OB and B9 OB. Beyond B9 OB they show a continuous decrease.

The average value of the dielectric constant $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ and the extrapolated isotropic value are not shown in figures 5.2-5.7 since the difference between ε_{is} and $\bar{\varepsilon}$ is less than 0.5%. This is in contrast to the large difference (4 - 5%) observed in strongly positive compounds (see chapters ifI and IV).

In the temperature range measured, all the compounds except the undecyloxy derivative show the normal behaviour of increasing $\varepsilon_{\parallel}$ and decreasing $\varepsilon_{\perp}$

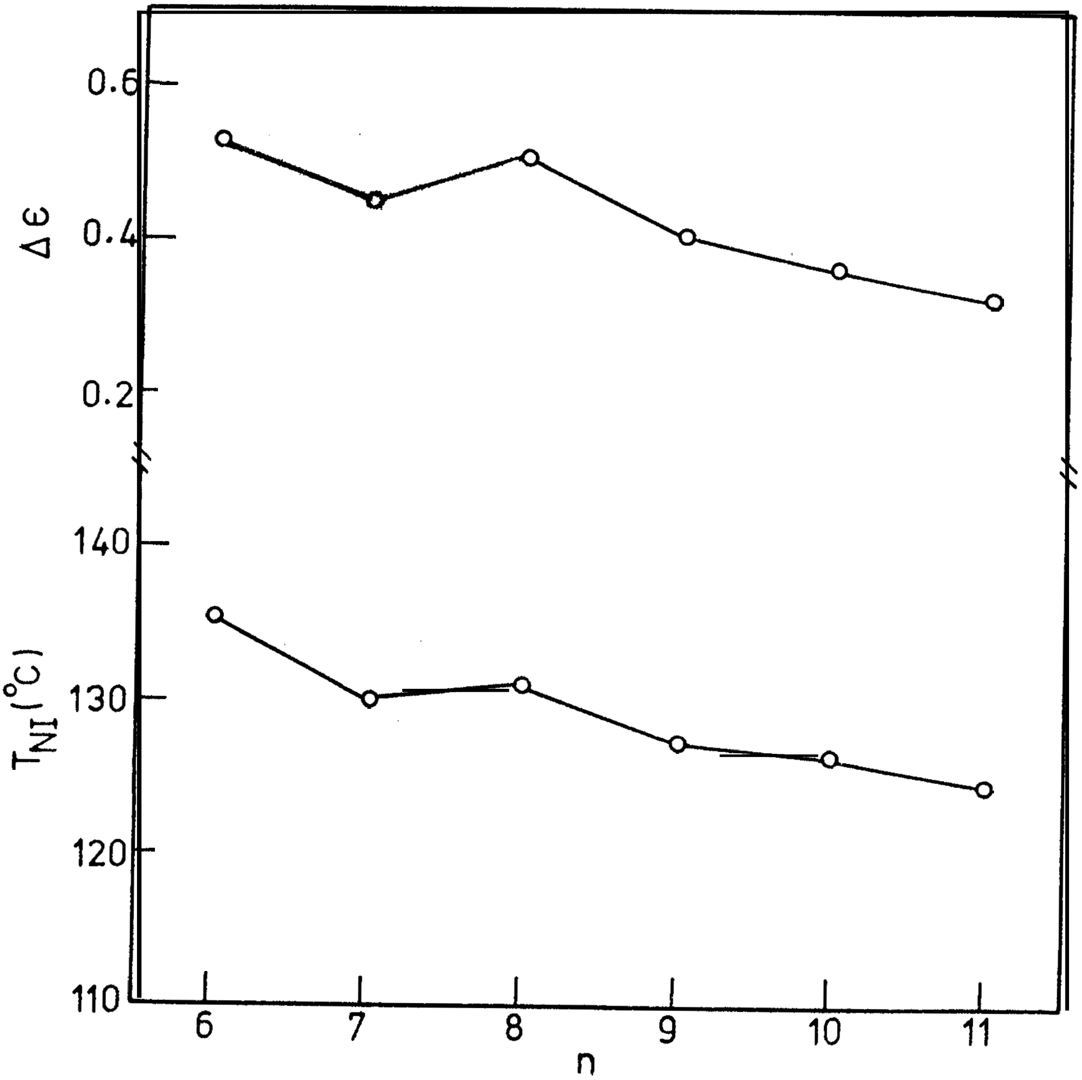

Figure 5.8

The dielectric anisotropy (Δε) taken at a common relative temperature of $(T_{NI} - 2)$°C and nematic-isotropic transition temperature (T_{NI}) as functions of the number of carbon atoms in the alkoxy chain for Bn OB.

with decrease of temperature. In the undecyloxy compound, at temperatures below $(T_{NI} - 6)°C$, $\varepsilon_{\parallel}$ decreases while $\varepsilon_{\perp}$ increases with decrease of temperature (figure 5.7). Unfortunately, owing to the difficulty in alignment, we could not measure the dielectric constants in the smectic phase to see whether this anomaly leads to a change in the sign of $\Delta\varepsilon$ as observed in alkyl azoxybenzenes.[4,5]

B. Dielectric dispersion

The low frequency dispersion of $\varepsilon_{\parallel}$ was measured for the four successive homologues, B7 OB - B10 OB. For each compound the dispersion was measured at different temperatures in the frequency range of 0.4-15.0 MHz. In figures 5.9-5.12 we have plotted $\varepsilon''_{\parallel}$ versus frequency for all the compounds. Figures 5.13-5.16 are the Cole-Cole plots at different temperatures. All the arcs are semicircles with their centres lying on the $\varepsilon'_{\parallel}$-axis characterising a single

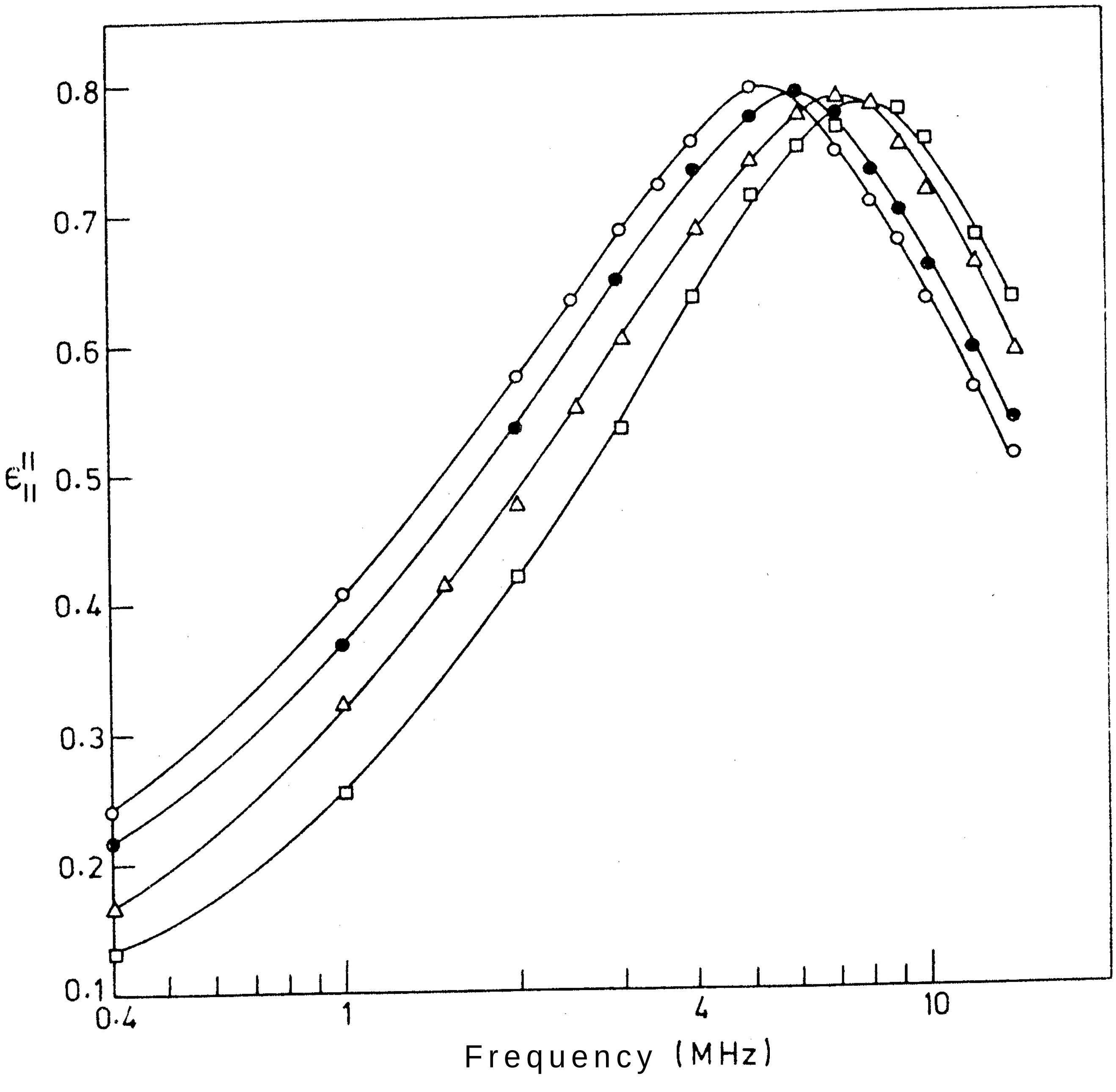

Figure 5.9

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

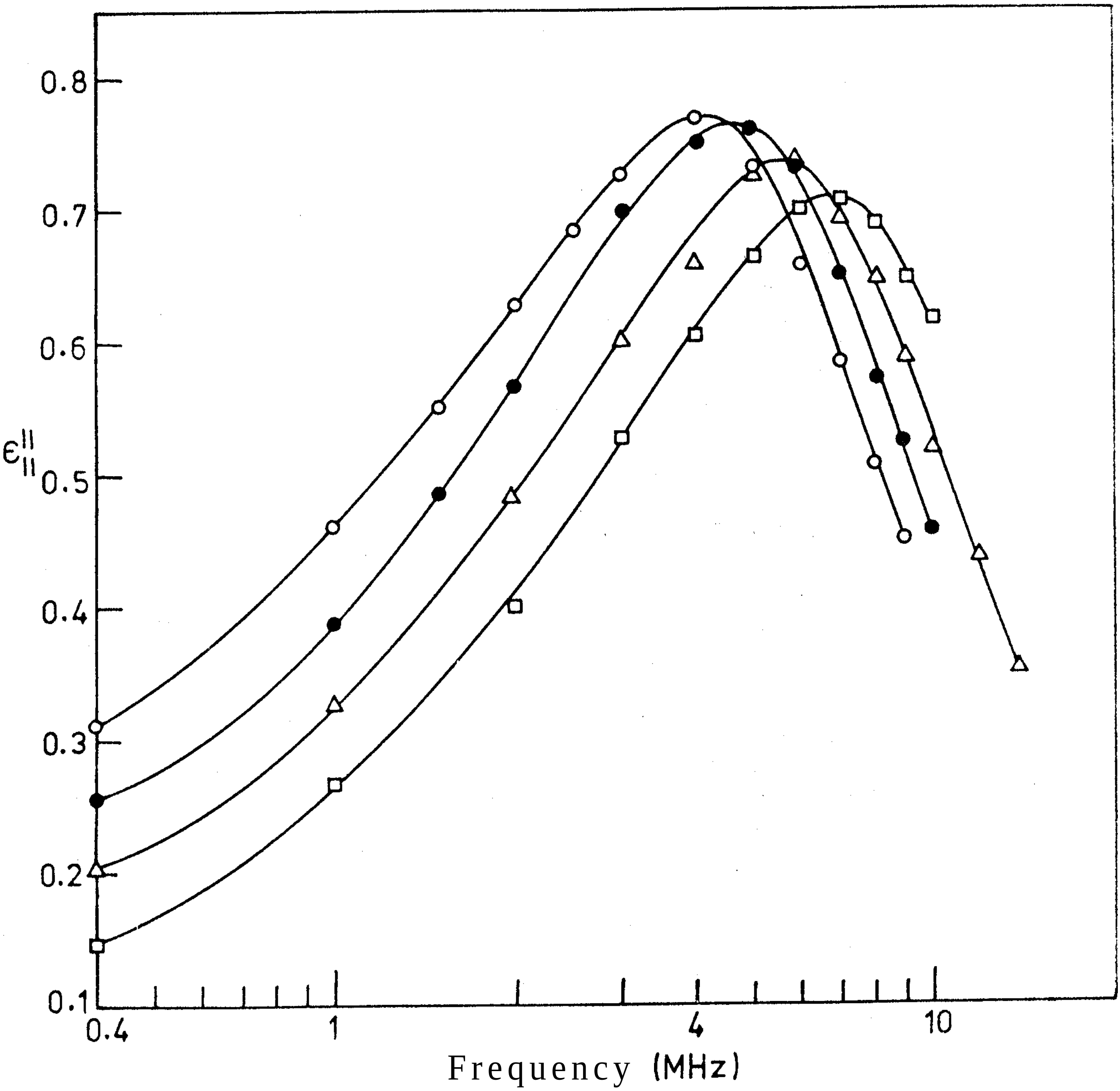

Figure 5.10

$\epsilon''_{\parallel}$ as a function of frequency for B8 CB at 107.9 °C (○), 110.25 °C (●), 113.3 °C (A) and 118.5 °C (□).

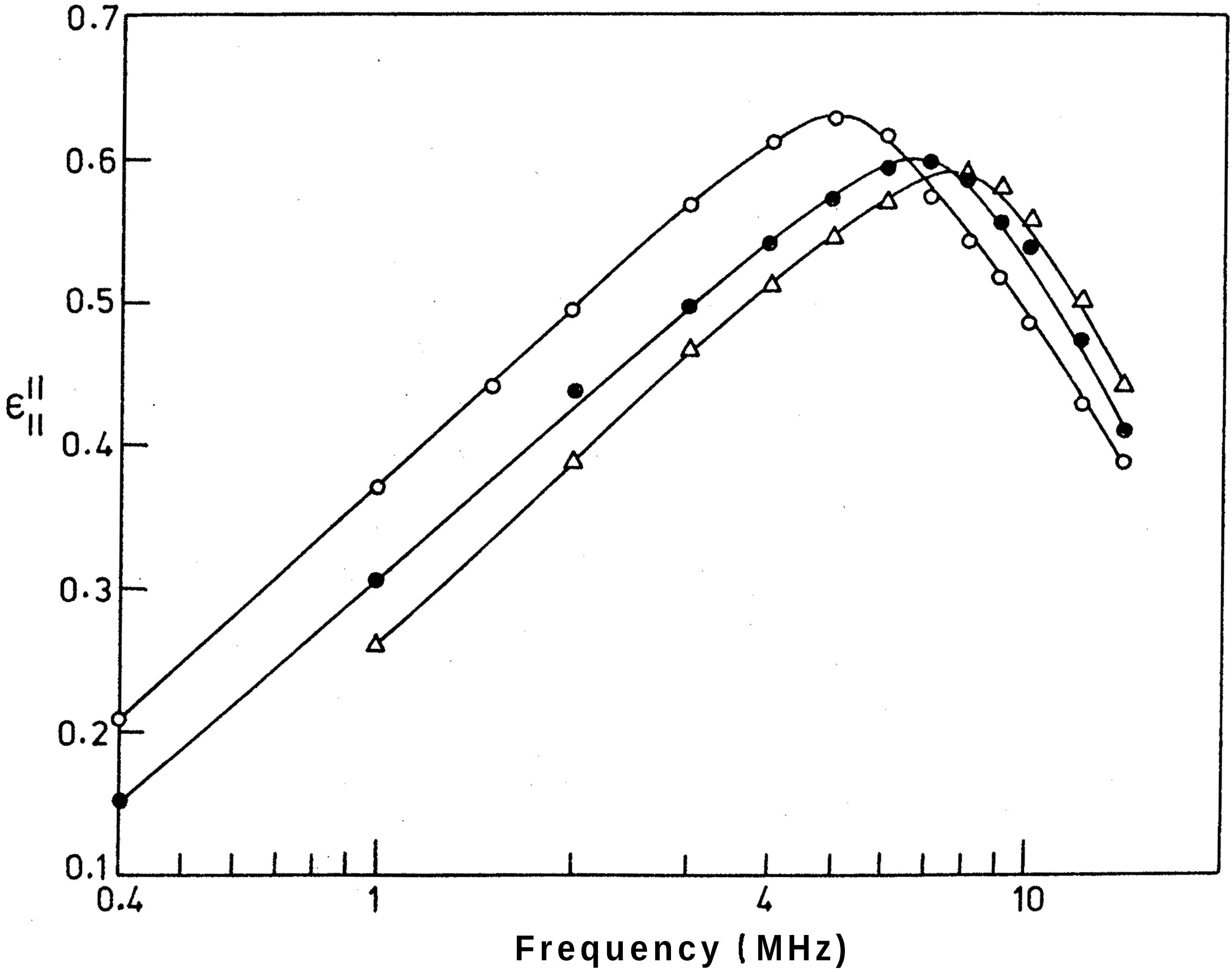

Figure 5.11

ε" as a function of frequency for B9 OB at 111.6 °C (o), 116.0 °C **(a)** and 119.1 °C (A).

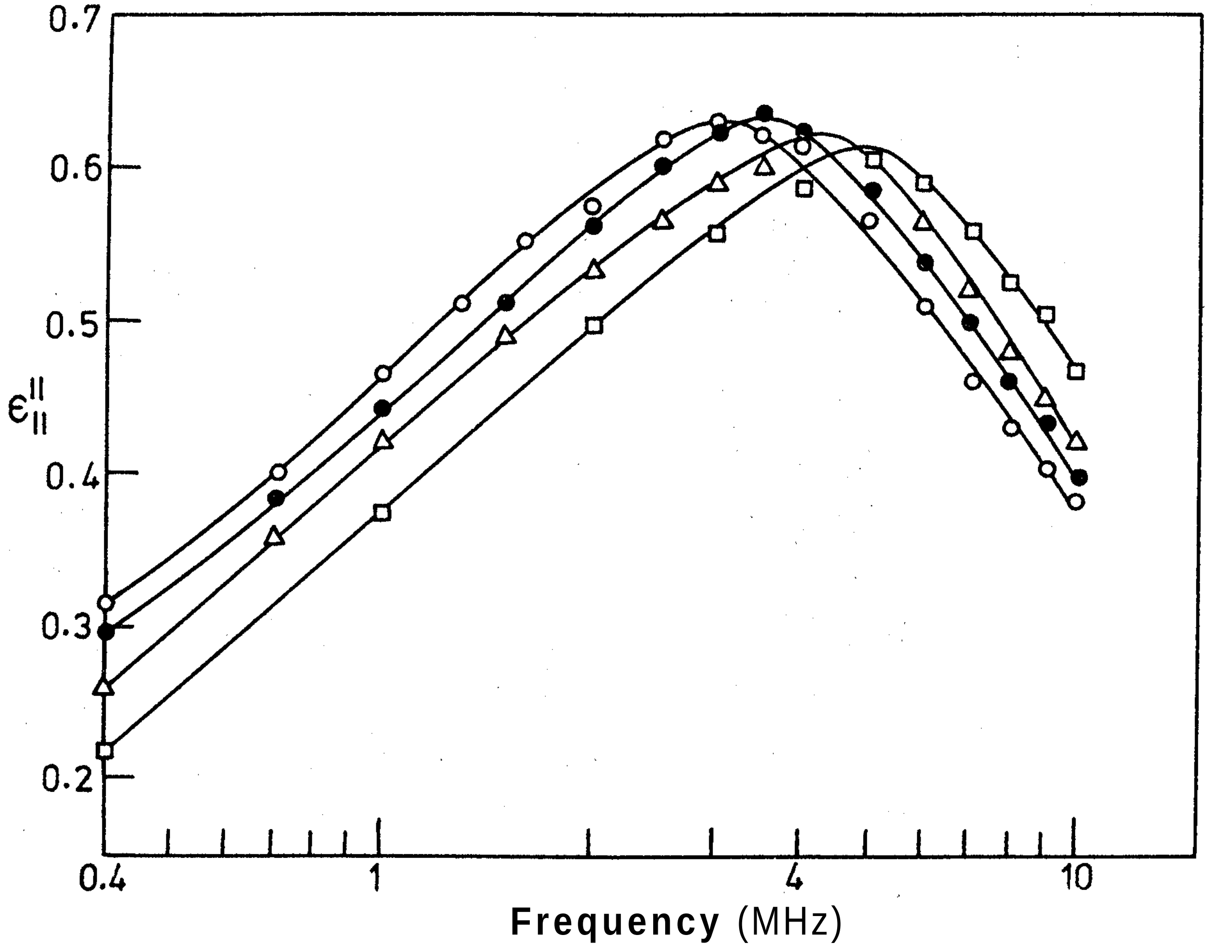

Figure 5.12

$\varepsilon''_{\parallel}$ as a function of frequency for B10 OB st 105.2 °C (○) 107.6 °C (●), 110.4 °C (A) and 113.6 °C (□).

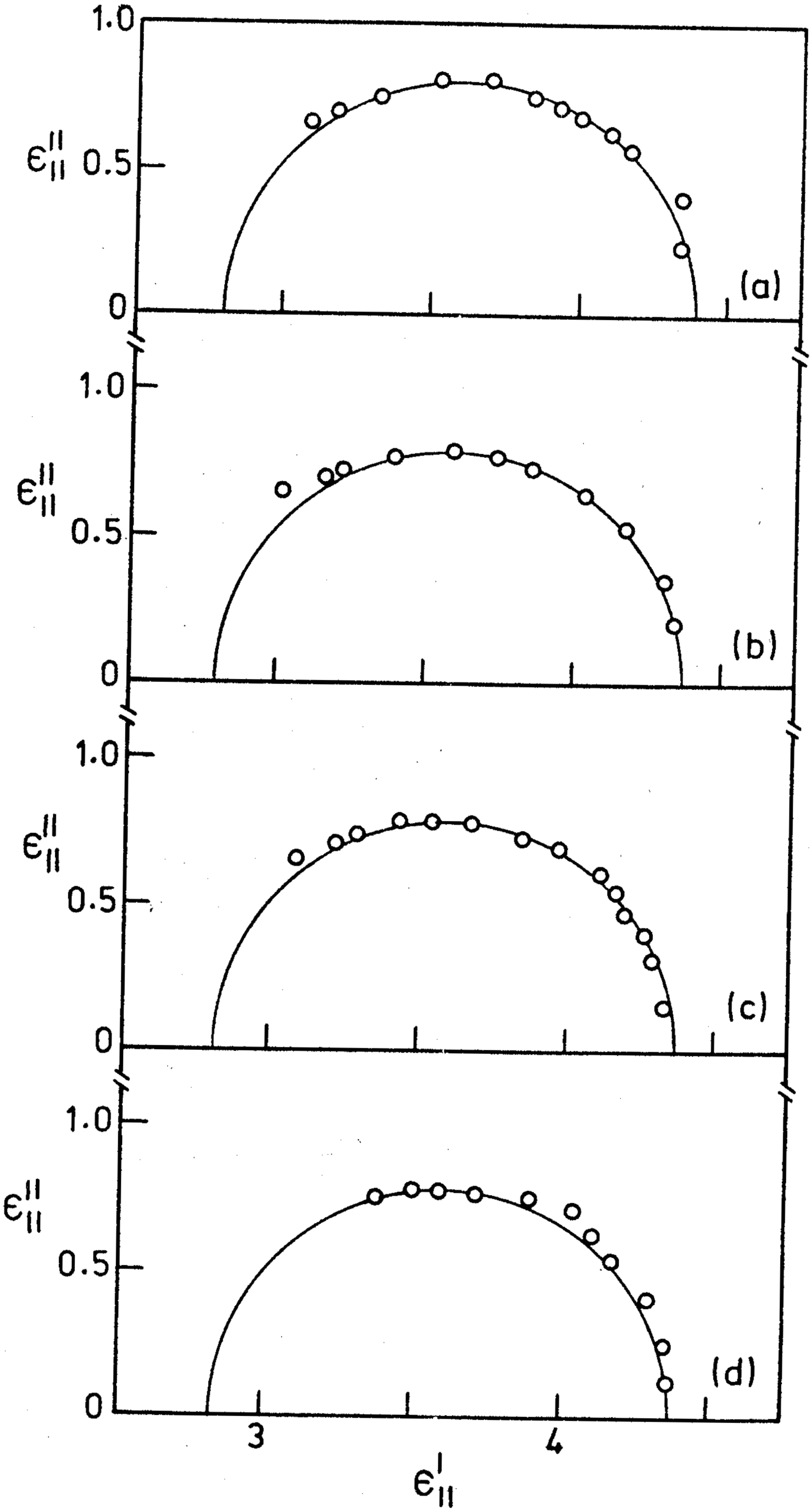

Figure 5.13

Cole-Cole plots for B7 OB at (a) 112.95 °C (b) 115.1 °C (c) 117.6 °C and (d) 121.3 °C

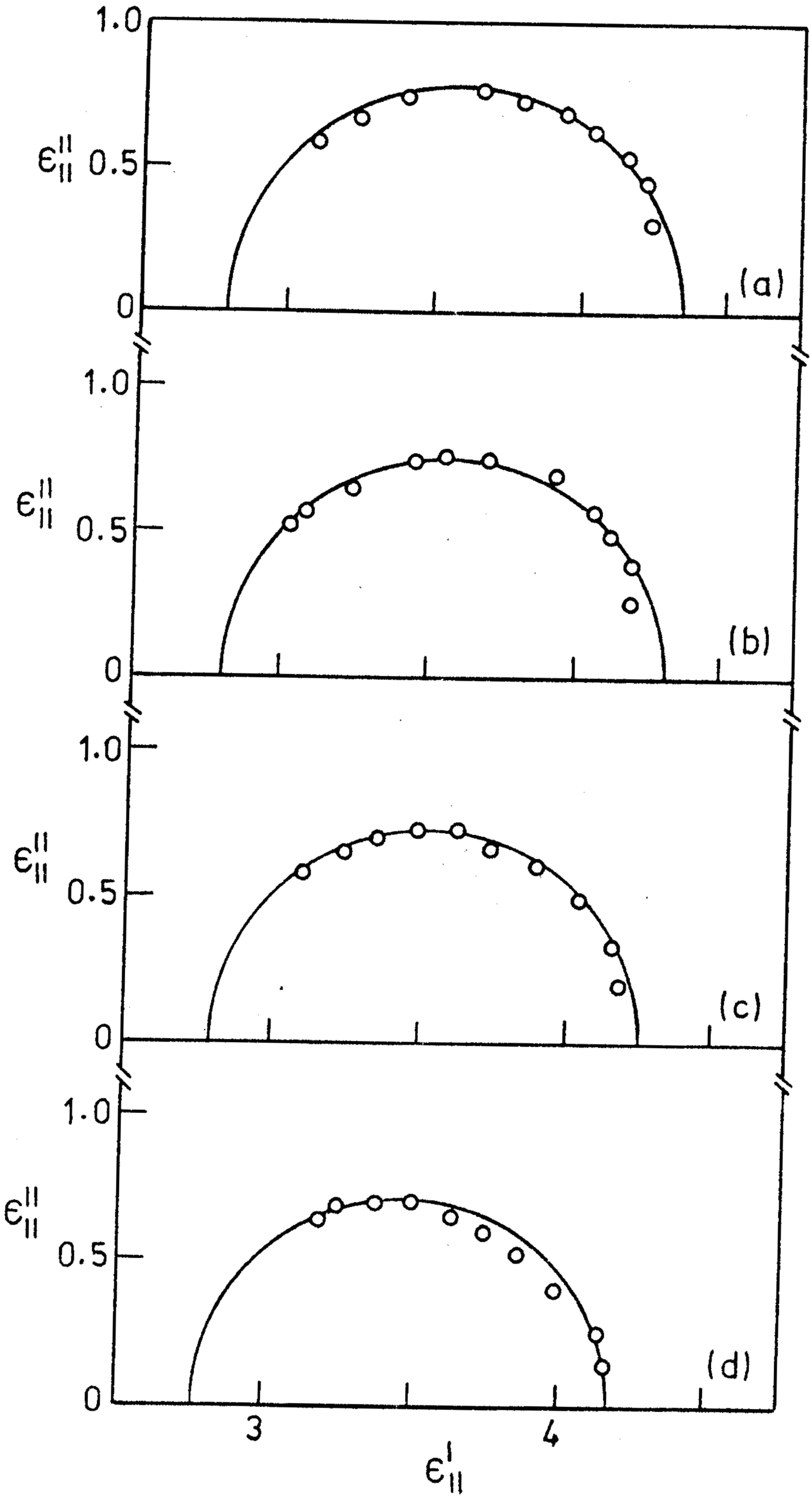

Figure 5.14

Cole-Cole plots fox B8 OB at (a) 107.9 °C (b) 110.25 °C (c) 113.3 °C and (d) 118.5 °C.

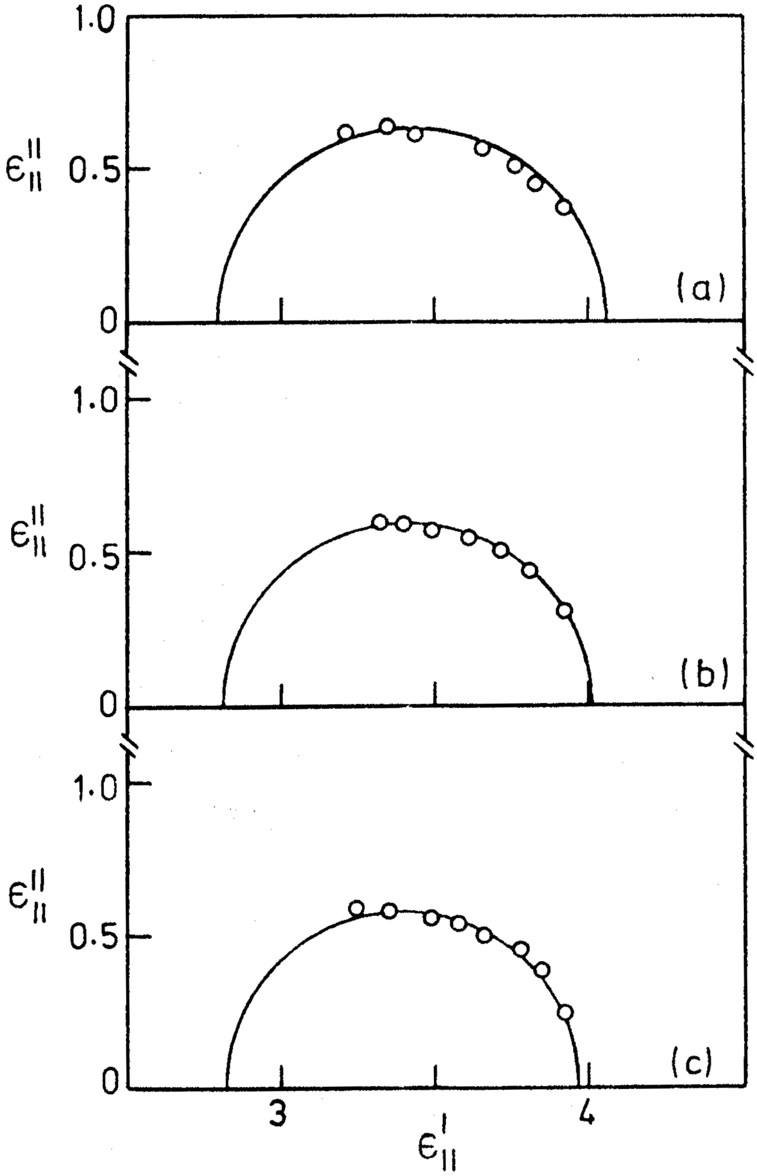

Figure 5.15

Cole-Cole plots for B9 OB at (a) 111.6 °C (b) 116.0 °C and (c) 118.1 °C.

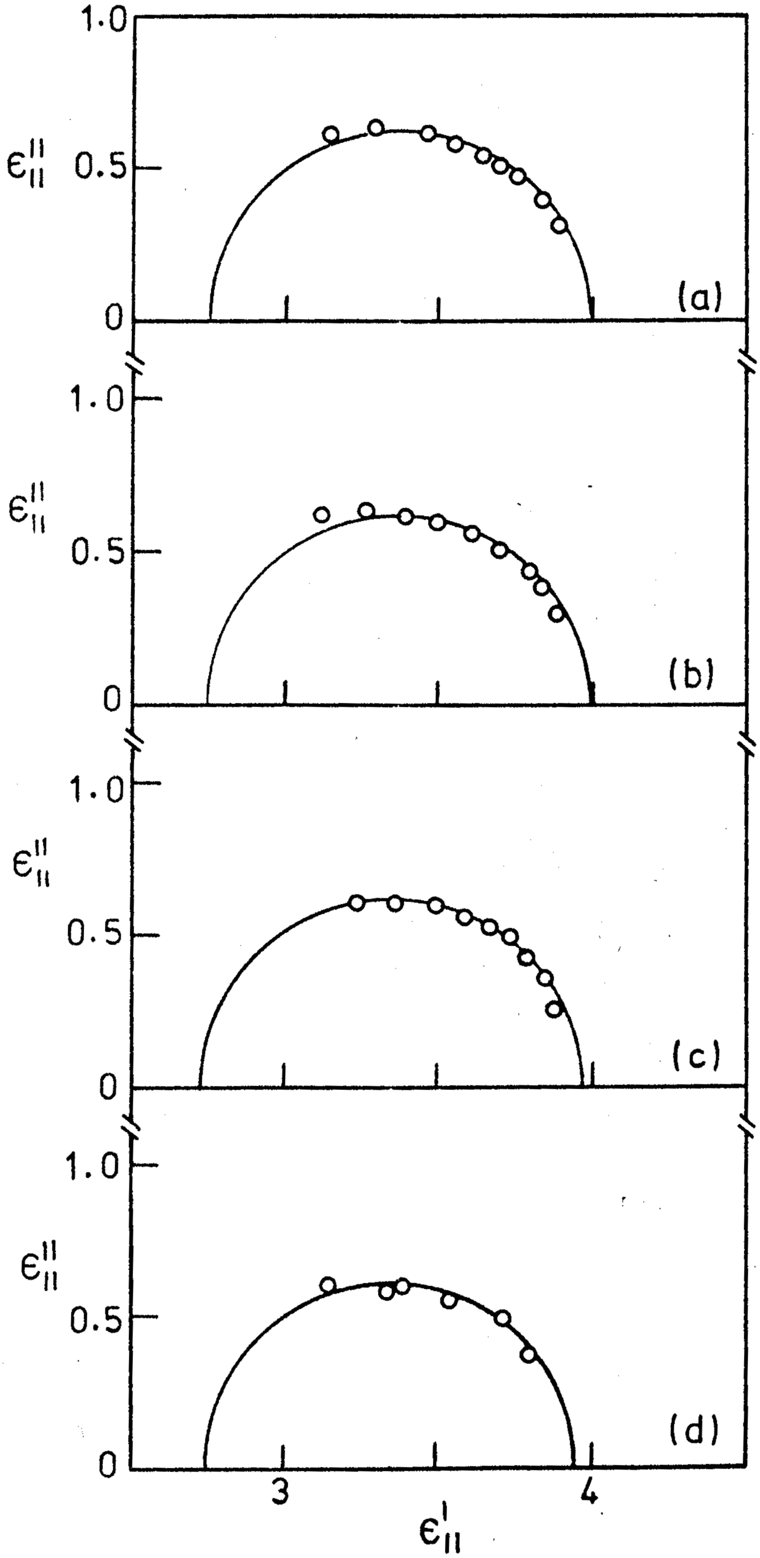

Figure 5.16

Cole–Cole plots for B10 OB at (a) 105.2 °C (b) 107.6 °C (a) 110.4 °C and (d) 113.6 °C relaxation time. We determined the relaxation frequency only in the supercooled region of the nematic phase since f_R at higher temperatures was beyond the frequency range of our experimental set up.

In all the compounds, the dielectric anisotropy shows a change in the sign and the frequency of dielectric isotropy f_0 is very close to f_R (see table 5.3). In figure 5.17 we have plotted log f_R and log f_0 taken at a common relative temperature of (T_{NI} - 2) °C and T_{NI} as functions of the number of carbon atoms in the alkoxy chain. All the three of them alternate in a similar fashion with increasing alkoxy chain length just as in nCB and n OMOPC.

In figures 5.18 and 5.19 we have plotted log f_R and log f_0 W functions of 1/T. For all the compounds both f_R and f_0 give the same value of W within the experimental error (see table 5.3). The

Table 5.3: The values of relaxation frequency (f_R), frequency of dielectric isotropy (f_0) and activation energy (W) for Bn CB (n = 7 - 10).

Compound	Temperature (°C)	f_R(MHz)	f_0(MHz)	W_{f_R}(eV)	W_{f_0}(eV)
B7 CB	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 CB	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 CB	111.6	5.0	4.5	0.718	0.736
	116.0	6.5	5.9		
	118.1	7.4	6.7		
B10 CB	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		

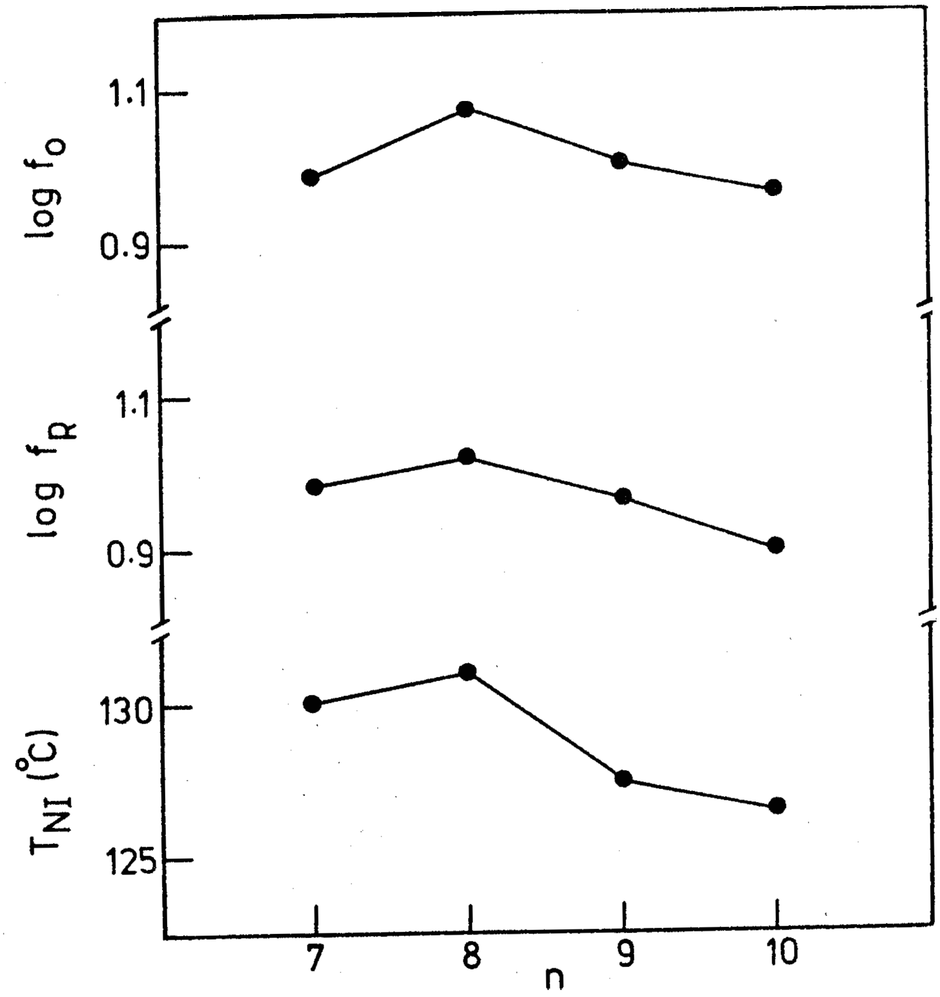

Figure 5.17

Log f_O 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 alkoxy chain of Bn OB.

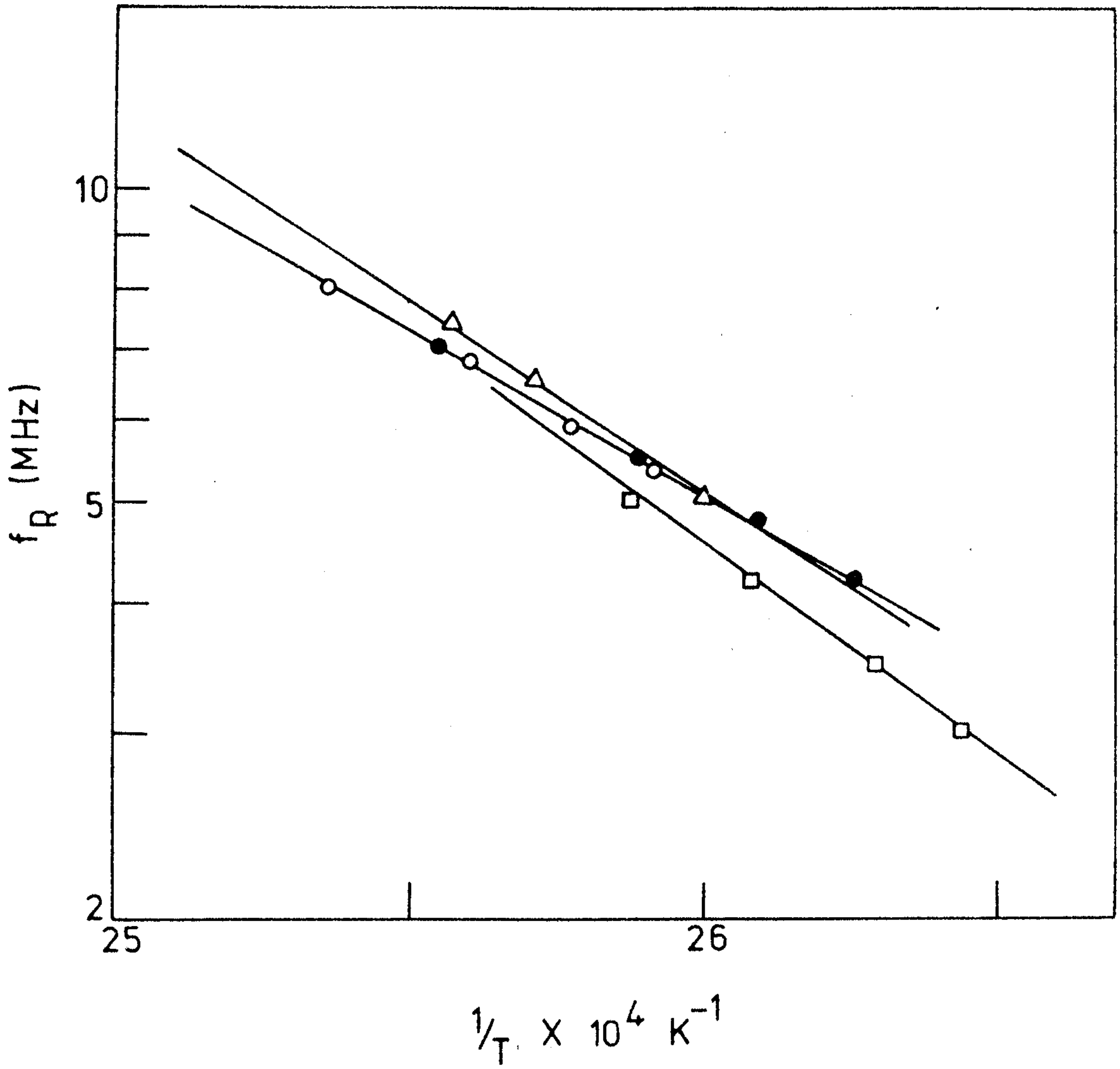

Figure 5.18

Log f_R as a function of 1/T for B7 OB (○), B8 OB (●), B9 OB (A) and B10 OB (□).

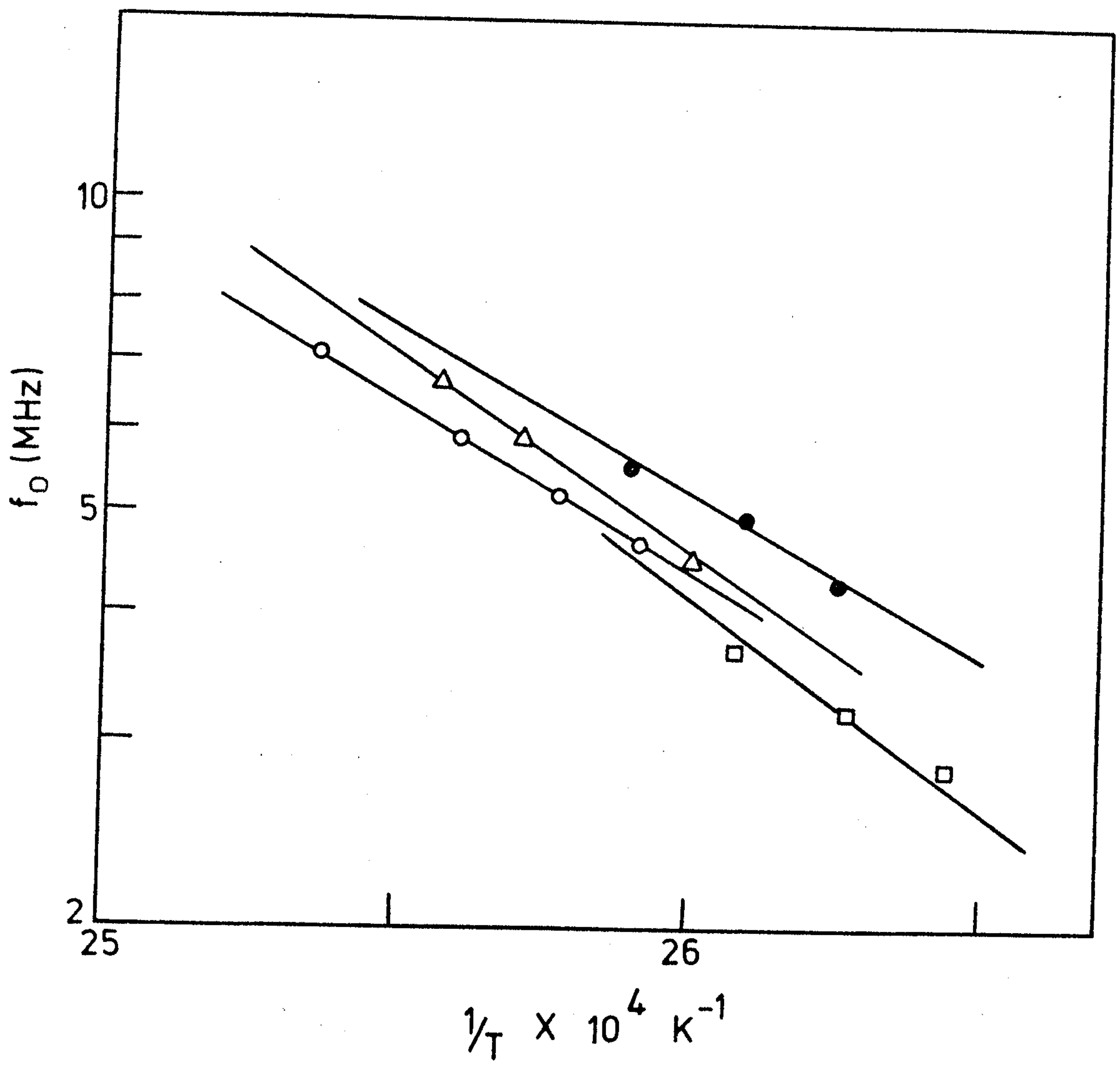

Figure 5.19

Log f_0 as a function of 1/T for B7 OB (○), B8 OB (●), B9 OB (A) end B10 OB (□).

value of W remains the same for heptyloxy and octyloxy derivatives but increases systematically for the nonyloxy and decyloxy derivatives. An increase of W may be expected for a compound which shows a smectic phase at a lower temperature, as has been observed in the case of 4,4'-di-n-alkoxy azoxybenzenes.[6] But this argument does not hold good for nCB and n OMCPC wherein no such increase in W is observed with the occurrence of the smectic phase. Neither does it hold good in the present case, viz., Bn OB for no increase is observed on going from the heptyloxy to the octyloxy derivative, even though the latter shows an additional monotropic smectic A phase. Thus the precise relationship between the activation energy and the chain length is yet to be explained in detail.

References

1. B.K. Sadashiva and G.S.R. Subba Rao, Curr. Sci., 44, 222 (1975).

   Subsequent to this note ths authors have submitted a more detailed paper to Mol. Cryst. Liquid Cryst. giving the thermodynamic data calculated from differential scanning calorimetry (Perkin-Elmer 2B) experiments.

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