CHAPTER III

DIELECTRIC PROPERTIES OF 4'-n-ALKYL 4-CYANOBIPHENYLS

Introduction

There has been a number of studies of the dielectric properties of nematic liquid crystals. Maier and Meier[1] were the first to measure the principal dielectric constants of di-alkoxy substituted azo- and azoxybenzenes. A systematic study of the di-alkyl substituted azo- and azoxybenzenes was carried out by de Jeu and Lathouwers[2] to evaluate the influence of the molecular structure on the dielectric properties. The molecules of a liquid crystal usually consist of at least two benzene rings that are bridged by rigid groups like CH=N, N=N, N=NO, etc., The effect of these bridging groups on the dielectric properties was also studied by de Jeu and Lathouwers.[3] All these measurements are on nematics with relatively small dielectric anisotropy.

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[4] which resulted in the development of a new type of electrooptic device.[5,6] Liquid crystals with large positive dielectric anisotropy are obtained by incorporating a strong dipole moment along the long molecular axis, e.g., the presence of a $C\equiv N$ as an end group contributes 4.05 debye[7] to the parallel component of the dipole moment of the molecule. Large negative dielectric anisotropies[8] can be obtained by introducing the cyano group in a lateral position. The principal dielectric constants of some strongly positive cyano compounds were first measured by Schadt.[9] Titov et al.[10] have recently synthesized a number of 4-substituted benzonitriles and cinnamonitriles and measured $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in some representative compounds. A systematic study of different members of a homologous series of strongly polar molecules was carried out for the first time by us.

There have also been a number of experimental studies of the low frequency dispersion of $\varepsilon_{\parallel}$. Maier and Meier[11] were the first to experimentally find out the relaxation region of $\varepsilon_{\parallel}$. From their measurements on 4,4'-di-n-alkoxyazoxybenzenes they showed that in the radio frequency region $\varepsilon_{\parallel}$ is frequency dependent whereas $\varepsilon_{\perp}$ remains constant. Later Weise and Axmann[12,13] measured the dielectric dispersion of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ as well as ε_{is} for the same compounds in the microwave frequency region. They calculated the polarizability, dipole moment and retardation factor for these compounds. A systematic investigation of the low frequency dielectric relaxation of $\varepsilon_{\parallel}$ in different members of the homologous series 4,4'-di-n-alkoxyazoxybenzenes was again carried out recently by Mircea-Roussel and Rondelez.[14] They measured the activation energy of these compounds and found that it is greater for a compound having a smectic phase at lower temperatures. We will be discussing their results in detail later.

Rondeles and Mircea-Roussel[15] have also measured the dielectric relaxation of p-methoxy benzylidene p'-n-butyalaniline (MBBA). The dielectric properties of low positive 5-n-hexyl-2-[4-n-alkyloxy-phenyl]-pyrimidines were measured by Kresse et al.[16] For all these compounds the relaxation frequency was in the MHz region. Relaxation in the KHz region has been observed in some phenyl benzoates[17] and a mixture of p-substituted benzylidene p'-cyanoaniline.[9] Measurements on the latter compound was the first to be made on nematics with strong positive dielectric anisotropy. The other measurements on strongly positive compounds are the one by Cummins et al.[18] on 4'-n-pentyl 4-cyanobiphenyl and the other by Davies et al.[19] on 4'-n-heptyl 4-cyanobiphenyl. Later we will be comparing their results with ours.

We have undertaken a systematic study of the static dielectric constants and the low frequency dispersion of $\varepsilon_{\parallel}$ in the nematic phase of four successive members of 4'-n-alkyl 4-cyanobiphenyls. These compounds were first synthesised by Gray et al.[20] Their structural formula is given in figure 3.1. Because of the cyano end group they exhibit a large value of $\varepsilon_{\parallel}$ and consequently a large positive dielectric anisotropy. They are highly suited for display devices since they have low melting points, are colourless, chemically and photochemically stable.

Experimental

(a) Materials

We have studied the pentyl to octyl derivatives of 4'-n-alkyl 4-cyanobiphenyl. For convenience let us call them nCB (n = 5-8). Of these the first three

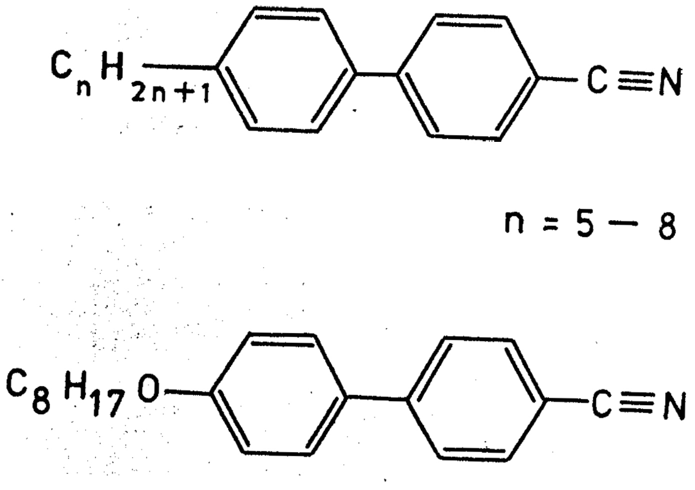

Figure 3.1

Structural formulae of 4'-n-alkyl 4-cyanobiphenyls (nCB, n = 5–8) and 4'-n-octyloxy 4-cyanobiphenyl (8 OCB).

are room temperature nematics and 8CB is a room temperature smectic A. Their transition temperatures are listed in table 3.1. The 5CB, 6CB and 7CB used in our measurements were synthesized in our chemistry laboratory and 8CB was obtained from BDH, England. Their transition temperatures agreed with those reported by Gray et al., except in the case of 6CB for which our value of T_{NI} was 2°C higher.

(b) Dielectric cell

The dielectric constants were evaluated by measuring the capacitances of a parallel plate capacitor without and with the sample. A schematic diagram of the dielectric cell is given in figure 3.2a. The cell consisted of two tin-oxide coated glass plates which served as electrodes. The separation between them was fixed by two narrow strips of mylar. The conductive coating in the area over which the mylar spacers are placed was removed to eliminate the

Table 3.1: Transition temperatures of 4'-n-alkyl 4-cyanobiphenyls (nCB, n = 5-8) and 4'-n-octyloxy 4-cyanobiphenyl (8 OCB)

Compound	Temperature of transition to		
	Smectic (°C)	Nematic (°C)	Isotropic (°C)
5CB	-	22.5	35.0
6CB	-	13.5	29.0
7CB	-	28.5	42.0
8CB	21.0	32.5	40.4
8 OCB	54.5	67.0	80.5

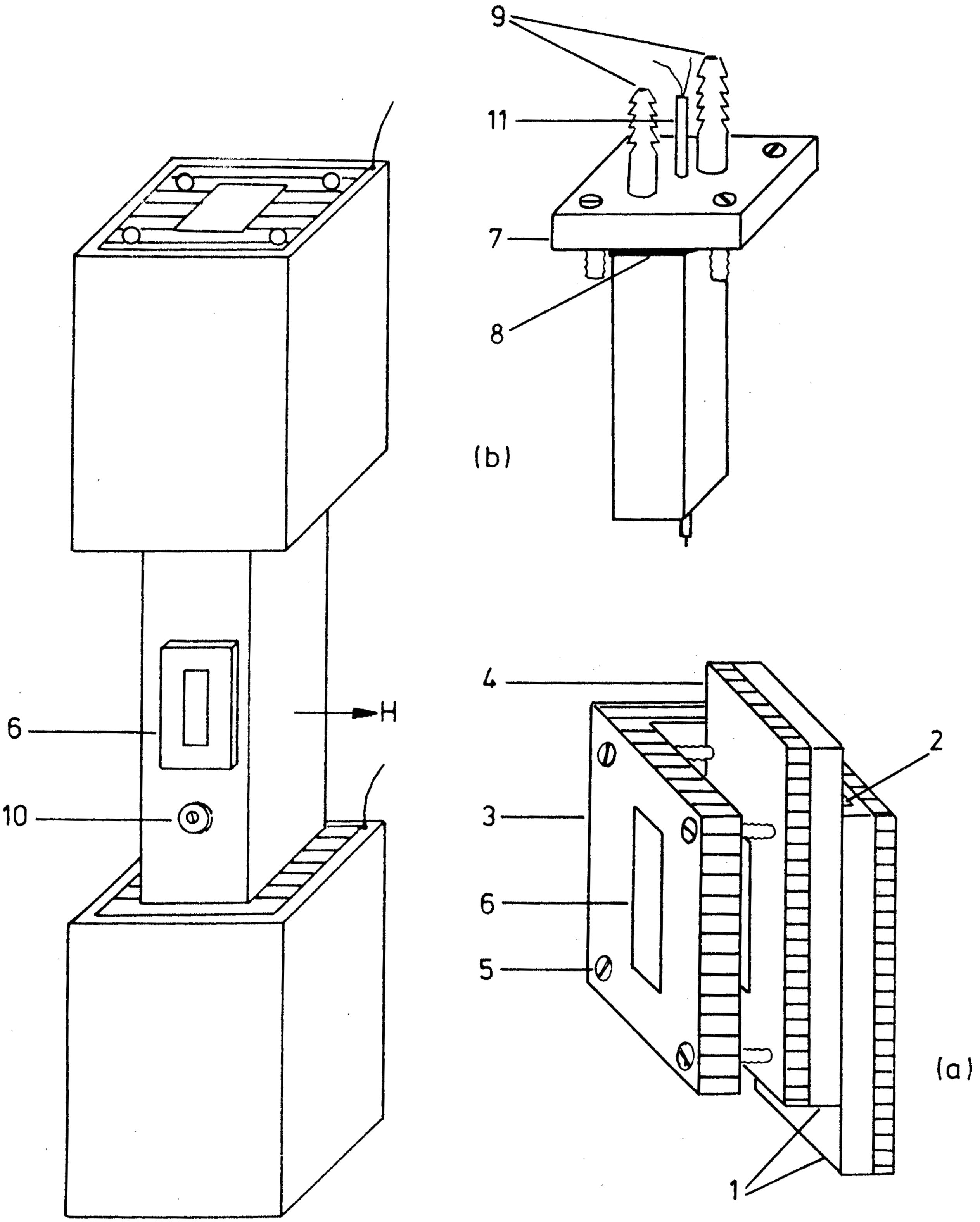

Figure 3.2

Schematic diagram of (a) dielectric cell and (b) heater.
1. Electrodes 2. Bevel 3. Copper clamp 4. Copper plate
5. Brass screws 6. Windows 7. Copper cap 8. Neoprene gasket
9. Nozzles 10. Brass nuts with pyrophilite bushes 11. Chromel-alumel thermocouple. H represents the direction of the magnetic field for $\varepsilon_{\perp}$-measurements.

contribution of the mylar to the capacitance of the cell. A bevel made on the shorter side of one of the plates was useful in filling the sample. The plates were offset along the length and the area jetting out was used to make the electrical contacts. The active area of the electrodes was 1 sq. cm. The electrode assembly was held rigidly in a copper frame shaped like a rectangular G clamp. A flat copper plate was used to cover the glass plates to avoid uneven pressing by the brass screws. The rectangular slots made in the copper plate and the frame served as observation windows.

(c) Heater

A schematic diagram of the heater used is shown in figure 3.2b. It consisted of a long rectangular copper tube. A thin sheet of mica was stuck over the surface of the tube so that nichrome wire could be wound over it. Asbestos sheet covering on the outside provided good thermal insulation. The length of the heater was deliberately made very large compared to the size of the dielectric cell to ensure that there are no temperature gradients in the sample. Its cross-sectional size in the central portion was minimized in order do obtain as high a magnetic field as possible. It was made sure that the dielectric cell when introduced into the heater from the top was always positioned at the centre of the heater. Two rectangular glass windows were provided in the heater which matched with the windows in the cell. The heater was sealed by the neoprene gasket in the copper cap. Before tha commencement of any experiment the heater was flushed with dry nitrogen for a long time through a pair of nozzles in order to prevent oxidation and hence deterioration of the sample.

Two brass nuts were fixed in the body of the heater, on the sides with windows. These were insulated from the heater by pyrophilite bushes. Two screws with springs mounted on the inner end could be made to move forward or backward in the nuts in order to make or break contact with the electrodes. The brass nuts were connected to the measuring bridge via two copper leads fixed rigidly on a wooden base.

(d) Temperature control and measurement

The electrical power to the heater was supplied by two stabilised d.c. power supplies (60 V and 5 A each). A rheostat in series with the nichrome winding was used for finer variations in temperature. The temperature of the sample could be controlled and maintained to better than 0.1°C over 4-5 hours. Such high thermal stability over long periods was especially necessary while measuring the frequency dependence of $\varepsilon_{\parallel}$.

A chromel-alumel thermocouple previously calibrated with respect to a standard thermometer was used to probe the temperature of the sample. Using similar probes at various positions inside the heater it was ascertained that the sample did not experience any temperature gradients. The temperature of the sample was measured to an accuracy of 0.025°C using a vernier potentiometer (OSAW-30071) and a multireflex galvanometer (OSAW-30274).

(c) Sample alignment

It is obvious from the definition of the principal dielectric constants in a nematic that the sample should be aligned homeotropically ($E \parallel \underline{n}$) for the measurement of $\varepsilon_{\parallel}$ while a homogeneous alignment ($E \perp \underline{n}$) is necessary for measuring $\varepsilon_{\perp}$.

The most common method of aligning the sample is the use of strong magnetic fields (H). Since nematics are diamagnetic with a positive anisotropy $\sim 10^7$ c.g.s. units, the molecules always align parallel to H. As a result the values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ can be determined by applying H parallel and perpendicular respectively to the measuring field E. In the absence of the magnetic field the dielectric constant has a value between the two principal dielectric constants. As H is increased continuously the measured values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ change until a saturation is reached. Once the saturation is attained any further increase in the magnetic field will not influence the value of the dielectric constants. The measurements are always carried out in this saturation region.

As the alignment of liquid crystals ore known to be strongly influenced by surface conditions, the electrodes were carefully selected and assidiously cleaned first with a detergent (Teepol, BDH Ltd.) and then with freshly prepared chromic acid. Both homeotropic and homogeneous alignments were achieved by applying a magnetic field of 17 kGauss which was more than twice the saturation field for the thickness of the sample used (25–50 μm). The homeotropic alignment was relatively easier since the molecules of nCB have a tendency to orient normal to the surface. The alignments in the smectic A phase were obtained by slowly cooling the well aligned nematic in the presence of the magnetic field. The magnetic field obtained by an electromagnet (BDS Electronics, Bangalore) with 25 mm tapered pole pieces was measured using a fluxmeter (Bell, USA). In figure 3.2b we have shown the position of the heater with respect to H for $\varepsilon_{\perp}$-measurements. In this case the alignment of the sample could be checked directly between crossed polaroids. For measuring $\varepsilon_{\parallel}$ the heater was turned through 90°. In this position we used two small mirrors fixed at 45° to the windows to check the alignment.

(f) Measurement of static dielectric constants

A GR1656 impedance bridge was used to measure the static dielectric constants. The capacitances were measured at 1 KHz to an accuracy of 0.1%. This frequency was high enough to avoid interfacial polarization effects at the electrodes.[21] The measured capacitance was always corrected for the lead capacitance. The bridge voltage across the sample was very low (~ 300 mV) and did not have any disturbing influence on the sample. The resistivities of the samples used were measured using the same bridge. They were quite high, of tho order of $10^{9}-10^{10}$ ohm-cm. Thus problems like heating of the sample did not arise.

The relative variation of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ could be determined to an accuracy of 0.1%. The value of the dielectric constant in the isotropic phase obtained independently from the two geometries matched to within 1%. The experimental set up was initially used to measure the dielectric constant of standard liquids like toluene and chlorobenzene. The value obtained for these liquids always agreed within 2% of the standard value which is therefore reckoned to be the absolute accuracy of our measurements.

((i) Measurement of tho dielectric relaxation of $\epsilon_{\parallel}$

We have measured the low frequency relaxation of $\epsilon_{\parallel}$ in 5CB-8CB. The experimental set up and the methods adopted to obtain homogeneous and homeotropic alignments were the same as those used in the static measurements. However the tin-oxide coated plates could not be used because of the high losses involved. Instead aluminium coated glass plates were used. The plates were thoroughly cleaned with Teepol and chromic acid and then vacuum coated with a thin layer of 99.99% pure aluminium. These plates were not optically transparent and therefore it was not possible to visually check the alignment. However a preknowledge of the value of the static dielectric constants helped us in ascertaining the perfectness of the alignment.

The dispersion was measured in the frequency range of 400 KHz-10 MHz using a GR 1606B RF bridge. A signal generator (Radart 923A) served as the source while a 15 MHz oscilloscope (Philips PM 3231) served as the detector. One of the electrode terminals was earthed and the other was connected to the lead from the unknown terminal of the bridge. The reactance (X_m) and resistance (R_m) as measured on the bridge were corrected for the lead capacitance to get the true values, X_x and R_x of the sample. If X_a is the reactance of the lead then

$$X_x = \frac{X_m - \frac{R_m^2}{X_a} - \frac{X_m^2}{X_a}}{(1 - \frac{X_m}{X_a})^2 + (\frac{R_m}{X_a})^2}$$

and

$$R_x = \frac{R_m}{\left(1 - \frac{X_m}{X_a}\right)^2 + \left(\frac{R_m}{X_a}\right)^2}$$

Using these relations the dielectric constant (ε') as well as the dielectric loss (ε'') of the sample were calculated. The measured reactance was corrected for the series inductance

For each compound the real and imaginary parts of both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured at 4-5 temperatures in the nematic phase. As expected $\varepsilon'_{\parallel}$ showed a dispersion in the frequency range covered while $\varepsilon'_{\perp}$ remained constant. However was not zero due to non-zero ionic conductivity. This value of $\varepsilon''_{\perp}$ was used to correct the $\varepsilon''_{\parallel}$ value as suggested by Rondelez and Mircea-Roussel.[15]

The maximum error in the measurement is estimated to be 3% for the dielectric constant and 7% for the dielectric loss. The relaxation frequency and the activation energy could be determined to an accuracy of 2-3%.

Results and Discussion

A. Static dielectric constants

The temperature variation of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{is} for 5CB are shown in figure 3.3. With increase of temperature $\varepsilon_{\parallel}$ decreases continuously while $\varepsilon_{\perp}$ increases. At T_{NI} they both change abruptly signifying a first order phase transition. Similar curves were obtained for 6CB and 7CB also (figures 3.4 and 3.5). In case of 7CB, measurements were carried out; in the supercooled region of the nematic phase also. No change in the trends of the curves were observed in this region. In figure 3.6 the principal dielectric constants of 8CB are shown as functions of temperature in both the smectic and nematic phases. Experiments were also conducted on 4'-n-octyloxy 4-cyanobiphenyl (8 OCB) in order to study the effect of changing the end group from alkyl to alkoxy. The results on this compound are shown in figure 3.7.

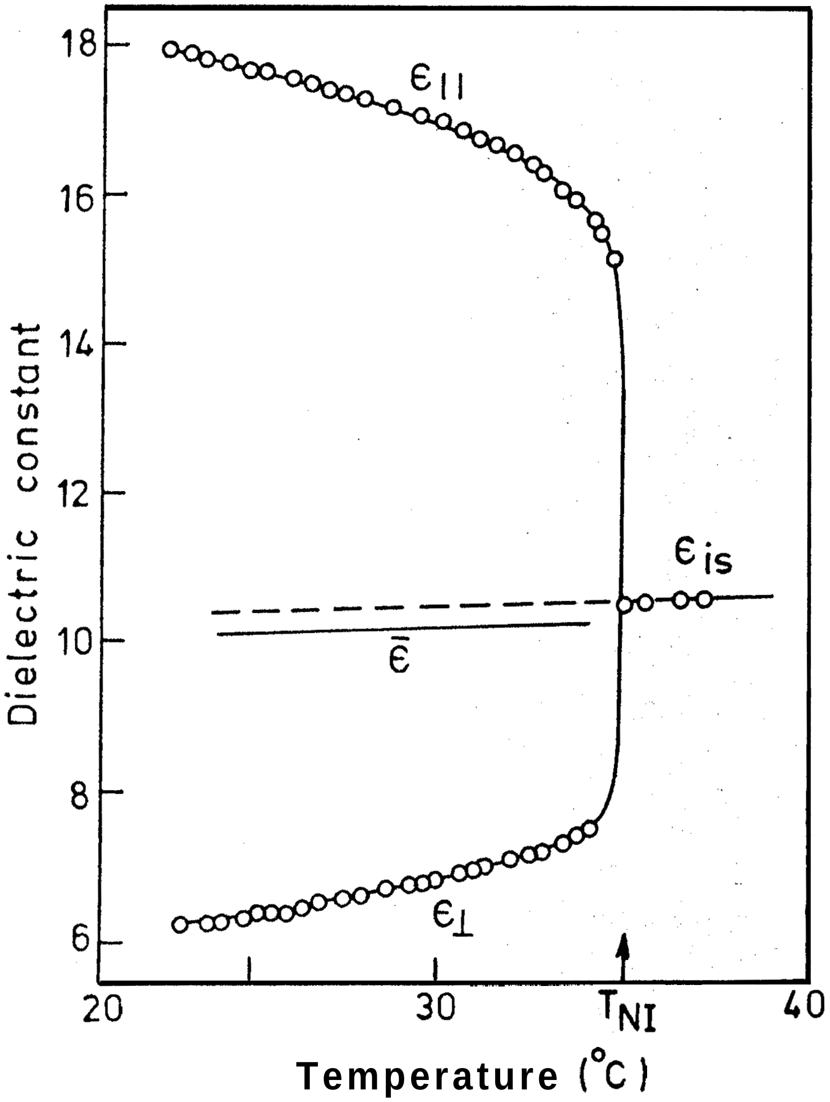

Figure 3.3

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} in the nematic phase. (Nematic-isotropic transition temperature T_{NI} = 35°C).

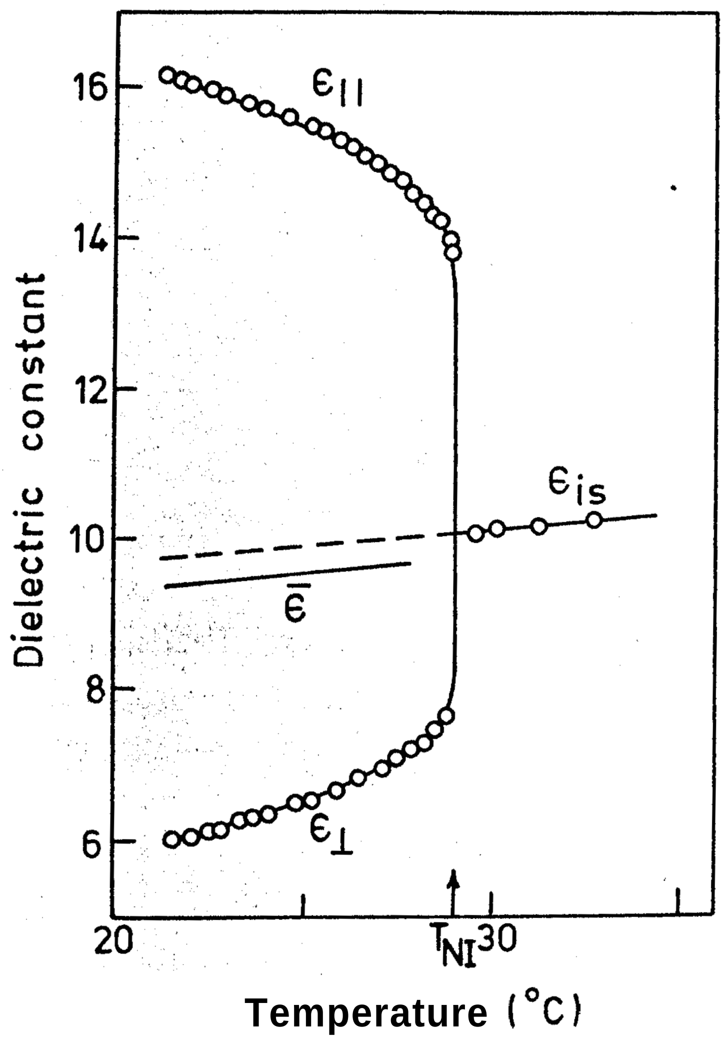

Figure 3.4

Principal dielectric constants of 6CB. (T_{NI} = 29°C).

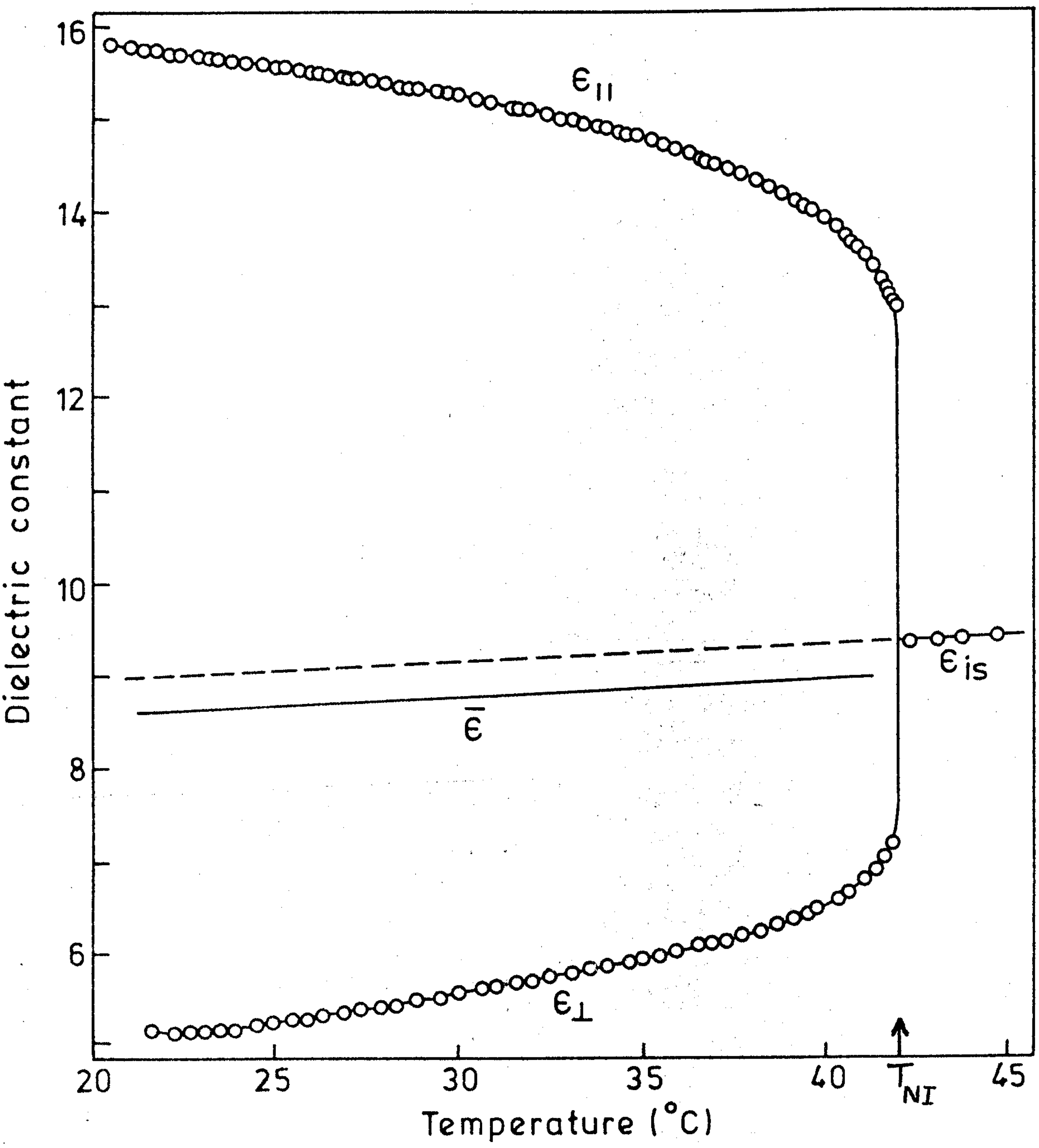

Figure 3.5

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

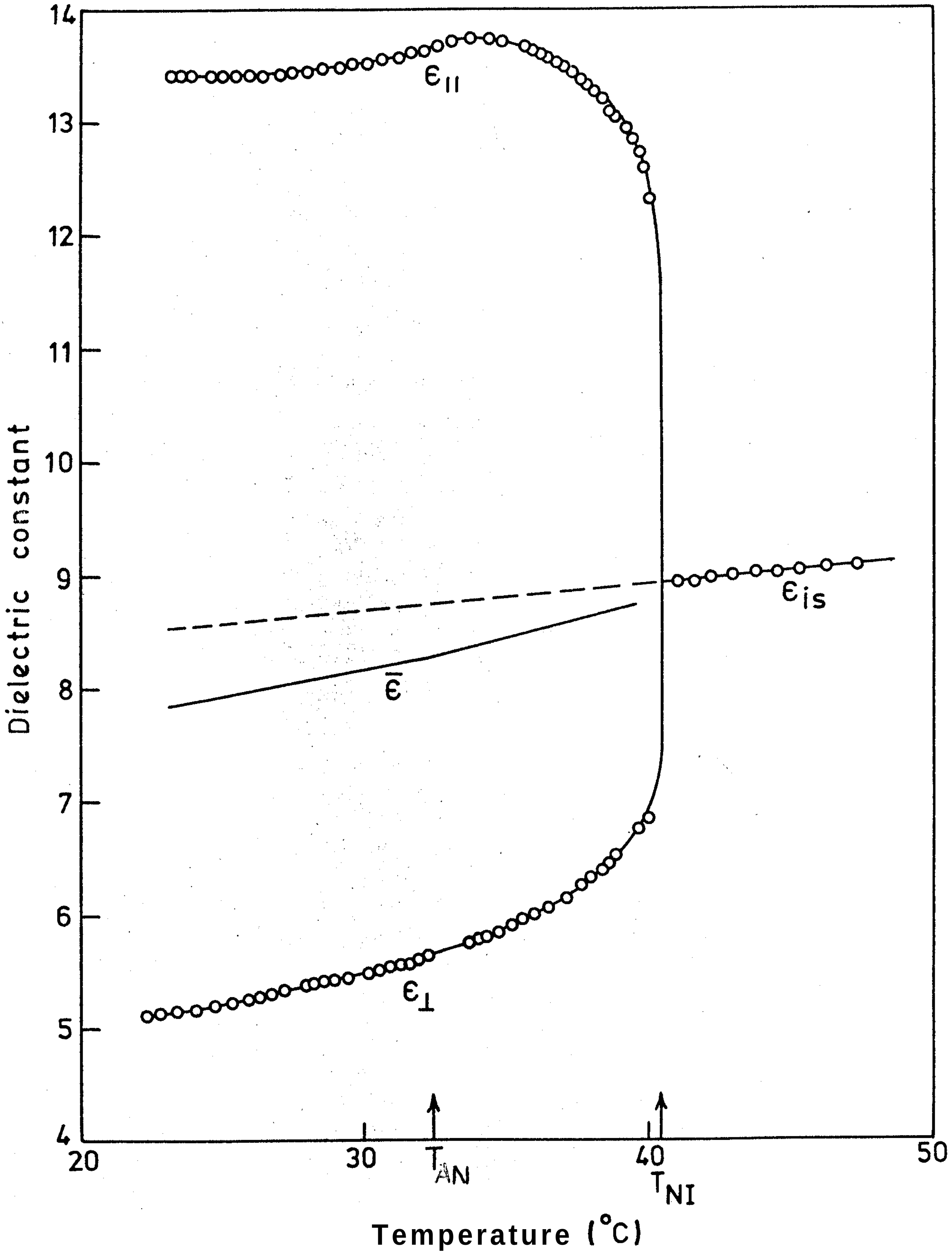

Figure 3.6

Principal dielectric constants of 8Q3 (smectic A–nematic transition temperature $T_{AN} = 32.5°C$, $T_{NI} = 40.4°C$).

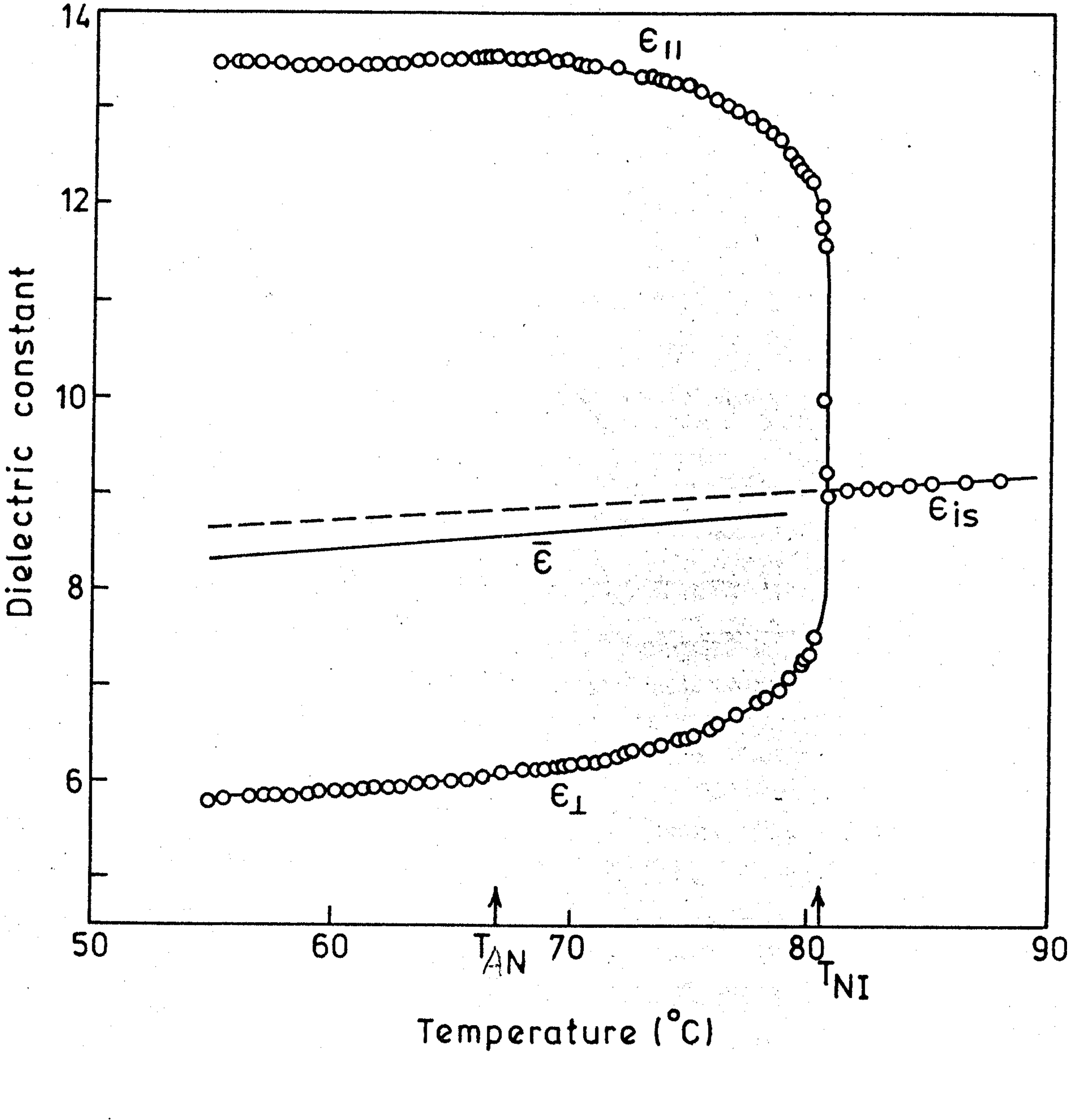

Figure 3.7

Principal dielectric constants of 8 OCB. (T_{AN} = 67 °C, T_{NI} = 80.5 °C)

In all these figures we have shown the mean dielectric constant $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ calculated from the measured values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. $\bar{\varepsilon}$ very near T_{NI} is not shown because of the decreased accuracy in the measurements of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in this region. We notice that in all cases $\bar{\varepsilon}$ is, throughout the nematic phase, less than the extrapolated isotropic value, the difference being $\sim 4\%$. A similar difference has been observed by Schadt[9] in the case of p-substituted benzylidene p'-cyanoanilines. This is in contrast to the behaviour of nonpolar molecules[2] wherein it has been observed that $\bar{\varepsilon}$ and ε_{is} coincide at T_{NI}.

The increase in $\bar{\varepsilon}$ at T_{NI} can be understood on the basis of the theory of antiferroelectric short range order discussed in chapter II. The theory is applicable to nematics composed of strongly polar molecules like nCB. In such compounds there will be a greater tendency for the nearest neighbours to assume an antiparallel orientation. This —tiparallel correlation is greater in the nematic phase than in the isotropic phase resulting in an increase of $\bar{\varepsilon}$ on going over from the nematic to the isotropic phase.

In fact the presence of such antiparallel local ordering has been confirmed by X-ray studies[22] on 5CB and 7CB. It was found that the meridional reflections correspond to a repeat distance of about 1.4 times the molecular length. This indicates that there is a smectic A type of short range order in the medium wherein each layer is made up of two molecules antiparallel to each other, probably with their polar ends interdigitated. A possible configuration is shown in figure 3.8.

An increase in $\bar{\varepsilon}$ on going from the nematic to the isotropic phase has been observed in some materials of negative dielectric anisotropy also. It was first

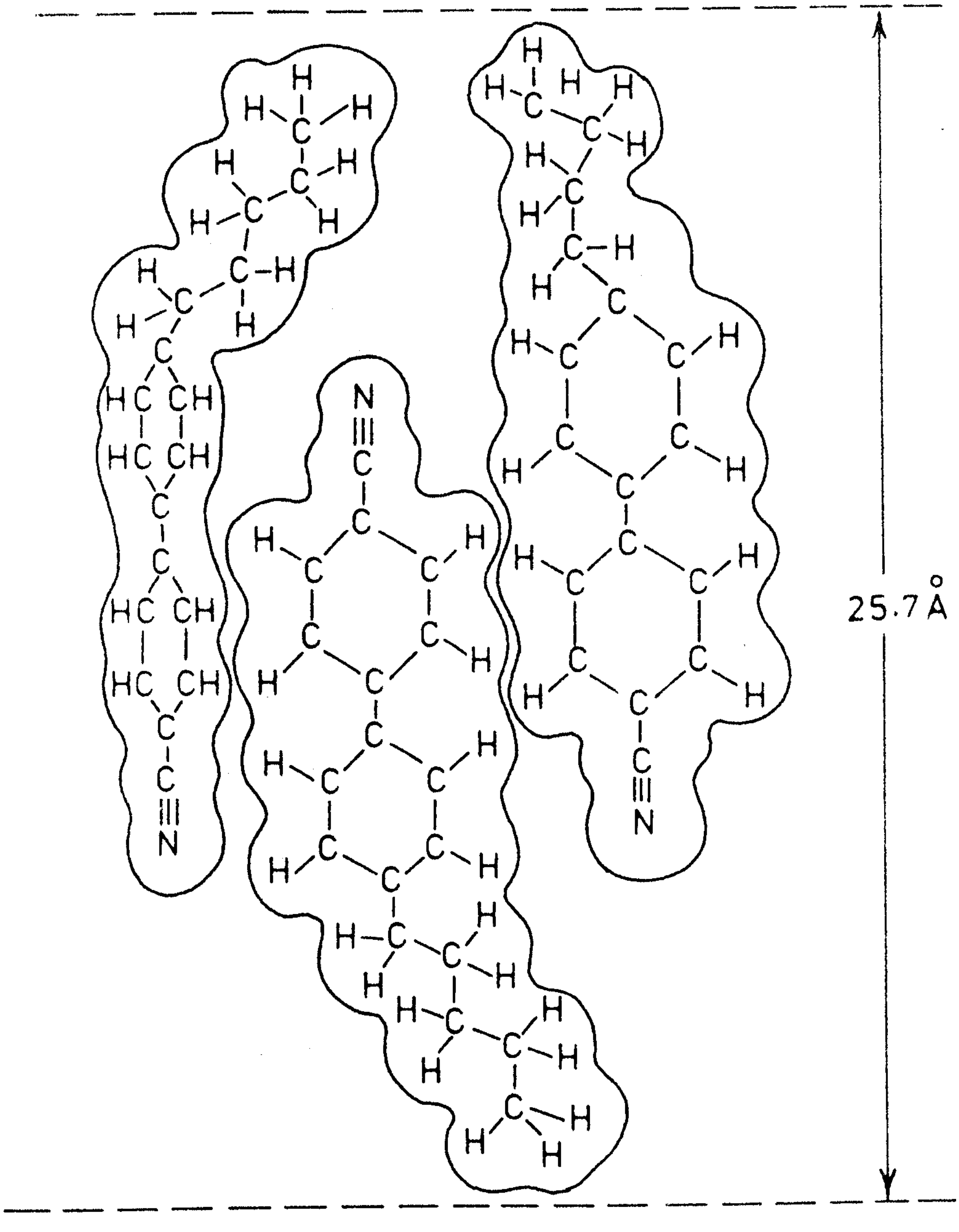

Figure 3.8

Schematic representation of antiparallel local order in 5CB. The repeat distance along the nematic axis is about 1.4 times the molecular length. (After Leadbetter, Richardson and Colling[22]).

observed in PAA by Maier and Meier[1] which they could not account for in their theory (see chapter II). Dershanski and Petrov[23] suggested that the difference between $\bar{\varepsilon}$ and ε_{is} may be due to a second order piezoelectric effect which diminishes the polarizability. However this can now be explained as due to an antiparallel correlation between the longitudinal components of the dipole moments of the neighbouring molecules. As far as the transverse components are concerned, there will not be, on the average, any orientation correlation because of the cylindrically symmetric distribution about the optic axis.

Further we notice that for all the compounds $\bar{\varepsilon}$ decreases with decrease of temperature, as a result of the increase in antiparallel order at lower temperatures. In the case of 5CB, 6CB and 7CB the difference between $\bar{\varepsilon}$ and the extrapolated ε_{is} remains the same throughout the nematic range. On the other hand, for

8CB and 8 OCB this difference increases with decrease of temperature obviously due to the presence of a smectic phase at lower temperatures.

Another interesting point observed in these strongly positive compounds is that the isotropic value increases with increase of temperature, evidently due to a decrease in the local order. Indeed X-ray data[22] reveal that there is considerable local order in the isotropic phase of nCB.

In table 3.2 we have given $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as well as $\Delta\varepsilon$ at a common relative temperature of $(T_{NI} - 1)$ °C. We notice that for all the compounds $\varepsilon_{\parallel} \simeq 2\varepsilon_{\perp}$ Further both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ decrease with increasing alkyl chain length. It was suggested

Table 3.2: Principal dielectric constants and dielectric anisotropy of 5CB–8CB and 8 OCB 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
8 OCB	12.35	7.20	5.15

by Schadt[9] that this may be partly due to the decrease in the molecular density. According to the density data available the decrease in density with increasing length is less 1%. This is too low to account for the 5–8% change in $\epsilon_{\parallel}$ and $\epsilon_{\perp}$.

T_{NI} and a number of other physical properties show a pronounced alternation as the homologous series is ascended. A detailed statistical thermodynamic treatment of this odd-even effect has been given by Marcelja.[24] In the case of nCB the even-numbered carbon atom in the alkyl chain makes a large angle with the long axis of the molecule while the odd-numbered carbon atom is along the long molecular axis.

Thus the polarisability anisotropy ($\triangle\alpha$), T_{NI} and the order parameter (s) are lowered in even members of the series while they are enhanced in the odd members. Such an alternation in the order parameter[25] though not very pronounced is observed in 5CB-7CB. But there is an increase in s between 7CB and 8CB. although T_{NI} decreases between them. This increase in s is attributed to an increased near neighbour correlation and the presence of smectic A phase at lower temperatures.

According to the theory of Maier and Meier discussed in chapter II, $\triangle\varepsilon$ has contributions from $\triangle\alpha$ and μ (see equation 2.16). For a molecule with zero dipole moment $\triangle\varepsilon$ is directly proportional to $\triangle\alpha$. Since $\triangle\alpha$ alternates we expect $\triangle\varepsilon$ also to alternate as is indeed observed in 4,4'-di-n-alkyl azobenzenes.[2] A similar alternation in $\triangle\varepsilon$ is also exhibited[2] by weakly positive as well as negative compounds. However $\triangle\varepsilon$ shows only a continuous decrease with increasing alkyl chain length in strongly polar nCB (see figure 3.9). This may be partly due to the fact that an increase in the order parameter increases the effect of antiparallel correlation which as discussed earlier results in a diminution of the dielectric anisotropy.

In figure 3.1 we have given the chemical structure of 8 OCB also. The only difference between 8CB and 8 OCB is that the octyl group in 8CB has been replaced by an octyloxy group in 8 OCB. The dipole moment of 8CB has contributions from C≡N and the octyl group, both acting along the line joining the centres of the two benzene rings in the same direction. Then the dipole moment has practically no perpendicular component. But in 8 OCB the octyloxy group has a perpendicular component of ~ 1.2 Debye. This results in an increase in the value of $\varepsilon_{\perp}$ and hence $\Delta\varepsilon$ of 8 OCB is less than that of 8CB (see table 3.2).

We shall now discuss the behaviour of the

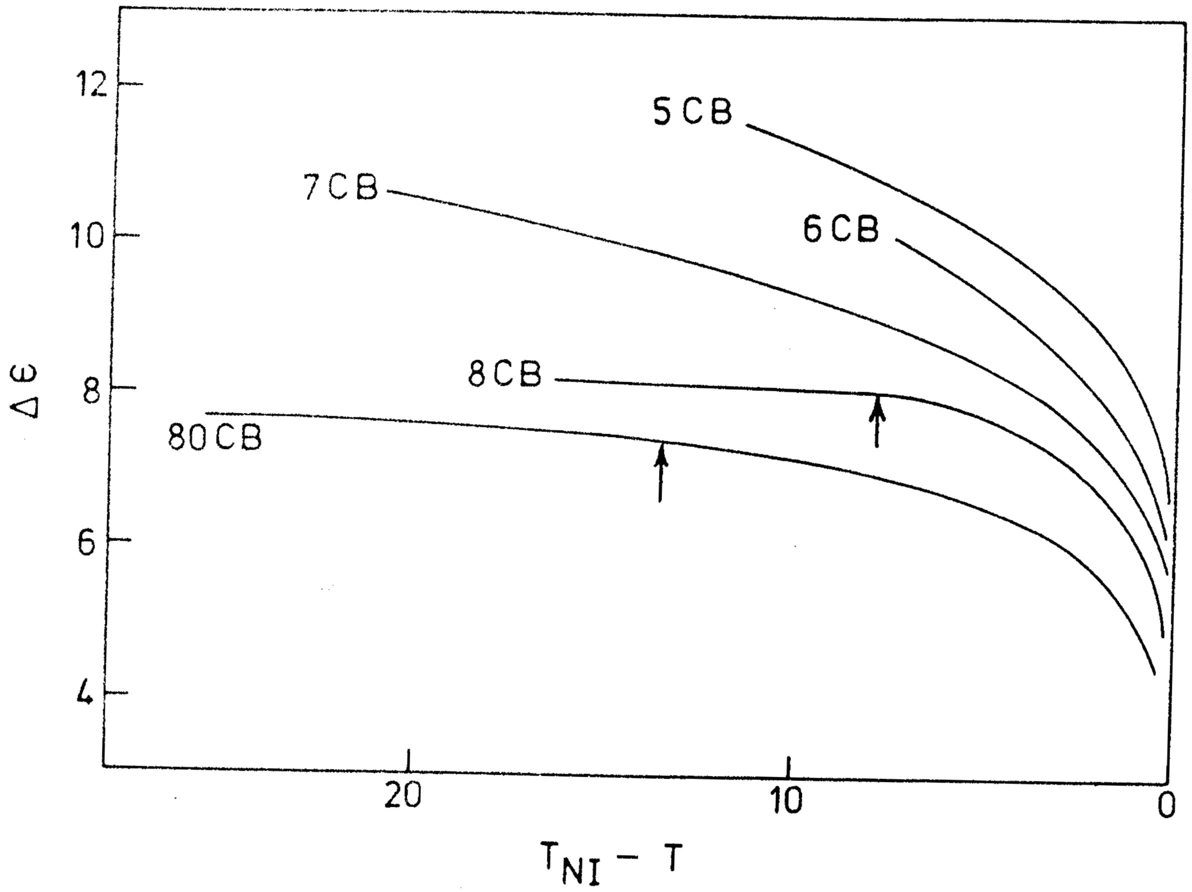

Figure 3.9

Dielectric anisotropy (Ae) of nCB and 8 OCB as functions of T_{NI} - T. The arrow indicates T_{AN}.

dielectric constants near T_{AN} in 8CB and 8 OCB. In the nematic phase $\varepsilon_{\parallel}$ shows the normal increase with decrease of temperature. However in the smectic phase it decreases with temperature near T_{AN} and remains constant at lower temperatures. On the other hand, $\varepsilon_{\perp}$ decreases continuously in both the nematic and smectic phases. The decrease in $\varepsilon_{\parallel}$ in the smectic A phase near T_{AN} is more prominent in 8CB than in 8 OCB (see figures 3.6 and 3.7). However this decrease is not reflected in the behaviour of A (see figure 3.9).

de Jeu et al.[26,27] have measured the dielectric constants in the smectic A phase of 4,4'-di-n-alkyl azoxybenzenes (hexyl to octyl). They observed that in the nematic phase $\varepsilon_{\parallel}$ decreases and $\varepsilon_{\perp}$ increases as T_{AN} is approached leading to a change in the sign of $\Delta\varepsilon$ at $T < T_{AN}$. This was explained as due to the increase in the dipolar correlation between neighbouring molecules in the smectic layer.

It may be relevant to mention here that the temperature dependence of the ratio of the principal electrical conductivities $\sigma_{\parallel}/\sigma_{\perp}$ of 4,4'-di-n-heptylazoxybenzene[28] is rather similar to the curve for $\varepsilon_{\parallel}$ in that it decreases fairly rapidly with decrease of temperature. On the other hand, $\sigma_{\parallel}/\sigma_{\perp}$ for 8CB and 8 OCB[28] shows a small decrease in the smectic phase very near T_{AN} and remains constant at lower temperatures

B. Dielectric dispersion

The dielectric dispersion was measured in the 0.1-10 MHz range. In figures 3.10-3.13 we have plotted the dielectric loss ($\varepsilon''_{\parallel}$) as a function of frequency at different temperatures for 5CB-8CB. For all the compounds, the maximum of $\varepsilon''_{\parallel}$ decreases with increase of temperature while the relaxation frequency (f_R) given by the maximum value of $\varepsilon''_{\parallel}$ increases. The values of f_R at different temperatures are given in table 3.3.

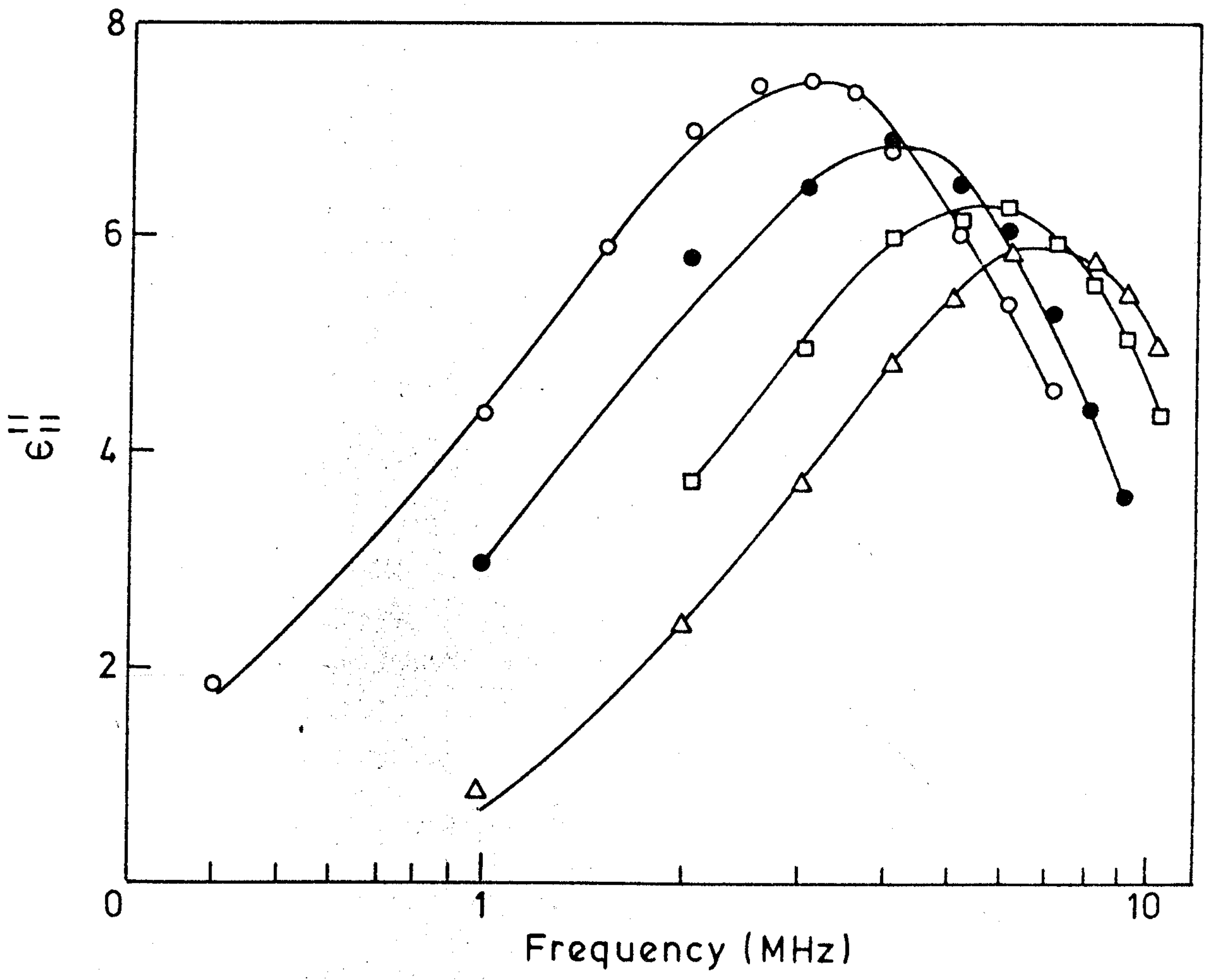

Figure 3.10

Dielectric loss ($\varepsilon''_{\parallel}$) as a function of frequency for 5CB at temperatures 19.5 °C(○), 24.0 °C (e), 28.0 °C (□) and 31.0 °C (△).

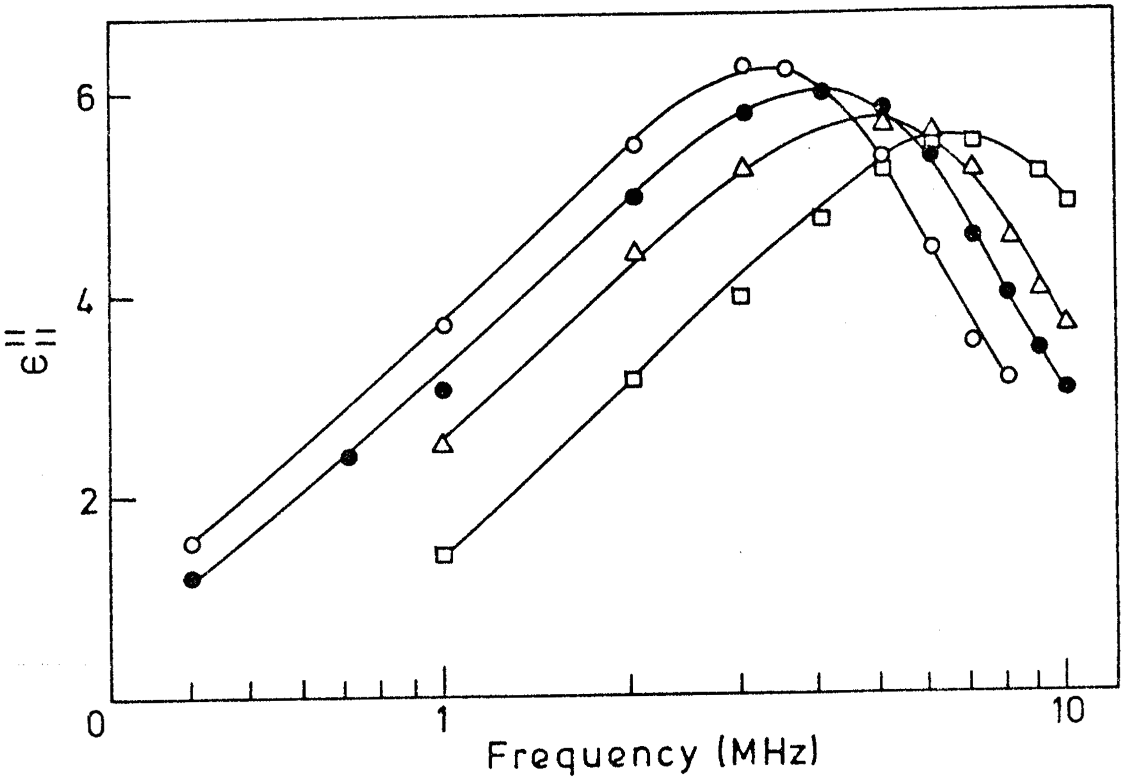

Figure 3.11

$\varepsilon''_{\parallel}$ as a function of frequency for 6CB at 18.0 °C (○), 20.2 °C (●), 22.5 °C (△) and 25.5 °C (□).

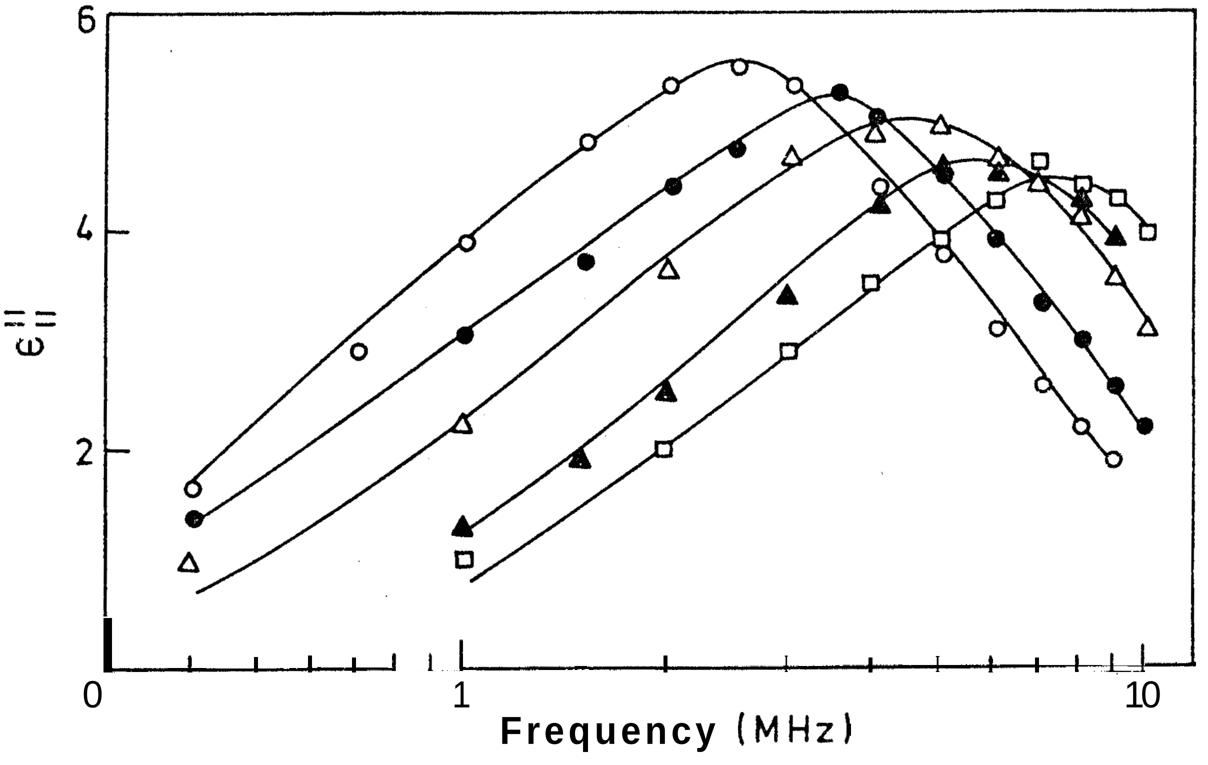

Figure 3.12

$\varepsilon''_{\parallel}$ as a function of frequency for 7CB at 23.0 °C (○), 27.5 °C (●), 31.5 °C (△), 35.0 °C (▲) and 38.0 °C (□).

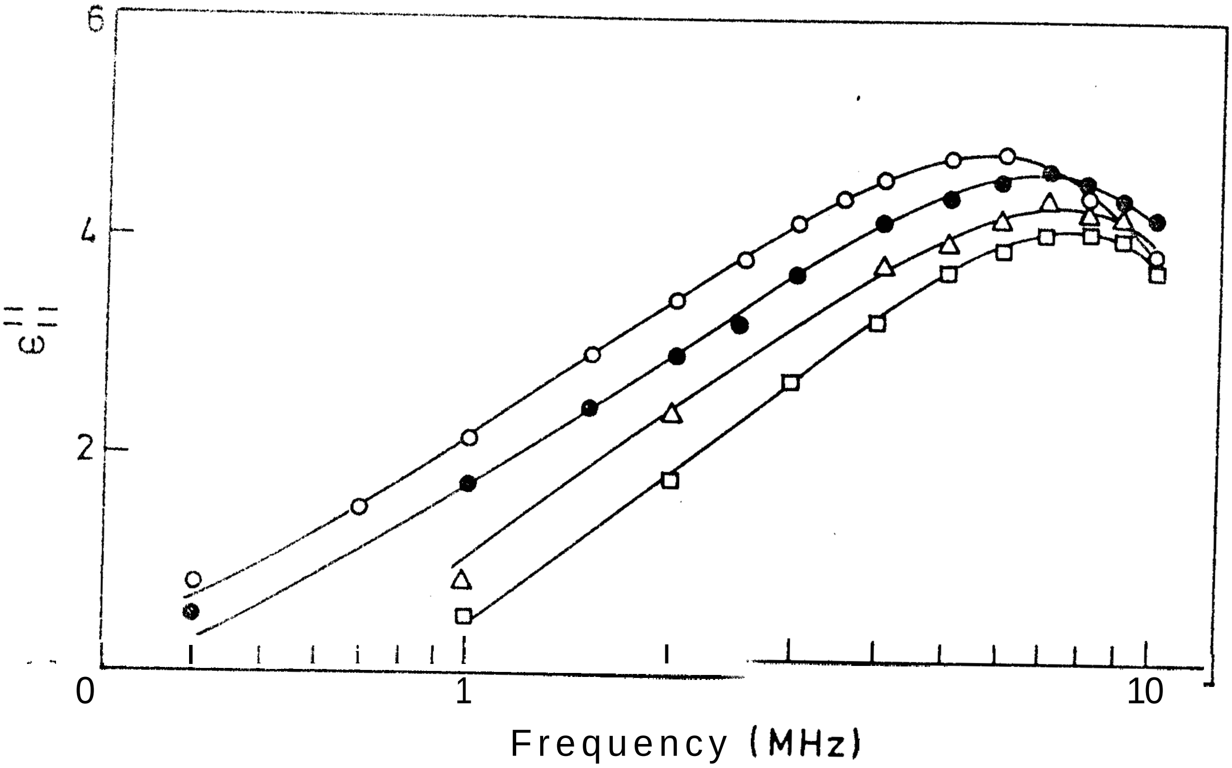

Figure 3.13

as a function of frequency far 8CB at 33.5 °C (○), 34.6 °C (●), 35.6 °C (A) and 36.5 °C (□).

Table 3.3: Relaxation frequency (f_R), frequency of dielectric isotropy (f_0) and activation energy (W) for 5CB-8CB

Compound	Temperature (°C)	f_R(MHz)	f_0(MHz)	W_{f_R}(eV)	W_{f_0}(eV)
5CB	19.5	3.0	5.0	0.560	0.560
	24.0	4.2	7.0		
	28.0	5.7	9.5		
	31.0	7.0	11.0		
6CB	18.0	3.5	6.5	0.570	0.562
	20.2	4.2	8.0		
	22.5	5.0	9.2		
	25.5	6.5	10.9		
7CB	23.0	2.6	5.7	0.560	0.565
	27.5	3.6	7.5		
	31.5	4.6	9.7		
	35.0	5.8	-		
	38.0	7.5	-		
8CB	33.5	5.8	-	0.560	-
	34.6	6.6	-		
	35.6	7.0	-		
	36.5	7.5	-		

A plot of ε'_{II} versus ε''_{II} is a semicircle with the centre lying on the ε'_{II}-axis, denoting a single relaxation time. These Cole-Cole arcs are plotted in figures 3.14-3.17. For all the compounds the radius of the semicircle decreases with increase of temperature and the centre shifts to lower ε'_{II}-values. Since a plot of ε''_{II} versus frequency along with the Cole-Cole plot is enough to describe the relaxation process completely we have not given the ε'_{II} versus frequency curves. The relaxation frequency is also defined as the frequency at which the ε'_{II} drops to half its static value. Thus we can determine f_R from the ε'_{II} vs. f curves also. The value of f_R determined in this manner agreed with that determined from the ε''_{II} vs. f curve to better than 2% in all cases.

Equation (2.47) can be rewritten as

$$\tau_R = A \exp(W/kT) ,$$

where $\tau_R = 1/23\ f_R$, $W = q + q_\eta$ and A is a constant.

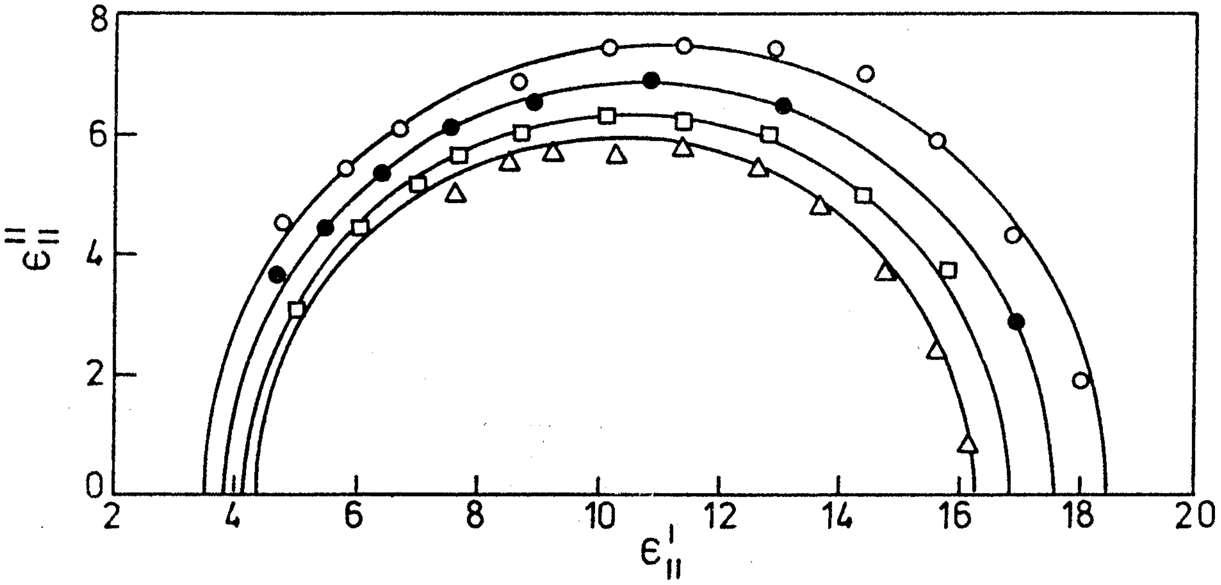

Figure 3.14

Cole-Cole plots for 5CB at 19.5 °C (○), 24.0 °C (●), 28.0 °C (□) and 31.0 °C (A)

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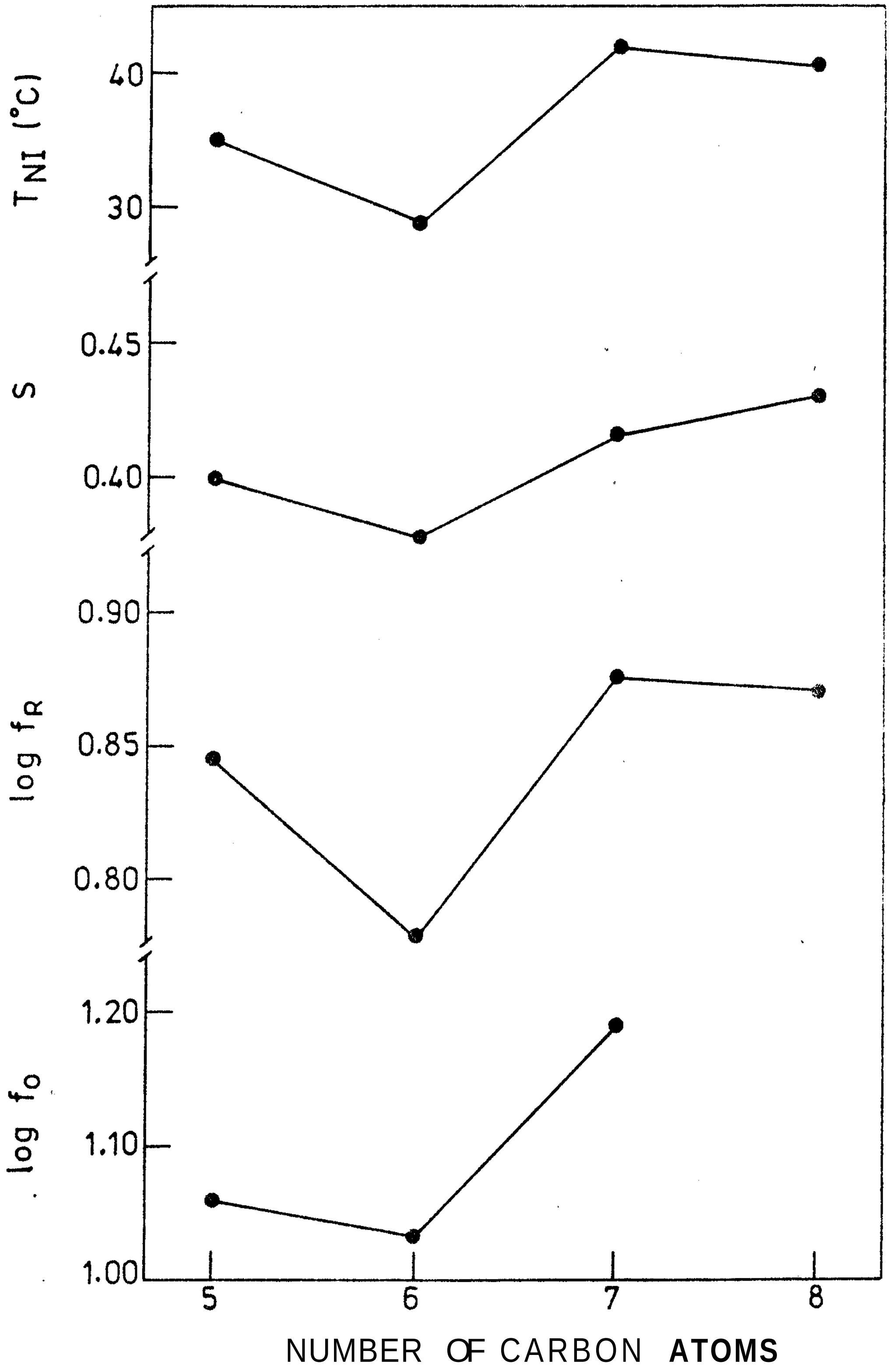

Figure 3.21

Order parameter (s), log f_R and log f_O taken at a common relative temperature of (T_{NI} - 4)°C and T_{NI} as functions of tho number of carbon atoms in the alkyl chain of nCB.

5CB or 7CB at the same temperature (see figure 3.18). However an entirely different picture emerges when we compare f_R of these compounds at a common relative temperature. Log f_R now exhibits an alternation with increasing alkyl chain length very similar to that of T_{NI} and s as shown in figure 3.21. As far as we are aware this is the first observation of such an alternation in f_R in successive members of a homologous series. Log f_0 which was found to alternate in a similar fashion is also shown in figure 3.21.

The similarity in the alternation of f_R and s is rather difficult to understand. With the increase of molecular order one would expect a greater hindrance to the rotation of the molecule about its short axis leading to a lowering of f_R while the opposite is observed here. This seems to suggest that the mechanism of dispersion of $\epsilon_{\parallel}$ is not influenced by the long range order alone, but also to a considerable extent by the short range order.

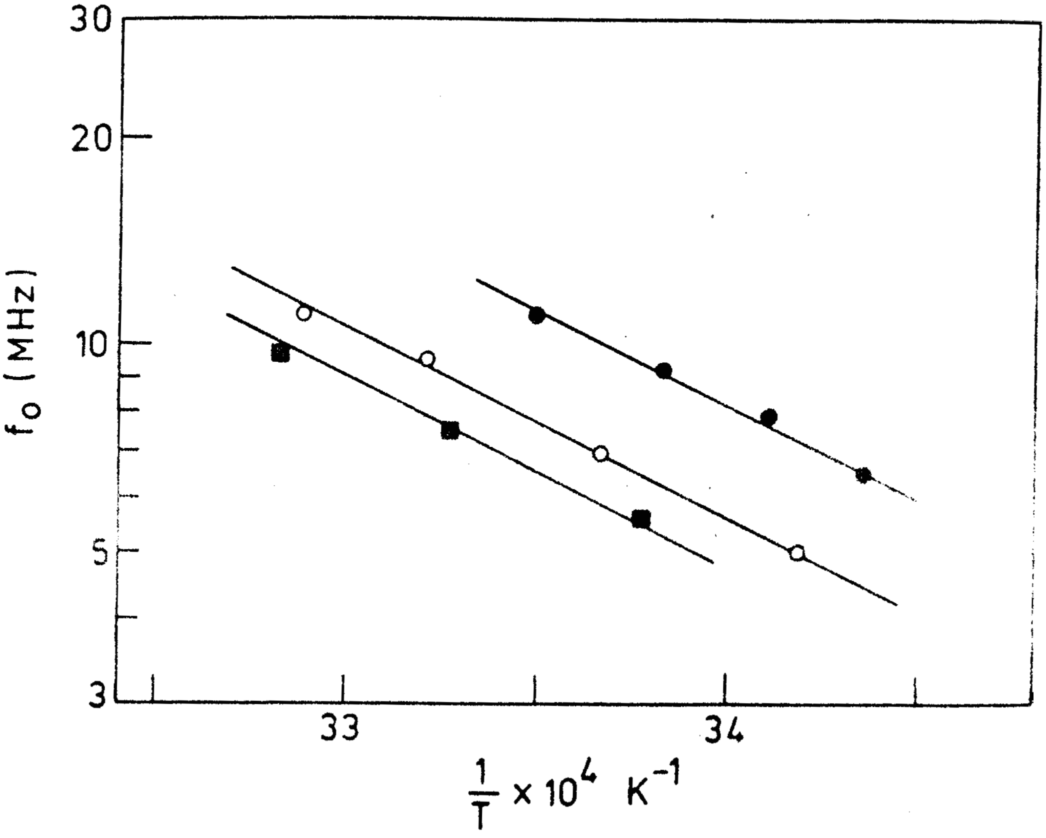

Figure 3.20

Frequency of dielectric isotropy (f_0) versus 1/T for 5CB (○), 6CB (●) and 7CB (■).

reason for the occurrence of such reversals in the sign of $\Delta\varepsilon$ in nCB has not yet been understood.

We have determined f_0 from the plot of $\varepsilon'_{\parallel}$ versus frequency for 5CB, 6CB and 7CB (see table 3.3). The experimental limitations prevented us from determining f_0 of 7CB for temperatures above 31.5°C and of 8CB at all temperatures. A plot of f_0 versus 1/T for 5CB-7CB is a straight line (figure 3.20) giving the same value of W as determined from f_R.

Whenever the low frequency relaxation was measured[9,11,16] for two members belonging to a homologous series, it was noticed that the relaxation frequency of the higher homologue is less than that of the lower one. It was suggested that this may be due to the greater alkyl chain length of the higher homologue. This was found to be the case with our data for 5CB and 7CB at any given temperature, but not for 6CB which has a higher value of f_R than either

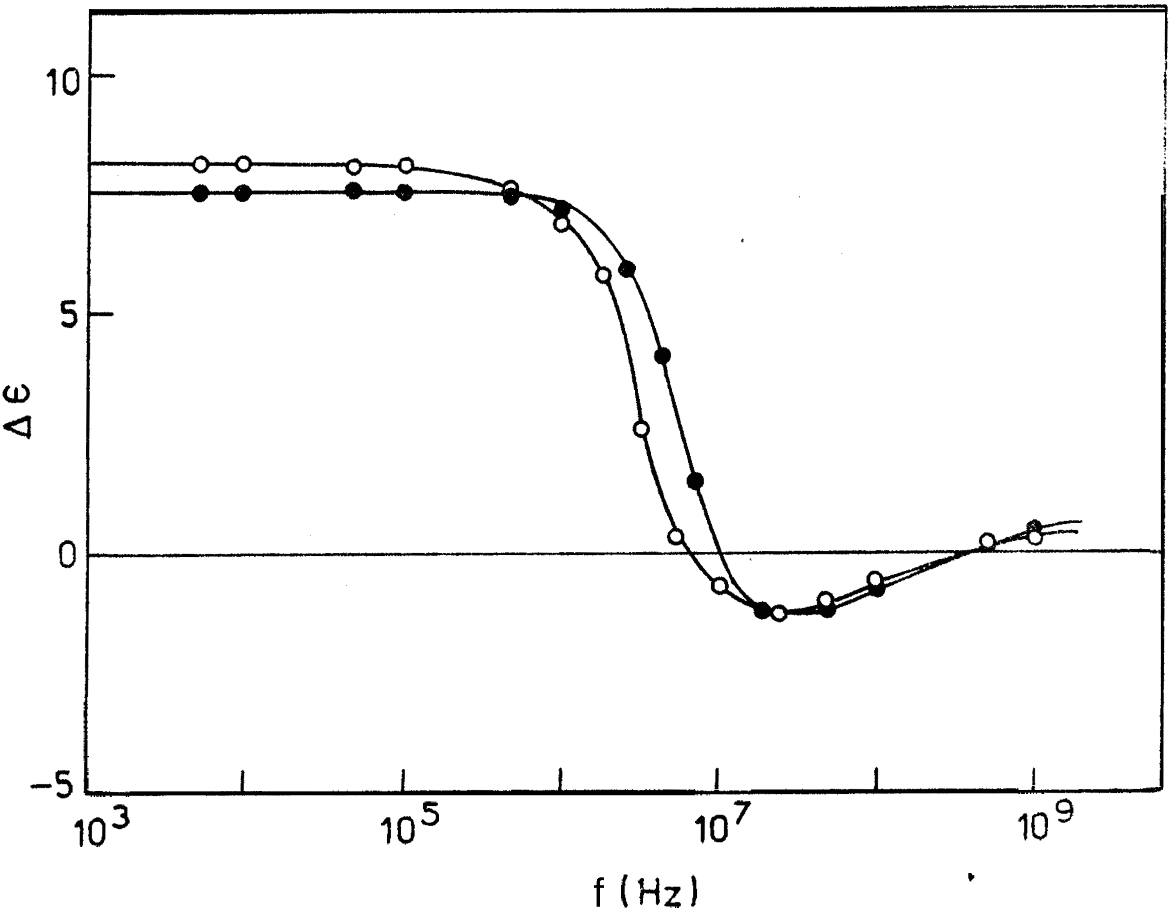

Figure 3.19

Dielectric anisotropy as a function of frequency for 8CB at T = 27°C (○) in the smectic phase and at T = 37 °C (●) In the nematic phase. (After Druon and Wacrenier[29]).

fa probably due to the presence of strong smectic like short range order even in the lower homologues.[22]

The high frequency limit of the dispersion, viz., $\varepsilon'_{\parallel}(\infty)$ could only be determined indirectly from the Cole-Cole plot, since the relaxation was not complete in the measured frequency range. $\varepsilon'_{\parallel}(\infty)$ is the intercept made by the Cole-Cole arc on the $\varepsilon'_{\parallel}$-axis at the high frequency side. For all the compounds $\varepsilon'_{\parallel}(\infty)$ was found to be less than $\varepsilon_{\perp}$ resulting in a change of sign of $\Delta\varepsilon$. The frequency of dielectric isotropy f_0, i.e., the frequency at which $\Delta\varepsilon$ becomes zero was in the 5–35 MHz region. A similar reversal in the sign of $\Delta\varepsilon$ of 5CB was observed previously by Cummins et al.[18] Recently Druon and Wacrenier,[29] from their measurements on 8CB over a wide range of frequency, showed that there are in fact two reversals; one around 10 MHz when $\Delta\varepsilon$ goes from positive to negative and the other above 100 MHz when $\Delta\varepsilon$ becomes positive again (figure 3.19). The

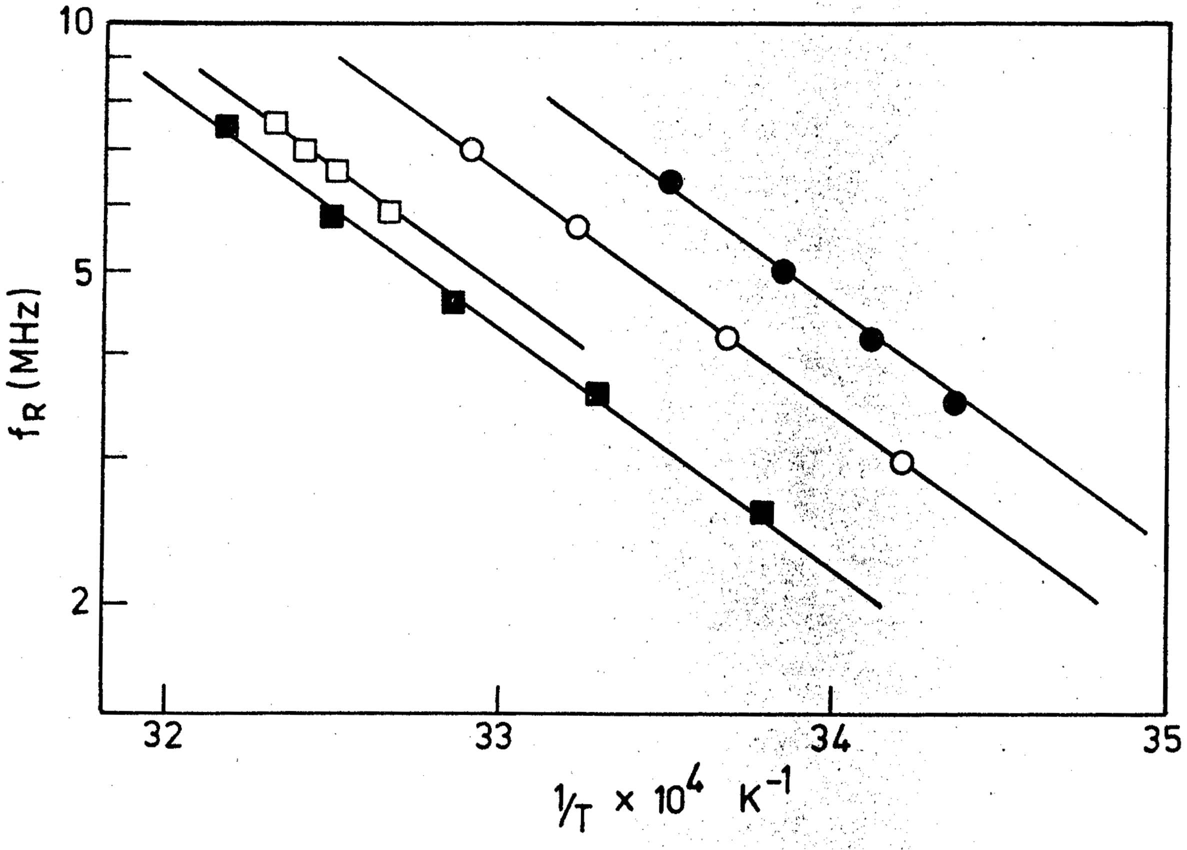

Figure 3.18

Relaxation frequency (f_R) versus 1/T for 5CB (○), 6CB (●), 7CB (■) and 8CB (□).

According to this equation, a plot of f_R versus 1/T on a log-linear scale (figure 3.18) gives a straight line the slope of which is the activation energy W. The value of W calculated in this manner is given in table 3.3 for 5CB–8CB. We find that W is the same for all compounds, the value being 0.56 ± 0.01 eV. Our value of W is in good agreement with that obtained by Cummins et al.[18] for 5CB and Davies et al.[19] for 7CB.

Measurements[14] of τ_R for six successive members of 4,4'-di-n-alkoxyazoxybenzenes showed that the value of W is the same for lower homologues which have only a nematic phase. But with the occurrence of a smectic C phase the value of W systematically increased from one homologue to the next higher one. This has been attributed partly to the presence of smectic like short range order in the nematic phase. In the case of nCB no such increase in W between the heptyl and the octyl derivatives has been observed even though the latter has an additional smectic A phase. This

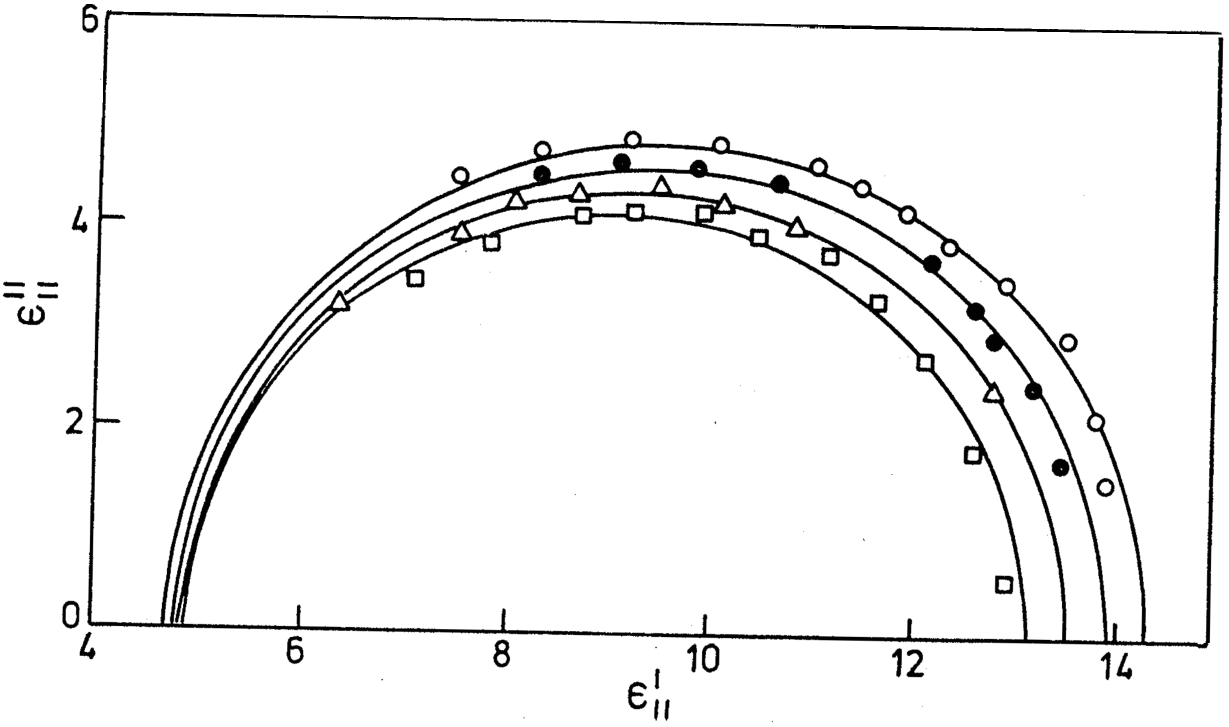

Figure 3.17

Cole–Cole plots *for* 8CB at 33.5 °C (○), 34.6 °C (●), 35.6 °C (A) and 36.5 °C (□).

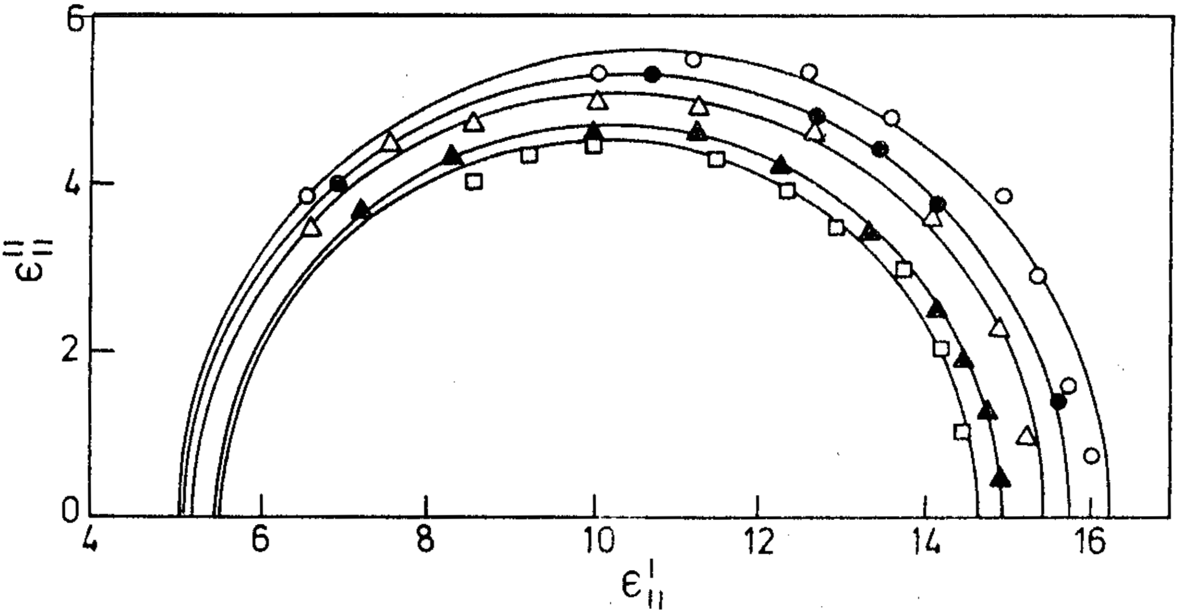

FIGURE 3.16

Cole-Cole *plots for 7CB* st 23.0 °C (○), 27.5 °C (●), 31.5 °C (△), 35.0 °C (A) and 38.0 °C (□).

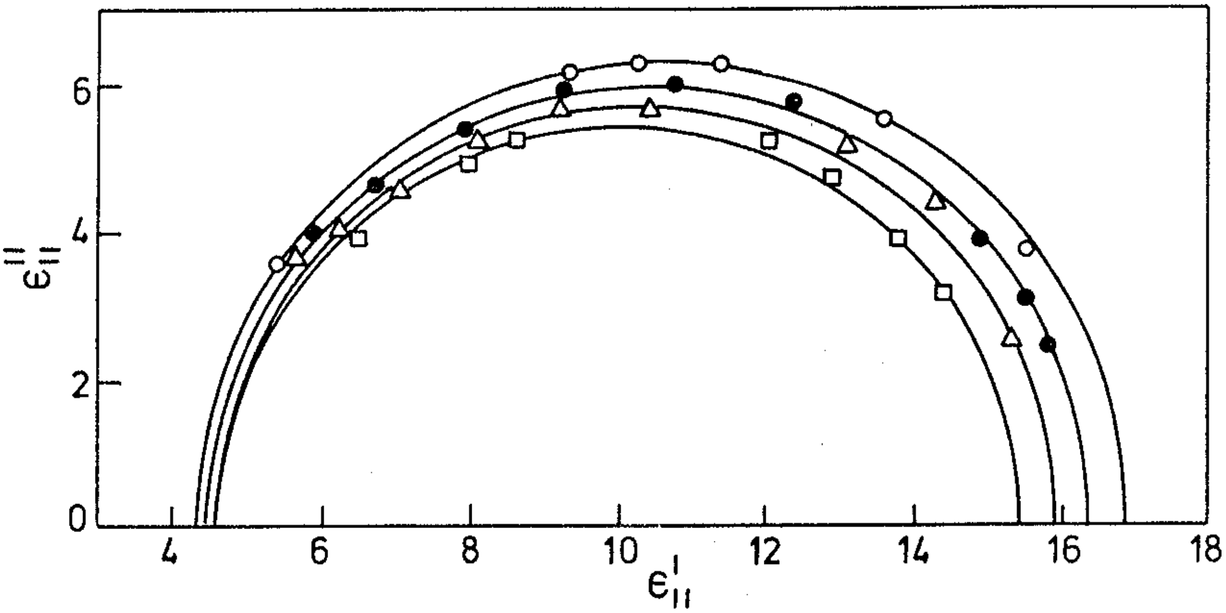

Figure 3.15

Cole-Cole plots for 6CB at 18.0 °C (○), 20.2 °C (●), 22.5 °C (A) and 25.5 °C (□).

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