

CHAPTER IV

TEMPERATURE DEPENDENCE OF THE SMECTIC A LAYER SPACING IN RE-ENTRANT NEMATOGENS

4.1 Introduction

We saw in chapter III that the formation of the re-entrant nematic phase at high pressures is associated with an expansion of the smectic A layer spacing with increase in pressure as was indeed predicted by Gladis et al.¹ In the light of the above result, it would be of importance to study the variation of the layer spacing with temperature in compounds exhibiting re-entrant behaviour at atmospheric pressure. The first X-ray investigation of such a compound was by Guillon et al.,² who studied the smectic A layer spacing as a function of temperature for a mixture of N-(p-hexyloxybenzylidene)-p-aminobenzonitrile (HBAB) in N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA). This mixture is known to exhibit the re-entrant nematic phase over a range of concentrations.³ They found that for a sample of 7.7% HBAB in CBOOA, the

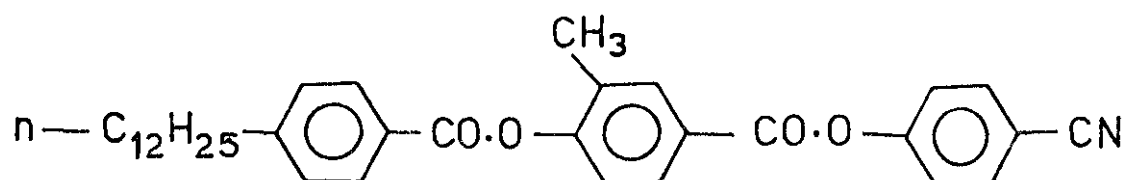
layer spacing in the smectic A phase increases continuously with decrease in temperature, over the entire smectic A phase. The layer spacing varied from 33.5 Å at the smectic A-nematic transition to 33.8 Å very close to the smectic A - re-entrant nematic transition. This represents a variation of about 1% over a temperature range of about 30°C. The re-entrant nematic phase has also been observed in binary mixtures of some terminal nonpolar liquid crystals with 8 OCB and CBOOA, at atmospheric pressures by Engelen et al.⁴ For an equimolar sample of 8 OCB/CBOOA, which shows the re-entrant nematic phase, they have studied the variation of layer thickness as a function of temperature. They did NOT find any temperature dependence of layer spacing for the mixture.

Re-entrant nematic phases have been discovered in pure compounds at atmospheric pressure by Madhusudana et al.⁵ in our laboratory. At about the same time, Hardouin et al.⁶ also reported the observation of re-entrant behaviour in some other pure compounds at atmospheric pressure.

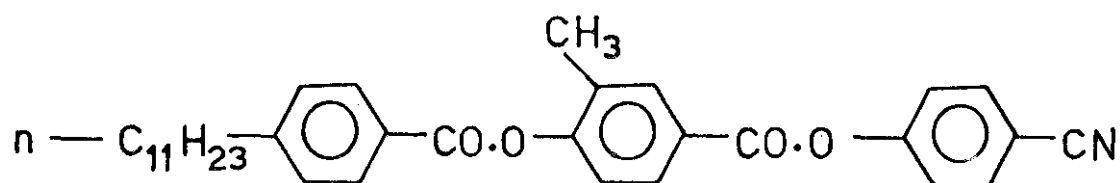
With the availability of pure compounds exhibiting the re-entrant nematic phase at atmospheric pressure, it was felt that it would be most interesting to carry out an accurate determination of the temperature dependence of the smectic A layer spacing. In this chapter, we present the results of our investigation on two pure re-entrant nematogens. We will compare our results with the X-ray studies in some other pure compounds showing the re-entrant behaviour at atmospheric pressure by Hardouin et al.⁷ and by Levelut et al.⁸, later in the chapter.

4.2 Experimental

a) Compounds. The compounds used in our experiments are 4-cyanophenyl-3-methyl-4-(4-n-dodecylbenzoyloxy)benzoate (12 CPMBB) and the corresponding undecyl homologue (11 CPMBB).⁹ Their structural formulae are shown in figure 4.1. Both compounds were first reported by Madhusudana et al.⁵ to show a monotropic re-entrant nematic phase. The transition temperatures as determined by thermal microscopy using a Mettler FP52 used in conjunction with FP5 temperature controller are tabulated in Table 4.1.



4-cyanophenyl-3-methyl-4-(4-n-dodecylbenzoyloxy) benzoate
(12 CPMBB)



4-cyanophenyl-3-methyl-4-(4-n-undecylbenzoyloxy) benzoate
(11 CPMBB)

FIGURE 4.1

Structural formulae of 12 CPMBB and 11 CPMBB

Table 4.1

Transition temperatures in °C (en cooling) for 12 CPMBB
and 11 CPMBB st atmospheric pressure

	<u>12 CPMBB</u>	<u>11 CPMBB</u>
Isotropic-nematic	148	152.5
Nematic-smectic A	138.5	127
Smectic A-Reentrant nematic	59.8	78.5
Reentrant nematic-solid	~56	~ 65

It is seen that both these compounds have a wide temperature range of smectic A phase - about 80°C for 12 CPMBB and about 50°C for 11 CPMBB.

b) The monochromator set-up. The determination of the layer spacing was carried out photographically using CuK_α radiation (from Philips PW1730 X-ray generator) reflected from a monochromator (Carl Zeiss Jena). The monochromator is of Johansson's type. In this a quartz crystal plate is concavo-cylindrically ground to the radius $2R$ while the cylinder axis is parallel to $(10 \bar{1} 1)$

crystal lattice planes. Subsequent bending of the crystal plate to the radius R results in strict focussing of radiation of a narrow wavelength range due to selective reflection from the planes according to Bragg's law. For the CuK_α radiation, the radius of deflection (i.e., the radius of curvature of the crystal) is 316 mm, the distance from the tube focus to crystal centre is 80 mm and the distance from the crystal centre to the focal line (focal length) is 210 mm. The sample was placed at the focus of the monochromator. The exact focus was determined by taking a series of trial photographs of the beam, close to the expected focal spot. To minimise the divergence of the X-ray beam, the exit slit of the monochromator was narrowed down to about 3 mm. The set up is shown in figure 4.2.

a) The sample holder and the heater. The sample holder and the electrical furnace used to maintain the temperature of the sample at any desired value are given schematically in figure 4.3. The sample holder is made of copper. It has a 1 mm hole to collimate the X-ray beam. The diffracted X-ray beam emerges out of the sample holder

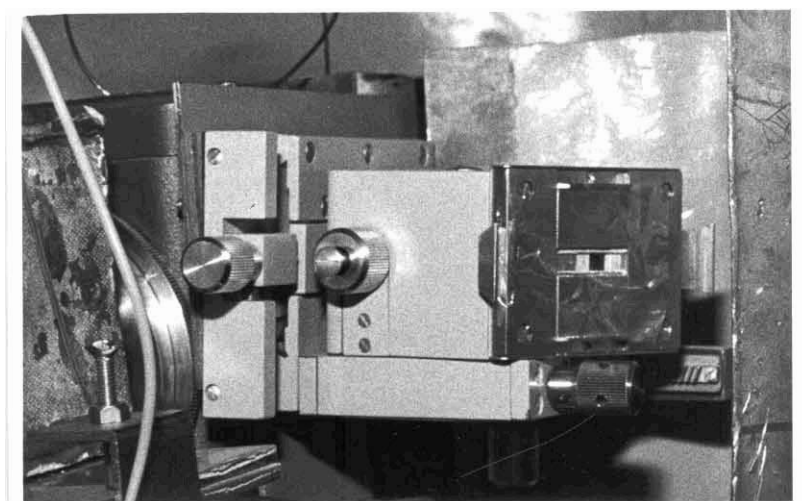
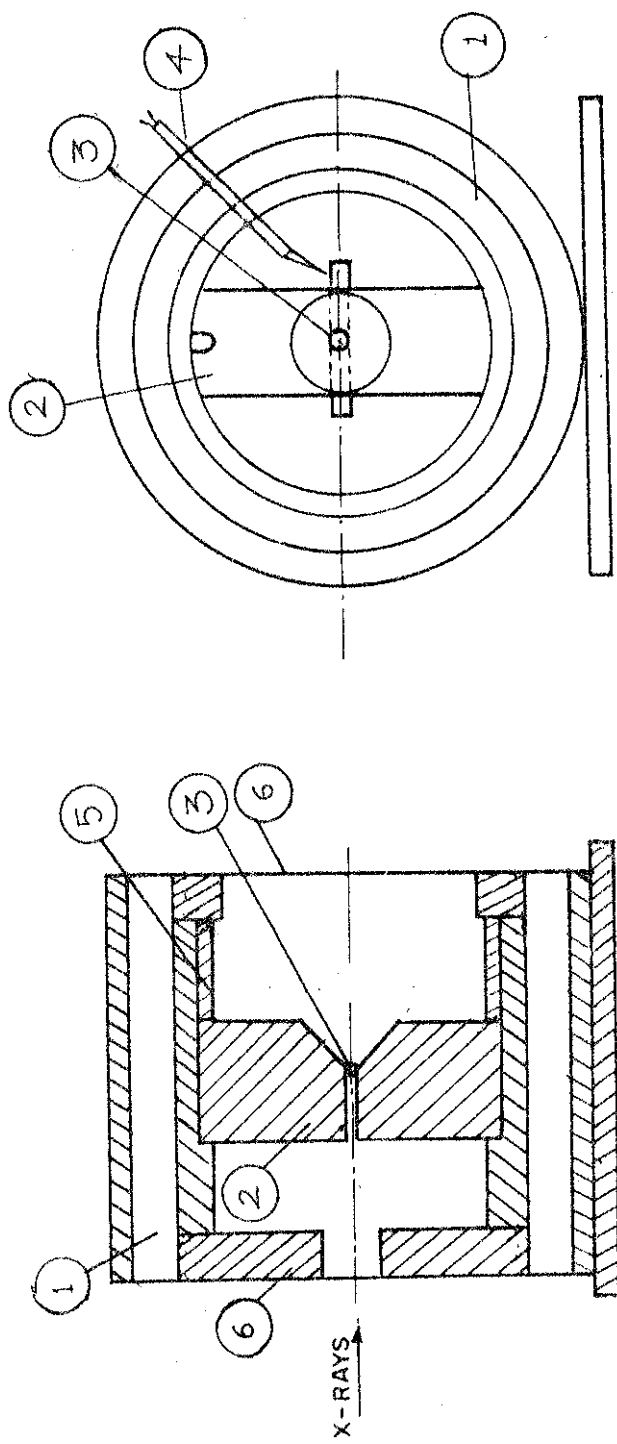


FIGURE 4.2

The monochromator **used** in the experiment



- 1. HEATER
- 2. SAMPLE HOLDER
- 3. SAMPLE
- 4. THERMO COUPLE
- 5. SPACER
- 6. WINDOWS

FIGURE 3: Schematic diagram of the sample holder and the heater.

through a conical aperture, whose axis coincides with that of the collimator. The conical angle of the aperture is about 45° , which is more than adequate for the X-ray diffraction studies of these compounds. There is a 0.75 mm diameter hole at the centre of the sample holder, at right angles to the incident X-ray beam. Through this hole, a Lindemann capillary containing the sample can be inserted.

The heater consists of a circular copper tube of about 6 cm length and 5 cm diameter. Nichrome wire is wound round its outer surface. By adjusting the current through the wire the temperature inside the heater can be maintained at any desired value. A highly stabilised power supply was used to minimise electric current fluctuations.

A projection is provided in the heater to match the notch at the top of the sample holder. This helps to place the sample holder exactly in the same position everytime the sample is mounted. The sample-to-film distance thus remains unaltered. Mylar sheets of thickness 6 microns, glued to copper rings that are screwed into the body of the

heater, serve as the windows. These prevent air currents and thereby avoid temperature fluctuations inside the hater.

d) Measurement of temperature. A chromel-alumel thermocouple, one junction of which is in contact with We Lindemann capillary, was used in conjunction with a 4½ digit panel meter to measure the temperature of the pimple. The thermocouple was calibrated by taking standard samples like azobenzol, benzil, phenacetin, benzanilid, para-azoxyanisole in Lindemann capillaries and observing the transitions visually. The temperature of the sample in the capillary could be read and maintained for long periods of time to within $\pm 0.25^{\circ}\text{C}$.

e) X-ray measurements. As the aim of the study was to measure small changes in the layer spacing, the sample-to-film distance was kept quite large (approximately 400 mm). The sample was taken in the powdered form in a Lindemann capillary whose diameter is about 0.5 mm. The capillary was then evacuated and sealed to prevent the decomposition

of the compound. It was placed in the sample holder in position, normal to the X-ray beam.

The intensity of the diffraction maxima obtained for the aligned samples will be high since these are concentrated in two spots. The distance between the spots obtained can be accurately measured. In our experiments, an aligned sample could be obtained since the compounds having terminal cyano groups have a tendency to align homeotropically. The homeotropically aligned sample used in our experiments was obtained by slowly cooling the sample in the Lindemann capillary from the isotropic phase to the smectic phase. Using the aligned sample along with monochromatic beam gave very sharp X-ray reflections. A contact print of the X-ray photograph is given in figure 4.4.

The exposure time was around twenty hours at each temperature, the temperature itself, as said earlier, being maintained to $\pm 0.25^{\circ}\text{C}$. The diffraction maxima became very diffuse on approaching the higher temperature

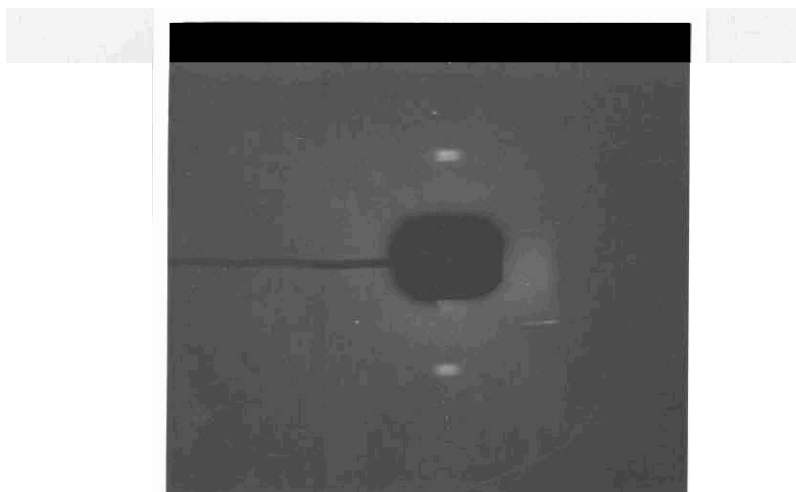


FIGURE 4.4

X-ray diffraction pattern of the aligned sample

nematic transition point. For this reason, the layer spacing was not determined in this region. After the completion of the experiment, the nematic-isotropic transition temperature of the sample in the sealed capillary was redetermined and was found to be unaltered (within the experimental error of $\pm 0.25^{\circ}\text{C}$) even after twenty days. This showed that the compound did not undergo any decomposition during the experiment.

The diameters of the diffraction rings obtained were measured by taking traces of the film, magnified five times, in a microdensitometer (Joyce Loebel, Model, 30S) and also by using an accurate comparator (Adam Hilger Ltd). The experiment was repeated with two or three different samples at each temperature and the data was highly self consistent. From the internal consistency of the data evaluated from the different measurements at each temperature, it is estimated that the relative accuracy of the Payer spacing measurement is better than $\pm 0.1 \text{ \AA}$. The data were brought to the absolute scale by using the 100 reflection of p-decanoic acid, the 'd' value of this

reflection being taken to be $23.10 \text{ \AA}$.¹⁰

4.3 Results and Discussion

a) 12 CPMBB. X-ray photographs were taken at thirteen temperatures covering the entire smectic range of this compound. The diameters of the rings and the layer spacings evaluated from them at different temperatures are given in table 4.2. The data are plotted in figure 4.5. It is seen that the spacing, which is $43.78 \text{ \AA}$ at 130°C starts decreasing with decrease of temperature till about 106°C when the spacing becomes $43.07 \text{ \AA}$. On further cooling, the variation of layer spacing reverses sign and the spacing starts increasing with decrease of temperature. This increasing trend of layer spacing continues right up to the re-entrant nematic phase. The spacing is $44.45 \text{ \AA}$ at 62°C , at about 2°C away from the re-entrant nematic phase. It is significant to note that the increase in the layer spacing is about $1.4 \text{ \AA}$ which is about 3% variation in the layer spacing.

b) 11 CPMBB. The data for 11 CPMBB are given in

TABLE 4.2

Layer spacing in smectic A phase of 12 CPMBB at
different temperatures
Sample-to-film distance = 398 mm

Temperature (°C)	Diameter of the rise; (mm)	Layer spacing (Å)
62	27.625	44.44
65	27.886	44.03
70	28.05	43.77
76	28.11	43.68
82	28.31	43.37
88	28.36	43.29
94	28.38	43.26
100	28.42	43.20
106	28.51	43.06
112	28.42	43.20
118	28.34	43.32
124	28.24	43.47
130	28.047	43.77

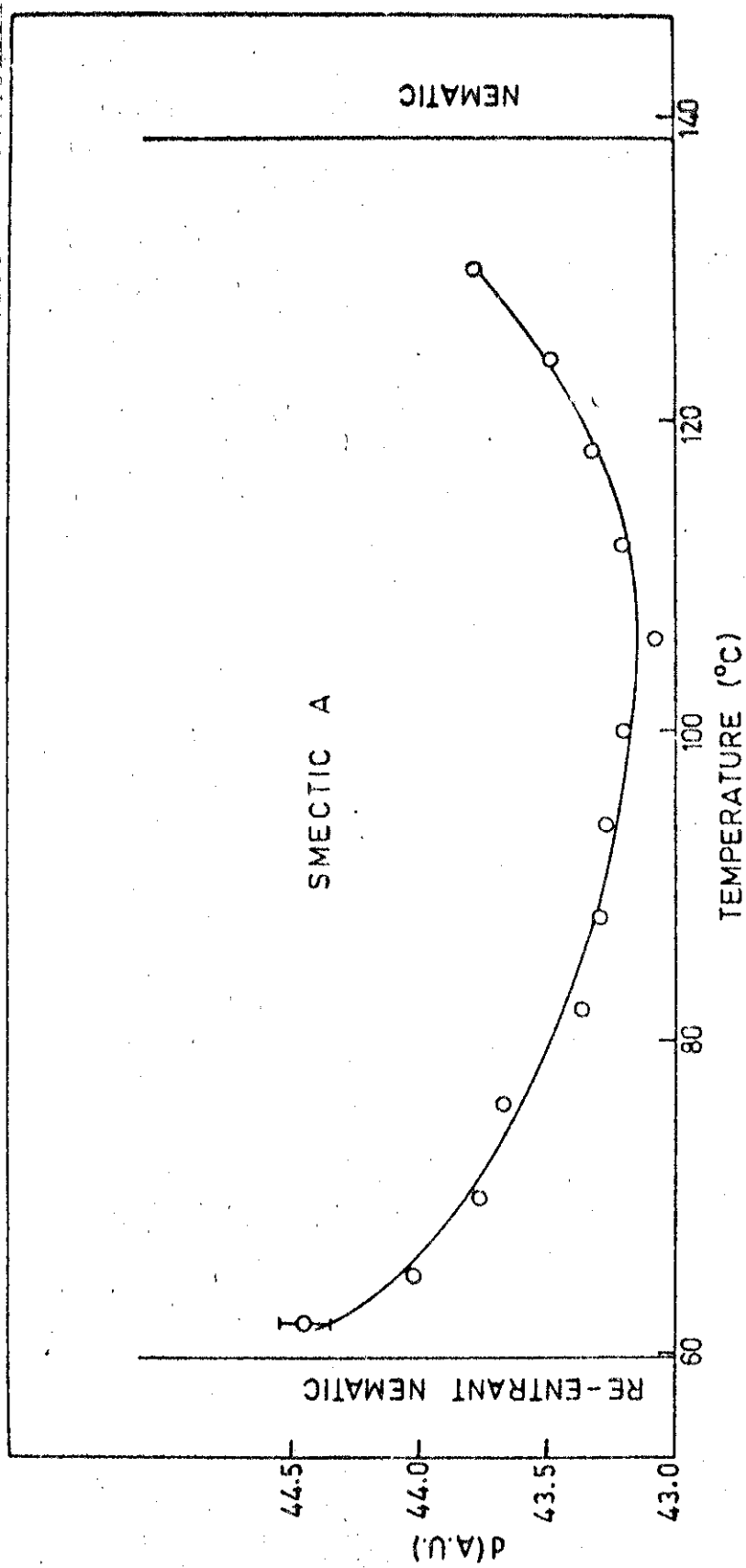


FIGURE 4.5: The variation of layer spacing in the smectic A phase of 12 CPMB as a function of temperature.

table 4.3 which are plotted in figure 4.6. The range of the smectic A phase for this compound is smaller than that in 12 OPMBB. The increase in the layer spacing in this compound is less pronounced than in 12 OPMBB. This increase is about $0.6 \text{ \AA}$, which is about 1.4% variation in the spacing.

The error bar in the determination of the layer spacing is marked in both the figures 4.5 and 4.6.

The results therefore provide a clear evidence of a structural change taking place in the smectic bilayer as a precursor to the formation of the re-entrant nematic phase.

We may mention here the results reported recently by the French group on other pure compounds which show the re-entrant behaviour at atmospheric pressure. Hardouin et al.⁷ have investigated the different phases of the eighth homologue of the 4-cyanobiphenyl-4'-n-alkoxybenzoate esters by X-ray diffraction. Within the accuracy of Weir experimental error ($\pm 0.4 \text{ \AA}$) they did not find any variation

TABLE 4.3

Layer spacing of the smectic A phase of
11 CPMBB at different temperatures.

Sample-to-film distance = 407 mm

Temperature (°C)	Diameter of the ring (mm)	Layer spacing (Å)
80	29.905	41.98
81	29.915	41.97
83	30.036	41.80
88	30.09	41.73
93	30.168	41.62
98	30.226	41.54
103	30.328	41.40
108	30.236	41.52
113	30.194	41.58
117	30.14	41.66
120	29.98	41.88

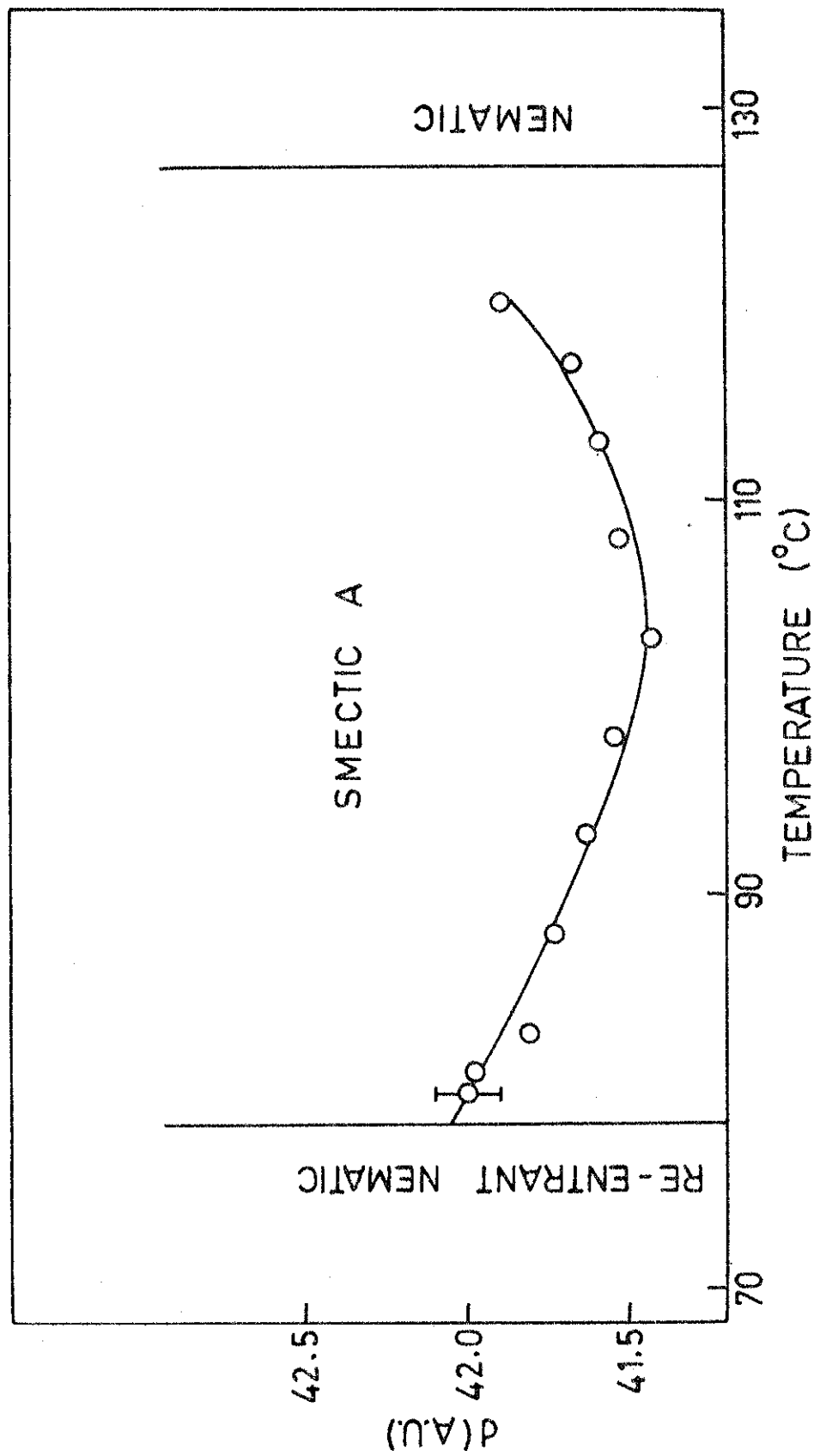


Figure 4.6: Variation of layer spacing in the smectic A phase of 11 CPMBB as a function of temperature.

of layer spacing with temperature in the smectic A phase. Levelut et al.⁸ have also studied the variation of layer spacing in 4-n-octyloxybenzoyloxy-4'-cyanostilbene. The sequence of phase transitions in this compound in the cooling mode is, Isotropic $\rightarrow$ nematic $\rightarrow$ smectic A $\rightarrow$ nematic $\rightarrow$ smectic A $\rightarrow$ solid. It thus shows two re-entrant phases. The X-ray study performed on this pure compound showed that the higher temperature smectic A has a layer spacing 'd' greater than the molecular length 'L'. It has thus a bilayer structure. In the re-entrant smectic A phase, the layer spacing is approximately equal to the molecular length. Hence it is a 'monolayer' smectic A. In the higher temperature smectic A with a bilayer structure, near the nematic-smectic A transition point, the value of (d/L) is found to be equal to 1.24. With decrease in temperature, the value of d/L continuously decreases. Near the smectic A - re-entrant nematic transition point, the value becomes 1.11. The change in the layer spacing is thus quite large, about 10% over a temperature range of about 100°C. No appreciable change

was found in the entire re-entrant smectic A phase.

The value of d/L in this phase is found to be 0.99.

Thus the behaviour observed in this compound is quite different from that observed in our compounds. Nevertheless the results do emphasize that structural changes in *the* bilayer arrangement are important for formation of the re-entrant nematic phase.

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CHAPTER V

PRINCIPAL DIELECTRIC CONSTANTS OF RE-ENTRANT NEMATOGENS

5.1 Introduction

It was mentioned in earlier chapters that the re-entrant phenomenon was observed¹⁻⁷ in almost all the compounds which have a cyano end group along the long axis of the molecule. This terminal group is the one which is responsible for the polar nature of the molecule. It was also stated earlier that in such strongly polar compounds the correlation between neighbouring molecules is antiparallel.⁸ Recently, this was confirmed in neutron studies of such compounds.⁹ An important consequence of antiparallel association of the molecules is that the mean dielectric constant $\bar{\epsilon}$ in the mesophase becomes less than the isotropic value (ϵ_{is}), because of the decrease in antiparallel ordering in the isotropic phase.⁸ Here $\bar{\epsilon}$, the average dielectric constant $= \frac{1}{3}(\epsilon_{||} + 2\epsilon_{\perp})$ where $\epsilon_{||}$ and $\epsilon_{\perp}$ are the principal dielectric constants measured parallel and perpendicular to the optic axis. Ratna and

Shashidhar^{10,11} have experimentally verified that $\bar{\epsilon}$ is less than the extrapolated isotropic value in a number of cyano compounds. The experimental curves also showed that $\bar{\epsilon}$ as well as ϵ_{13} decrease with decrease in temperature, which again may be attributed to the increase of antiparallel ordering at lower temperatures. In the first part of this chapter we present a more direct evidence of the antiparallel correlation and its influence on the dielectric properties.

We saw in chapters III and IV that subtle changes in the bilayer structure as evidenced by X-ray studies, are responsible for the re-entrant behaviour. A study of the dielectric properties of these compounds showing the re-entrant nematic phase is therefore of considerable importance, since St is expected to reveal the nature of the molecular associations in the different phases. We have undertaken a detailed investigation of the static dielectric constants ($\epsilon_{||}$ and $\epsilon_{\perp}$) in the normal nematic, smectic A and the re-entrant nematic phases of three systems. Two of these are pure compounds while the third

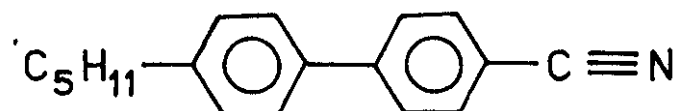
one is a mixture. These exhibit a monotropic re-entrant nematic phase on cooling the sample from the smectic A phase, at atmospheric pressure. The results obtained regarding the variation of the static dielectric constants with temperature are discussed in the latter part of this chapter.

5.2 Direct evidence of antiparallel correlation

Measurement of the dielectric constant of solutions of 5CB in benzene

We have determined the effective dipole moment per molecule of 4'-n-pentyl-4-cyanobiphenyl (SUB) by measuring the dielectric constant (ϵ_{12}) and the refractive index (n_{12}) of solutions of 5CB in a nonpolar solvent, viz., benzene. The chemical structure of 5CB is given in figure 5.1. It has a C≡N end group with a dipole moment $\mu = 4.05$ debye¹² acting along the long molecular axis.

The dielectric constants were measured using a Wayne Kerr B642 bridge and the refractive indices by the prism method¹³ using a goniometer spectrometer. The dipole moment μ is calculated using the Guggenheim equation¹⁴



4'- n - pentyl - 4 - cyanobiphenyl
(5 CB)

FIGURE 5.1

Structural formula of 5 CB

$$\mu^2 = \frac{27kT}{4\pi N_A (\epsilon_1 + 2)(n_1^2 + 2)} \cdot \frac{(\epsilon_{12} - n_{12}^2) - (\epsilon_1 - n_1^2)}{0}$$

where N_A is the Avagadro number,

k the Boltzmann constant,

ϵ_1 the dielectric constant of the solvent,

n_1 the refractive index of the solvent, and

0 the molar concentration.

All the measurements were carried out at the same temperature of 38°C , which is about 3°C above the nematic-isotropic transition temperature (35°C) of pure 5QB.

The dipole moment μ of pure 5QB at 38°C is calculated using the Maier-Meier equation¹⁵

$$\epsilon = 1 + \frac{4\pi N_A \rho h F}{M} \left(\bar{\alpha} + \frac{\mu^2}{3kT} \right)$$

where ρ is the density,

$$h \text{ (the cavity field factor)} = \frac{3\epsilon}{(2\epsilon + 1)},$$

$$F \text{ (the reaction field factor)} = \frac{1}{1 - \bar{\alpha}f},$$

$$f = \frac{4\pi N_A (2\epsilon - 2)}{3M(2\epsilon + 1)}$$

where M is the molecular weight and $\bar{\alpha}$, the mean polarisability.

The values that we have used in the calculations are

$$\epsilon = 10.62,^{10} \quad \rho = 1.007,^{16} \quad \text{and} \quad \bar{\alpha} = 32.9 \times 10^{-24} \text{ cm}^3.^{17}$$

The dipole moments which are evaluated at different concentrations are plotted in figure 52. It is seen that with the decrease of concentration (or increase of dilution), the dipole moment μ increases linearly at first. As the concentration decreases below about 10%, the variation of μ becomes much faster. For concentrations less than 5%, μ increases very rapidly. The value of μ obtained on extrapolation to infinite dilution is 5.30 debye. This is the dipole moment of an isolated molecule of 5CB. Lippens et al.¹⁸ have also reported a study of the determination of the dipole moment of 4'-n-heptyl-4-cyanobiphenyl (7CB). For solutions of different concentrations of 7CB in n-octane, they have obtained results which are similar to ours. The fact that the dipole moment decreases with increase of concentration (to 3.33D in the isotropic phase) proves conclusively that the near neighbour correlations are antiparallel in such compounds.

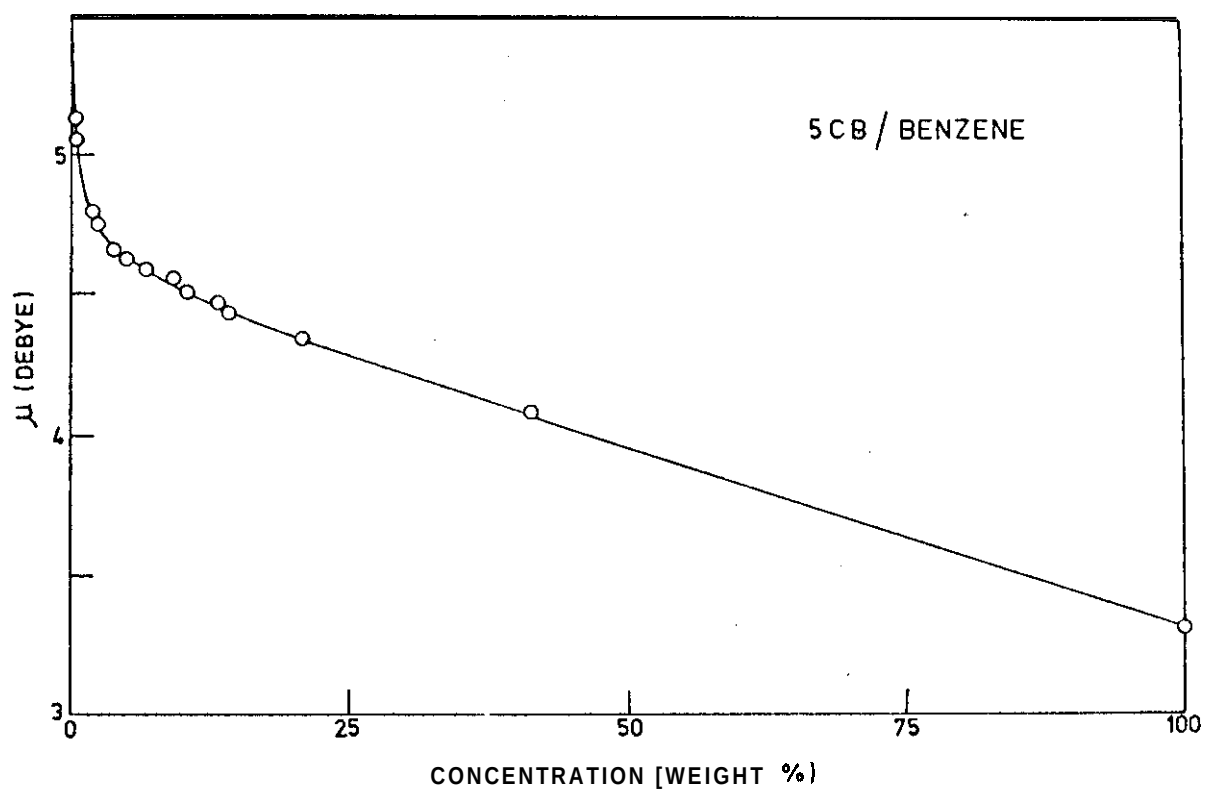


FIGURE 5.2

The dipole moment of 5CB molecule in benzene solution as a function of concentration.

5.3 Measurements on re-entrant nematogens

A. Experimental

a) Compound. The compounds studied are 11 CPMBB, 12 CPMBB⁴ and a mixture of 35.8% by weight of 4'-n-hexyloxy-4-cyanobiphenyl (6 OCB) in 8 OCB.¹⁹ The pure compounds were synthesised in our laboratory. The mixture was given to us by Dr. P.E.Cladis. The chemical structures of the pure compounds and those of the components of the mixture are given in figure 5.3. The transition temperatures of these re-entrant nematogens, while cooling the sample from the isotropic phase are given in table 5.1

Table 5.1

Transition temperatures (in °C) of 11 CPMBB, 12 CPMBB and 35.8 : 64.2 weight mixture of 6 OCB In 8 OCB on cooling

	11 CPMBB	12 CPMBB	6 OCB/ 8 OCB mixture
Isotropic - nematic	152.5	148	78.5
Nematic - smectic A	127	138.5	45.5
Smectic A - Re-entrant nematic	78.5	59.8	30
re-entrant nematic - solid	~ 65	~ 56	~ 25

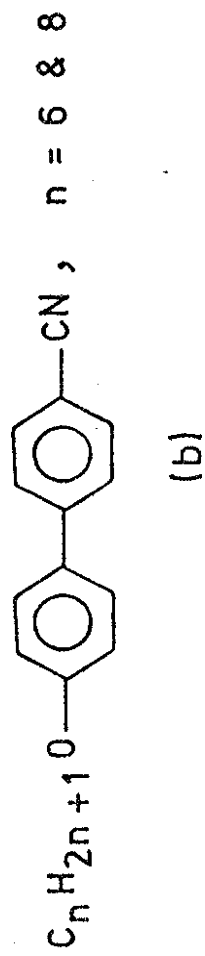
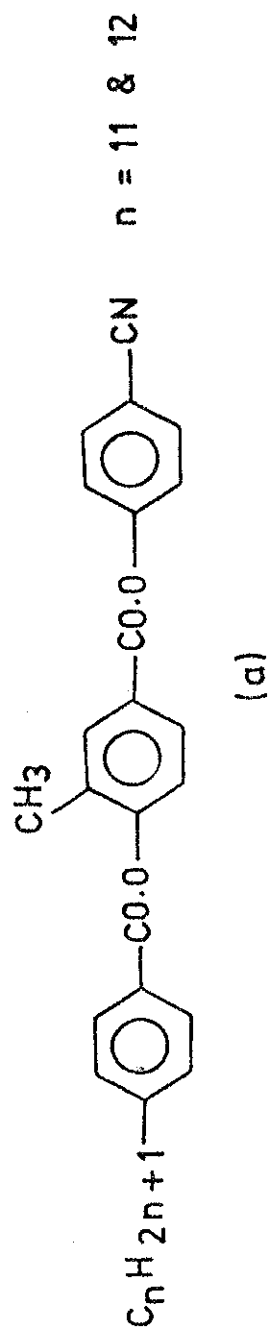


Figure 5.3

Structural formulae for (a) 11 CPMBB, and 12 CPMBB, and (b) 6 OCB and 8 OCB

Both the pure compounds have Wide mesomorphic ranges much greater than that of the mixture. As mentioned in 5.1 the re-entrant nematic phase in all the three systems was obtained by cooling the sample from the smectic A phase. Measurements could be made in the re-entrant phase of 11 CPMBB for a temperature range of about 8°C . In 12 CPMBB this range was less than 3°C . In the mixture, the readings could be taken for a range of about 6°C .

b) The dielectric cell. The dielectric constants were evaluated by measuring the capacitance of a parallel plate capacitor without and with the sample. The schematic diagram of the dielectric cell²⁰ used is shown in figure 5.4. The cell consisted of two tin oxide coated glass plates which served as electrodes. The separation between the two plates was fixed by mylar spacers. The conductive coating which was in contact with the mylar was removed to eliminate the contribution of mylar to the capacitance of the cell. The active area of the electrodes was about 1 sq.cm. The plates were held in a copper frame

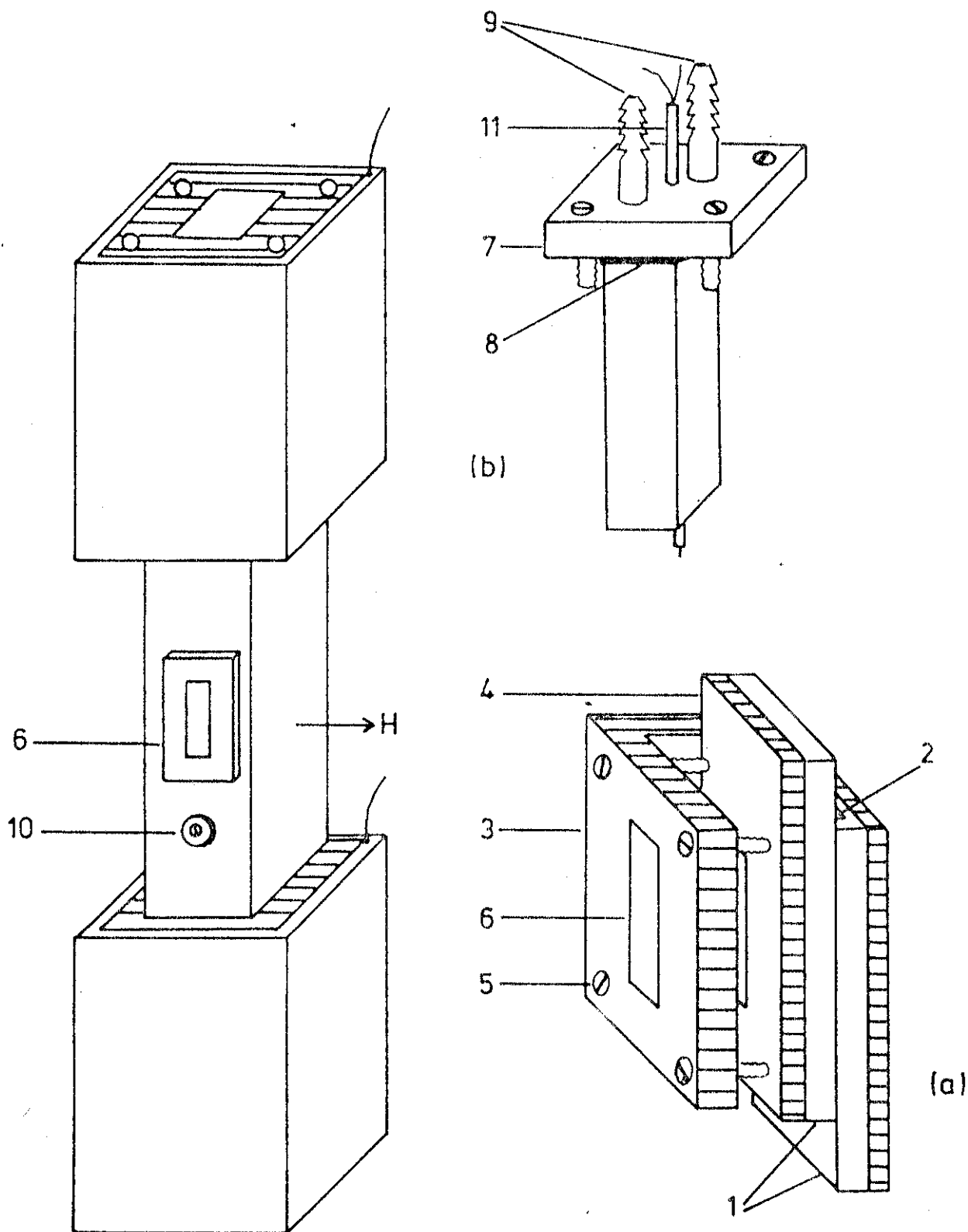


FIGURE 5.4

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 11. Thermocouple. H represents
 the direction of the magnetic field for $\epsilon_{\perp}$ measurements.

and were screwed tightly against each other using a copper plate as a buffer to avoid uneven pressing on the glass plates. The rectangular slots made in the copper plate and the frame served as observation windows.

c) Heater. The schematic diagram of the heater used is shown in figure 5.4(b). It consists of 8 long rectangular copper tube with nichrome windings on the outer surface for passing electrical current. The length of the heater was deliberately made large compared to the size of the dielectric cell to ensure that there is no temperature gradient within the sample. Also, the dimensions of the central region of the heater was reduced as far as possible, to obtain as high a magnetic field as possible. Two glass windows are provided in the heater to facilitate the checking of the alignment of the sample during the course of the experiment. By using a cap which can be screwed onto the top of the heater, the system was sealed after passing nitrogen through the nozzles. This was done as a precaution to prevent oxidation and hence the deterioration of the sample.

d) Temperature control and measurement. The electrical power to the heater was supplied by two highly stabilized DC power supplies (60 V, 6A each). A rheostat used in series with the nichrome winding served for finer variations in temperature. The temperature of the sample could be controlled and maintained to better than $\pm 0.025^{\circ}\text{C}$.

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 previously ascertained that the sample did not experience any temperature gradient. The temperature of the sample was measured to an accuracy of $\pm 0.025^{\circ}\text{C}$ using a Keithley digital multimeter (model 174).

e) Sample alignment. The compounds, especially 11 CPMBB, have a strong tendency for homeotropic alignment, i.e., to orient with director normal to the surface. However, to ensure a good alignment, both $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were measured in the presence of a magnetic field of 15 K Gauss which is

more than twice the saturation field for the thicknesses of the sample used (50 to 250 microns). The alignments in the smectic A phase were achieved by slowly cooling the well aligned nematic in the presence of the magnetic field. The magnet used was an electromagnet (BDS Electronics, Bangalore) with 25 mm tapered pole pieces. The field strength was measured by using a fluxmeter (Bell, USA).

f) Measurement of static dielectric constants. A Wayne Kerr bridge (E642) was used at 1592 Hz to determine the static dielectric constants. This frequency was high enough to avoid interfacial polarisation effects at the electrodes.²¹ The measured capacitance was always corrected for the lead capacitance. The bridge voltage across the sample was very low and did not have any disturbing influence on the sample.

The relative variation of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ could be determined to an accuracy of 0.1%. The value of ϵ_{is} obtained independently from the two different geometry matched to within 1%. The experimental set up was initially

used to measure the dielectric constants of standard liquids like toluene and chlorobenzene. The values obtained for these liquids agreed to within 2% of the standard value, which is therefore reckoned to be the absolute accuracy of our measurements.

B. Results and Discussion

The variation of $\epsilon_{||}$, $\epsilon_{\perp}$ and ϵ_{is} for 11 CPMBB, 12 CPMBB and for the 6 OCB/8 OCB mixture in their isotropic, normal nematic, smectic A and re-entrant nematic phases are shown in figures 5.5 to 5.7 respectively. In all the three systems, $\epsilon_{\perp}$ decreases with decrease in temperature, starting from the nematic-isotropic transition point (T_{NI}). In the pure compounds, $\epsilon_{||}$ increases rapidly in the beginning (close to T_{NI}) as the temperature is lowered. On further cooling, in 11 CPMBB, the rate of increase slows down near the normal nematic-smectic A transition temperature (T_1 , see figure 5.5). In 12 CPMBB, near the nematic-smectic A transition (T_1 , see figure 5.6), $\epsilon_{||}$ decreases and the decrease continues through part of the smectic phase. A

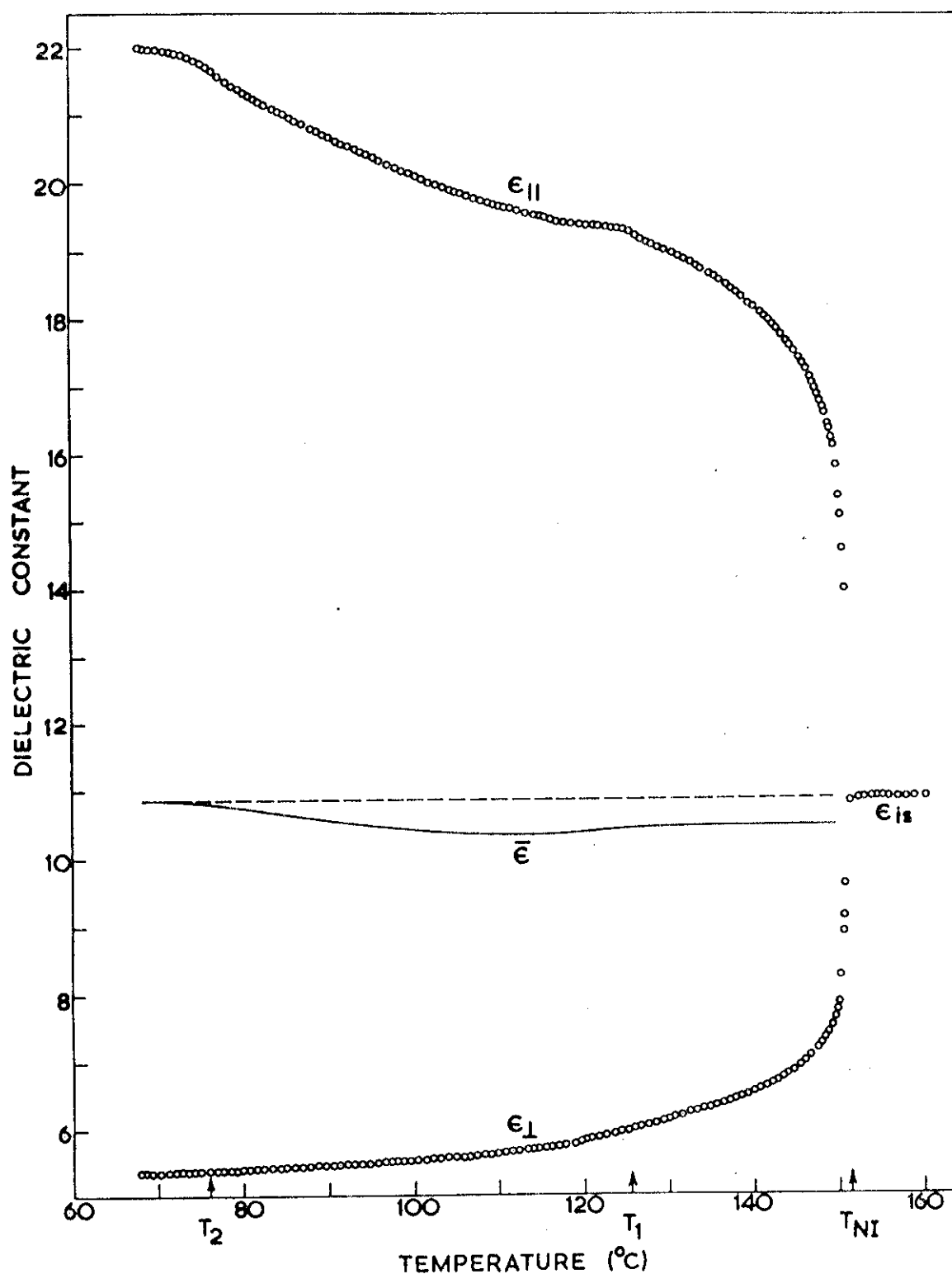


FIGURE 5.5

Principal dielectric constants of 11 CPMBB. $\bar{\epsilon}$ is the mean dielectric constant evaluated from the measured values of $\epsilon_{||}$ and $\epsilon_{\perp}$. The broken line is the extrapolation of $\epsilon_{\perp}$.

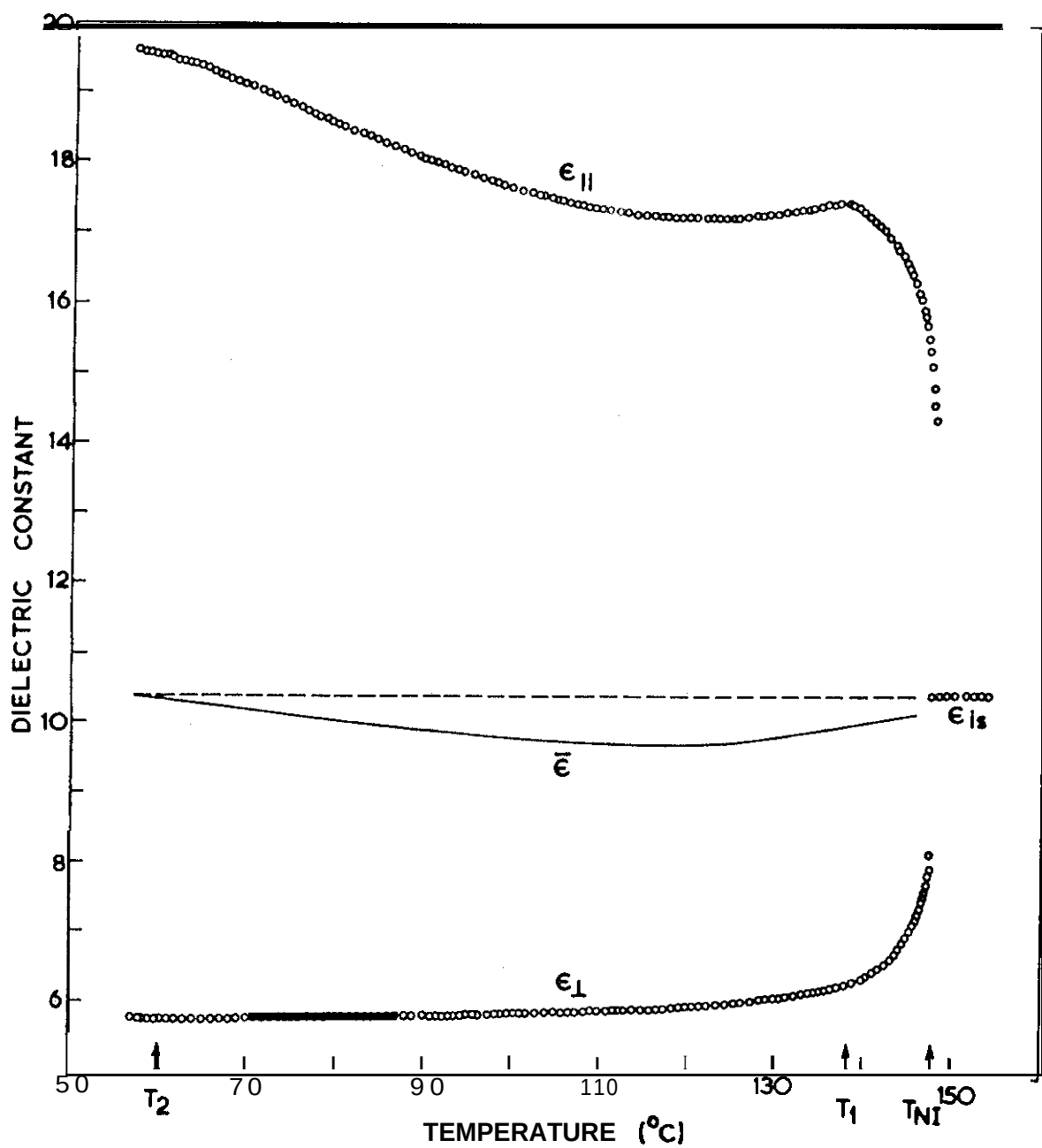


FIGURE 5.6

Principal dielectric constants of 12 CPMBB

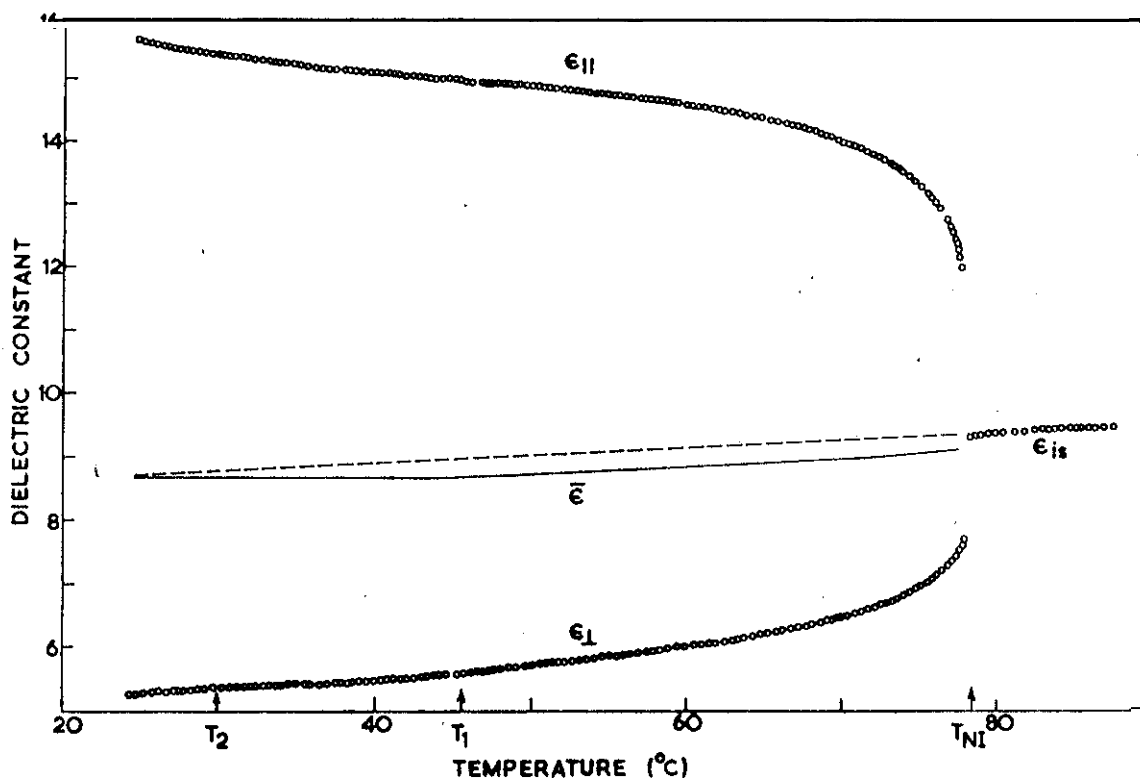


FIGURE 5.7

Principal dielectric constants of 6 OCB/8 OCB mixture

similar behaviour has been found by Bata and Buka²² in 4-nitrophenyl-4-octyloxybenzoate (NPOOB) which is also a strongly polar compound. The decrease of $\epsilon_{||}$ in the smectic A phase as compared to that in the nematic phase may be attributed to a relative increase in antiparallel correlations of the molecules in the smectic phase. In both the pure compounds, on further cooling, $\epsilon_{||}$ increases continuously till the sample is cooled to the re-entrant nematic phase. In the mixture, $\epsilon_{||}$ increases continuously with decrease in temperature throughout the mesomorphic range (figure 5.7).

At the normal nematic-isotropic transition temperature (T_{NI}), both $\epsilon_{||}$ and $\epsilon_{\perp}$ change abruptly, signifying a first order phase transition. Beyond this temperature, ϵ_{is} increases with increase of temperature due to the decrease of antiparallel ordering of the molecules at higher temperatures.

The value of $\epsilon_{||}$, $\epsilon_{\perp}$ and $\Delta\epsilon$, taken at a common relative temperature of $(T_{NI} - 5)^{\circ}\text{C}$, (where T_{NI} is the

normal nematic-isotropic transition temperature) are given in table 5.2. It is seen that the anisotropy in the pure compounds is larger than that in the mixture. This difference is mainly due to the two COO bridging groups present in 11 CPMBB and 12 CPMBB, which enhance the parallel component of the dipole moment. Consequently the dielectric anisotropy will be higher.

TABLE 5.2

$\epsilon_{\parallel}$, $\epsilon_{\perp}$ and $\Delta\epsilon$ at a common relative temperature of $(T_{NI} - 5)^{\circ}\text{C}$

Compound	$\epsilon_{\parallel}$	$\epsilon_{\perp}$	$\Delta\epsilon$
11 CPMBB	17.30	7.00	10.30
12 CPMBB	16.87	6.67	10.20
6 OCB/8 OCB mixture	13.68	6.75	6.93

In all three systems studied, the average dielectric constant $\bar{\epsilon}$, evaluated from the measured values $\epsilon_{\parallel}$ and $\epsilon_{\perp}$, shows an unusual behaviour. In the nematic phase, $\bar{\epsilon}$, as is to be expected from the theory of antiferroelectric short range order,⁸ is less than the extrapolated isotropic

value (ϵ_{1s}). This difference is similar to that observed in other strongly polar compounds.^{10,11,23} As the temperature is decreased, $\bar{\epsilon}$ decreases throughout the nematic phase and over a part of the smectic phase. On further decrease of temperature, $\bar{\epsilon}$ starts which seems to signify a decrease in antiparallel ordering as the re-entrant nematic phase is approached. This is perhaps related in some way with the reversal in the sign of the thermal expansion of the layer spacing discussed in chapter IV. This increasing trend in $\bar{\epsilon}$ continues right through up to almost the lowest temperature of the re-entrant nematic phase where it practically merges with the extrapolated value of ϵ_{1s} . Also in all the three systems studied, the reversal in the trend of $\bar{\epsilon}$ occurs closer to the normal nematic-smectic A transition temperature (T_1) than to the smectic A - re-entrant nematic transition temperature (T_2).

It is also seen that the unusual behaviour of $\bar{\epsilon}$ is not at all reflected in the variation of $\epsilon_{\perp}$. For both the pure compounds and for the mixture, it shows a continuous decrease with decreasing temperature. On the other

hand, ϵ_{11} does not show such a smooth variation as discussed earlier. The maximum difference between *extrapolated* ϵ_{1s} and $\bar{\epsilon}$ is about 4% for 11 CPMBB, about 7% for 12 CPMBB, and about 3% for the mixture.

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