PRINCIPAL DIELECTRIC CONSTANTS OF RE-ENTRANT NEMATOGENS

5.1 Introduction

It was mentioned in earlier chapters that the re-entrant phenomenon was observed 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. Recently, this was confirmed in neutron studies of such compounds. An important consequence of antiparallel association of the molecules is that the mean dielectric constant \( \bar{\varepsilon} \) in the mesophase becomes less than the isotropic value \( (\varepsilon_{\text{is}}) \), because of the decrease in antiparallel ordering in the isotropic phase. Here \( \bar{\varepsilon} \), the average dielectric constant \( = \frac{1}{3}(\varepsilon_{\|} + 2\varepsilon_{\perp}) \) where \( \varepsilon_{\|} \) and \( \varepsilon_{\perp} \) are the principal dielectric constants measured parallel and perpendicular to the optic axis. Ratna and
Shaahidharr have experimentally verified that $\varepsilon$ is less than the extrapolated isotropic value in a number of cyano compounds. The experimental curves also showed that $\varepsilon$ as well as $\varepsilon_{is}$ 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 it 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 ($\varepsilon_{||}$ and $\varepsilon_{\perp}$) 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 (5CB) by measuring the dielectric constant ($\varepsilon_{12}$) 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 $\mu = 4.05$ debye acting along the long molecular axis.

The dielectric constants were measured using a Wayne Kerr B642 bridge and the refractive indices by the prism method using a goniometer spectrometer. The dipole moment $\mu$ is calculated using the Guggenheim equation.
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$\text{C} \equiv \text{N}$

$4'-n$-pentyl-4-cyanobiphenyl

($5 \text{ CB}$)

Figure 5.1

Structural formula of $5 \text{ CB}$
\[ \mu^2 = \frac{27kT}{4\pi N_A (\epsilon_1 + 2)(n_1^2 + 2)} \left( (\epsilon_{12} - n_{12}^2) - (\epsilon_1 - n_1^2) \right) / c \]

where \( N_A \) is the Avagadro number,
\( k \) the Boltzmann constant,
\( \epsilon_1 \) the dielectric constant of the solvent,
\( n_1 \) the refractive index of the solvent, and
\( C \) 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 5CB.

The dipole moment \( \mu \) of pure 5CB at 38°C is calculated using the Maier-Meier equation\(^{15}\)

\[ \epsilon = 1 + \frac{4\pi N_A f \hbar F}{M} \left( \bar{\alpha} + \frac{\mu^2}{3kT} \right) \]

where \( f \) 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
\[ \varepsilon = 10.62, \quad \rho = 1.007, \quad \alpha = 32.9 \times 10^{-24} \text{ cm}^3. \]

The dipole moments which are evaluated at different concentrations are plotted in figure 5.2. It is seen that with the decrease of concentration (or increase of dilution), the dipole moment \( \mu \) increases linearly at first. As the concentration decreases below about 10\%, the variation of \( \mu \) becomes much faster. For concentrations less than 5\%, \( \mu \) increases very rapidly. The value of \( \mu \) 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 CPMBB and a mixture of 35.8% by weight of 4'-n-hexyloxy-4-cyanobiphenyl (6 OCB) in 8 OCB. 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 | 76.5 |
| 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 cell 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
the direction of the magnetic field for $\varepsilon_\perp$ 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 a 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 ±0.025°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 ±0.025°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 $\varepsilon_\parallel$ and $\varepsilon_\perp$ 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 (B642) was used at 1592 Hz to determine the static dielectric constants. This frequency was high enough to avoid interfacial polarisation effects at the electrodes. 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 $\varepsilon_\parallel$ and $\varepsilon_\perp$ could be determined to an accuracy of 0.1%. The value of $\varepsilon_\parallel$ 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 $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\varepsilon_{is}$ 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, $\varepsilon_{\perp}$ decreases with decrease in temperature, starting from the nematic-isotropic transition point ($T_{NI}$). In the pure compounds, $\varepsilon_{\parallel}$ 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), $\varepsilon_{\parallel}$ decreases and the decrease continues through part of the smectic phase. A
Principal dielectric constants of 11 CPMEEB. \( \bar{\varepsilon} \) is the mean dielectric constant evaluated from the measured values of \( \varepsilon_n \) and \( \varepsilon_\perp \). The broken line is the extrapolation of \( \varepsilon_{1s} \).
Principal dielectric constants of 12 GPMHB
FIGURE 5.7

Principal dielectric constants of 6 OCB/8 OCB mixture
similar behaviour has been found by Bata and Buka\textsuperscript{22} in 4-nitrophenyl-4-octyloxybenzoate (NPOOB) which is also a strongly polar compound. The decrease of $\varepsilon_{||}$ 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, $\varepsilon_{||}$ increases continuously till the sample is cooled to the re-entrant nematic phase. In the mixture, $\varepsilon_{||}$ increases continuously with decrease in temperature throughout the mesomorphic range (figure 5.7).

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

The value of $\varepsilon_{||}$, $\varepsilon_{\perp}$ and $\Delta \varepsilon$, taken at a common relative temperature of $(T_{\text{NI}} - 5)\degree C$, (where $T_{\text{NI}}$ is the
normal nemato-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 CO.O 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_{\parallel}$</th>
<th>$\varepsilon_{\perp}$</th>
<th>$\Delta \varepsilon$</th>
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<tr>
<td>11 CPMBB</td>
<td>17.30</td>
<td>7.00</td>
<td>10.30</td>
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<tr>
<td>12 CPMBB</td>
<td>16.87</td>
<td>6.67</td>
<td>10.20</td>
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<td>6 OCB/8 OCB</td>
<td>13.68</td>
<td>6.75</td>
<td>6.93</td>
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<td>mixture</td>
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In all three systems studied, the average dielectric
constant $\tilde{\varepsilon}$, evaluated from the measured values $\varepsilon_{\parallel}$ and
$\varepsilon_{\perp}$, shows an unusual behaviour. In the nematic phase,
$\tilde{\varepsilon}$, as is to be expected from the theory of antiferroelectric
short range order, is less than the extrapolated isotropic
value ($\epsilon_{is}$). This difference is similar to that observed in other strongly polar compounds.\textsuperscript{10,11,23} As the temperature is decreased, $\tilde{\epsilon}$ decreases throughout the nematic phase and over a part of the smectic phase. On further decrease of temperature, $\tilde{\epsilon}$ starts increasing 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 $\tilde{\epsilon}$ continues right through up to almost the lowest temperature of the re-entrant nematic phase where it practically merges with the extrapolated value of $\epsilon_{is}$. Also in all the three systems studied, the reversal in the trend of $\tilde{\epsilon}$ 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 $\tilde{\epsilon}$ is not at all reflected in the variation of $\epsilon_{i\perp}$. For both the pure compounds and for the mixture, it shows a continuous decrease with decreasing temperature. On the other
hand, $\varepsilon_\parallel$ does not show such a smooth variation as
discussed earlier. The maximum difference between extra-
polated $\varepsilon_{is}$ and $\bar{\varepsilon}$ is about 4% for 11 CPMBB, about 7% for 12 CPMBB, and about 3% for the mixture.
References


