CHAPTER III

STUDIES ON DIELECTRIC PERMITTIVITY OF LIQUID CRYSTALS AND THEIR ORDER PARAMETERS.


**Introduction:**

Measurements of the anisotropy of dielectric permittivity of liquid crystals in mesophase provide, apart from being of practical importance, information on molecular properties and structure of these substances. The knowledge of dielectric constants $\varepsilon_1$ and $\varepsilon_2$ parallel and perpendicular to the long molecular axis helps us to select a liquid crystal for a specific electro-optical display device.

The dielectric anisotropy of nematic liquid crystals and the effects of electric and magnetic fields on dielectric properties have been the subject of many investigations. The principal dielectric constants for a series of alkoxy derivatives of azo and azoxy benzenes have been reported by Maier and Meier. The dispersion over a range of microwave and audio frequencies has been studied by Maier and Saupe and Axmann et al. Car and his coworkers have made an extensive study of molecular ordering due to electric and magnetic fields and also the dielectric loss.

The first theory relating the components of the dielectric permittivity tensor of ordered liquid crystal $\varepsilon_1$ and $\varepsilon_2$ to the dipole moment $\mu$, mean polarizability $\bar{\kappa}$, and the polarizability anisotropy $\Delta \kappa$ of the molecules was developed by W. Maier and G. Meier. They treated the liquid crystal to be a continuous isotropic medium. The local field inside the medium and the effective dipole moment was determined on the basis of Onsager model of spherical cavity of a volume equal to the mean volume per
single molecule in liquid crystal. The relevant equations connecting the dielectric permittivities with the order parameter according to Meier and Maier is given by:

\[ \varepsilon_\parallel = 1 + 4\pi N h F \left[ \frac{2}{3} \Delta \chi S + \frac{\mu^2}{3kT} \left\{ 1 - (1 - 3\cos^2 \beta) \right\} S \right] \]

\[ \varepsilon_\perp = 1 + 4\pi N h F \left[ \frac{2}{3} \Delta \chi S + \frac{\mu^2}{3kT} \left\{ 1 - \frac{1}{3} (1 - 3\cos^2 \beta) \right\} S \right] \]

\[ \Delta \varepsilon = 4\pi N h F \left[ \Delta \chi - \frac{\mu^2}{2kT} (1 - 3\cos^2 \beta) \right] S \]

\[ N = \text{The number of molecules/c.c.} \]

\[ h = \frac{\bar{\varepsilon}}{2\bar{\varepsilon} + 1} \quad \text{cavity field factor.} \]

\[ F = \frac{1}{1 - 2F} \quad \text{reaction field factor} \]

\[ f = \frac{4\pi N (2\bar{\varepsilon} + 2)}{3(2\bar{\varepsilon} + 1)} \]

\[ \mu = \text{dipole moment of free molecule.} \]

\[ \Delta \chi = \text{polarizability anisotropy.} \]

\[ \Delta \varepsilon = \text{dielectric anisotropy.} \]

\[ \beta = \text{angle formed by the permanent dipole moment of a molecule with the long axis.} \]

\[ S = \text{The degree of orientational ordering of the long axis of the nematic molecules.} \]

\[ \chi_\parallel \text{ is the polarizability along the long axis of the molecule and } \chi_\perp \text{ is the polarizability in the direction normal to the axis.} \]

From the measurements of dielectric constants \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) parallel and perpendicular to the long axis of the molecule de Jue
and Lathouwers observed that in the case of liquid crystals with small dipole moment, the average dielectric constant 
\[ \bar{\varepsilon} = \frac{1}{3} (\varepsilon_{\parallel} + 2\varepsilon_{\perp}) \] practically coincides with the dielectric constant \( \varepsilon_{\text{iso}} \) in the isotropic phase. This fact, they pointed out, was an indicator that Maier and Meier's, equations 1, 2, and 3 give qualitatively the correct picture of dielectric properties of liquid crystals with small dipole moment. For lack of polarizability anisotropy and dipole moment, they could not evaluate the order parameter of the liquid crystals. The object of the present studies is to evaluate the order parameter \( S \) of liquid crystals of both strongly and weakly polar molecules from the measurements of dielectric anisotropy using Maier and Meier's equations and to compare these \( S \) values with those obtained from birefringences.

**Experimental**

The dielectric properties of the samples which were studied as follows:

- CPBB, CPPOB from Eastman Kodak.
- E-4, E-5, E-7 from B.D.H. Chemicals.
- Mixtures E-5 is composed of pentylycyanobiphenyl, 5-CB, 7-CB, 5-OCB, 7-OCB, 8-OCB, in the proportion of 45:24:10:9:12. The nematic range is -8 degree C - 50 degree C.

The structural formulae and the nematic isotropic transition temperatures of the other liquid crystals are given in chapter II.
All the samples were used for the experiment without any further purification. The transition temperatures of these liquid crystals were checked under a hot stage polarizing microscope of \( \text{mettler} \).

**Measurement of the dielectric permittivity.**

The static dielectric constants were measured at frequencies 1 KHz and 10 KHz using a GR - 1620 capacitance bridge.

A parallel plate capacitor with stainless steel electrodes of dimension 2 cm × 1 cm separated by a 1mm teflon spacer, served as the sample holder. The temperature of the sample was measured with a thermocouple. The thermocouple was mounted directly on one of the electrodes so that exact temperature of the electrodes can be obtained. A magnetic field of 10 K gauss was used to align the liquid crystal molecules parallel and perpendicular to the electrode surfaces. The temperature of the sample holder was maintained constant within 0.2 degree C by means of a thermostat.

The cell was calibrated using freshly distilled toluene and 11 chlorobenzene and the values agree to 0.1% of the standard value. The resistivities of the samples were above 10 Ohms cm. Dispersion was not observed for any of the samples at 10 kHz.

All the measurements of dielectric permittivities were carried out while cooling the liquid crystal. This process helps in the alignment of the samples also the compounds C P B B and C P P O B being monotropic the anisotropic property could be observed
only while slow cooling from isotropic state.

**Results and Discussions**

The experimental values of the dielectric constants $\varepsilon_{||}$ and $\varepsilon_{\perp}$ of the liquid crystals studied in the nematic state and $\varepsilon_{iso}$ in the isotropic phase are given in the Tables 3.1(a) to 3.1(l). The values of the average dielectric constant $\bar{\varepsilon} = \frac{1}{3} (\varepsilon_{||} + 2 \varepsilon_{\perp})$ are also included in these tables. Variation of the dielectric anisotropy with temperature is shown in the figures 3.1(a) - 3.1(l).

The values of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ obtained in this study for phenyl cyclohexanes are found to be in fair agreement with those obtained by Pohl et al. Also the dielectric anisotropy of E - 7 nematic mixture given by Raynes is similar to the values of the present investigation.

From the Figures 3.1(a) to 3.1(c) and 3.1(h) to 3.1(l) it can be seen that the average dielectric constant $\bar{\varepsilon}$ is always less than the dielectric constant $\varepsilon_{iso}$ at $T < T_{NI}$ extrapolated in the nematic range from $T \geq T_{NI}$ in all the PCH liquid crystals, mixtures E-4, E-5, E-7 and the cyanophenyl benzoates. These results are in agreement with the dielectric permittivities reported earlier for alkyl cyanobiphenyl, P aminobenzonitriles and some other liquid crystals which have got strong dipole moment.

The suggestion for the higher value of the dielectric constant at the nematic isotropic transition given by Schadt is due to a second order flexo electric effect. However the
Table 3.1 (a)

Temperature variation of $\varepsilon_1$, $\varepsilon_2$, $\bar{\varepsilon}$, and $\varepsilon_{iso}$ at nematic and isotropic phases for FCH - 3.

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<tr>
<th>Temp degree C</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>$\varepsilon_{iso}$</th>
<th>$\bar{\varepsilon}$</th>
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### Table 3.1 (b)

Temperature variation of $\varepsilon_{\|}$, $\varepsilon_{\perp}$, $\varepsilon$ and $\varepsilon_{\text{iso}}$ at nematic and isotropic phases for FCH - 5

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<th>$\varepsilon_{\perp}$</th>
<th>$\varepsilon_{\text{iso}}$</th>
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Dielectric Const. $\varepsilon$

$\varepsilon_{\parallel}$

$\varepsilon_{\perp}$

$\varepsilon_\ast$

$\varepsilon_{iso}$

Temp $T^\circ C$

Fig. 3.1 b
Temperature variation of $\varepsilon_{\parallel}$, $\varepsilon_\perp$, $\bar{\varepsilon}$ and $\varepsilon_{\text{iso}}$ at nematic and isotropic phases for FCH-7.

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<th>Temp degree $^\circ$C</th>
<th>$\varepsilon_{\parallel}$</th>
<th>$\varepsilon_\perp$</th>
<th>$\varepsilon_{\text{iso}}$</th>
<th>$\bar{\varepsilon}$</th>
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DIELECTRIC CONST. \( \varepsilon \)

\begin{align*}
\text{PCH - 7} & \\
\text{TEMP } ^\circ\text{C} & \\
\text{fig. 31c} & \\
\end{align*}
Table 3.1 (69)

Temperature variation of $\varepsilon_\parallel$, $\varepsilon_\perp$, $\varepsilon$ and $\varepsilon$ iso at nematic and isotropic phases for D 302.

<table>
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<th>$\varepsilon_\perp$</th>
<th>$\varepsilon$ iso</th>
<th>$\bar{\varepsilon}$</th>
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### Table 3.1 (C)

Temperature variation of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, $\overline{\varepsilon}$, and $\varepsilon_{150}$ at nematic and isotropic phases for 1402.

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<tr>
<th>Temp degree C</th>
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<th>$\varepsilon_{\perp}$</th>
<th>$\varepsilon_{150}$</th>
<th>$\overline{\varepsilon}$</th>
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Temperature variation of $\varepsilon_{ Nir}, \varepsilon_{Nir}, \varepsilon_{iso}$ and $\varepsilon_{iso}$ at nematic and isotropic phases for D-501.

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<tr>
<th>Temp degree C</th>
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</table>
D 501

TEMP T°C

fig. 3.14

DELECTRIC CONST. ε
Table 3.1 (q)
Temperature variation of $\varepsilon_{nn}$, $\varepsilon_{L}$, $\overline{\varepsilon}$ and $\varepsilon_{iso}$ at nematic and isotropic phases for D55

<table>
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<th>Temp degree $^\circ$C</th>
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Table 3.1

Temperature variation of $\varepsilon_{II}$, $\varepsilon_{II}$, $\varepsilon$ and $\varepsilon$ iso at nematic and isotropic phases for CF8

<table>
<thead>
<tr>
<th>Temp degree C</th>
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DIELECTRIC CONST \( \varepsilon \)

Fig. 31h

TEMP TC

\( \varepsilon_{iso} \)

\( \varepsilon_1 \)

\( \varepsilon_{11} \)
Table 3.1 (\(\omega\))
Temperature variation of \(\varepsilon_{\|}, \varepsilon_{\perp}, \varepsilon_{\text{iso}}\) and \(\bar{\varepsilon}\) at nematic and isotropic phases for CFPQB.

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<th>(\varepsilon_{\perp})</th>
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<th>(\bar{\varepsilon})</th>
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<td>9.033</td>
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<tr>
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<td>6.692</td>
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<td>8.901</td>
</tr>
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<td></td>
<td>8.927</td>
</tr>
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<td>14.536</td>
<td>6.215</td>
<td></td>
<td>8.9887</td>
</tr>
<tr>
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<td>14.964</td>
<td>6.853</td>
<td></td>
<td>9.0233</td>
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<td>5.811</td>
<td></td>
<td>8.9887</td>
</tr>
</tbody>
</table>
Table 3.1 (j)

Temperature variation of $\varepsilon_{ii}$, $\varepsilon_{44}$, $\varepsilon_{iso}$ and $\varepsilon$ iso at nematic and isotropic phases for E4

<table>
<thead>
<tr>
<th>Temp degree C</th>
<th>$\varepsilon_{ii}$</th>
<th>$\varepsilon_{44}$</th>
<th>$\varepsilon_{iso}$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>17.8666</td>
<td>5.7077</td>
<td></td>
<td>9.7607</td>
</tr>
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<td>17.7035</td>
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<td>40</td>
<td>17.4898</td>
<td>5.9470</td>
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<td>9.7946</td>
</tr>
<tr>
<td>45</td>
<td>17.0416</td>
<td>6.1375</td>
<td></td>
<td>9.7722</td>
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<tr>
<td>50</td>
<td>16.5517</td>
<td>6.4541</td>
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<td>9.8200</td>
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<td>15.2750</td>
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<td>9.6865</td>
</tr>
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<td>62.5</td>
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<td></td>
<td>10.3517</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td></td>
<td></td>
<td>10.4811</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td>10.3517</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td>10.2922</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td></td>
<td></td>
<td>10.1196</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3.11
Table 3.1

Temperature variation of $\varepsilon_n$, $\varepsilon_4$, $\varepsilon$ and $\varepsilon$ iso at nematic and isotropic phases for E5.

<table>
<thead>
<tr>
<th>Temp degree C</th>
<th>$\varepsilon_n$</th>
<th>$\varepsilon_4$</th>
<th>$\varepsilon$ iso</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>19.5601</td>
<td>6.3904</td>
<td></td>
<td>10.7803</td>
</tr>
<tr>
<td>35</td>
<td>19.1767</td>
<td>6.5500</td>
<td></td>
<td>10.7589</td>
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<td>38</td>
<td>18.9017</td>
<td>6.6940</td>
<td></td>
<td>10.7632</td>
</tr>
<tr>
<td>41</td>
<td>18.4750</td>
<td>6.9244</td>
<td></td>
<td>10.7746</td>
</tr>
<tr>
<td>44</td>
<td>17.9964</td>
<td>7.1928</td>
<td></td>
<td>10.774</td>
</tr>
<tr>
<td>47</td>
<td>17.2702</td>
<td>7.5969</td>
<td></td>
<td>10.8147</td>
</tr>
<tr>
<td>51</td>
<td></td>
<td></td>
<td></td>
<td>11.1553</td>
</tr>
<tr>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td>11.1970</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td>11.1851</td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td>11.1591</td>
</tr>
<tr>
<td>68</td>
<td></td>
<td></td>
<td></td>
<td>11.1100</td>
</tr>
</tbody>
</table>
Figure 3.1k: A graph showing the dielectric constant (ε) versus temperature (TEMP °C). The graph includes data points for different orientations: ε∥, ε⊥, and εiso. The dielectric constant values range from 6 to 19 across the temperature range of 40 to 70 °C.
Temperature variation of \( \varepsilon_{\parallel} \), \( \varepsilon_{\perp} \), \( \varepsilon \) and \( \varepsilon_{\text{iso}} \) at nematic and isotropic phases for E-7

<table>
<thead>
<tr>
<th>Temp degree $^\circ$C</th>
<th>$\varepsilon_{\parallel}$</th>
<th>$\varepsilon_{\perp}$</th>
<th>$\varepsilon_{\text{iso}}$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>19.5836</td>
<td>5.5488</td>
<td>10.2271</td>
<td></td>
</tr>
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<td>30</td>
<td>19.0425</td>
<td>5.6872</td>
<td>10.1403</td>
<td></td>
</tr>
<tr>
<td>35</td>
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<td>5.9099</td>
<td>10.0904</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>18.2208</td>
<td>6.0050</td>
<td>10.0769</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>17.7369</td>
<td>6.2080</td>
<td>10.0510</td>
<td></td>
</tr>
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<td>50</td>
<td>17.0681</td>
<td>6.5491</td>
<td>10.0528</td>
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</tr>
<tr>
<td>55</td>
<td>16.1613</td>
<td>7.2163</td>
<td>10.1980</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>*</td>
<td></td>
<td>10.5902</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td></td>
<td></td>
<td>10.6150</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td>10.5553</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td>10.4952</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td></td>
<td></td>
<td>10.3511</td>
<td></td>
</tr>
</tbody>
</table>
The explanation given by Madhusudana and Chandrasekhar is that the increase in the dielectric constant of the isotropic phase arises from the decrease in the antiferroelectric short range order at $T_N$. For liquid crystals having small and zero dipole moment it was shown by de Jeu et al that $\varepsilon$ coincides with the dielectric constant $\varepsilon_{iso}$ at the clearing temperature. From figures 3,1 d tc 3.1 g it can be noted that the average dielectric constants in the nematic phase for the alkyl/alkoxy phenylcyclohexane carbonylate liquid crystals practically coincide with the dielectric constants in the isotropic phase. These samples have a small dipole moment.

The dipole moments $\mu$ of the liquid crystals were determined in dilute solution of benzene and are included in the Tables 3.2.

$$\mu^2 = \frac{9 kT}{4 \pi N} \frac{\varepsilon_\infty - \varepsilon_x}{\varepsilon_\infty - \frac{\varepsilon_x}{2}} \left[ \varepsilon_\infty - \varepsilon_x \right]$$

0.1 cc of sample was mixed with 0.9 cc of benzene. The refractive index of the solution $\eta_d$ was observed, $\varepsilon_x = \eta_d^2$.

The dielectric permittivity of the solution $\varepsilon_\infty$ was also found. $T$ is the temperature of the solution given in kelvin, $k$ is the Boltzmann's constant.

$$N = \text{Avogadro's number}, \quad \rho = \text{density of the sample at a particular temperature}.$$
the resultant moment and the long axis of the molecules of the liquid crystals for alkyl cyanophenyles were negligible. Also the $\beta$ value for the mixtures E-4 and E-7 containing 55 to 70% of P-alkyl cyanobiphenyl were very small and assumed to be zero. In case of samples D-302, D-402, D-501 and D-55 the $\beta$ value was calculated from the alkoxy group moment and ester group moment reported in the literature. The angle $\beta$ for CPBB and CPPOB was estimated from the P-heptyl P cyanobiphenyl $\mu_D^P = 4.55$ and ester group moment of $\mu_D^{17}$ making an angle of 66 degree with the paraaxis. The value of the angle $\beta$ for each sample is included in the tables 3.2.

For the samples PCH-3, PCH-5, PCH-7, CPBB, CPPOB, E-4, E-7 we find from the Tables 3.2 (a, b, c, h, i, j and 1) that the values of the order parameters calculated from experimental results of dielectric anisotropy $\Delta \varepsilon$ using Maier and Meier's equation \( \varepsilon \) comes out to be much less than that obtained from birefringence or other methods. Similar results were reported earlier in the case of cyanobiphenyls and cyanophenyl heptyl benzoate.

Thus the results show that Maier and Meier's theory for dielectric constants in anisotropic media of strongly polar molecules fails to give consistent results with the experimental values. This is due to the fact that only long range order was considered in Maier and Meier's theory, existence of short range
TABLE 3.2 (a)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for FCH-3.

<table>
<thead>
<tr>
<th>T C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>9.68</td>
<td>.61</td>
<td>.20</td>
</tr>
<tr>
<td>43.5</td>
<td>9.19</td>
<td>.60</td>
<td>.19</td>
</tr>
<tr>
<td>44</td>
<td>8.92</td>
<td>.58</td>
<td>.18</td>
</tr>
<tr>
<td>44.5</td>
<td>8.49</td>
<td>.57</td>
<td>.18</td>
</tr>
<tr>
<td>45</td>
<td>8.02</td>
<td>.55</td>
<td>.17</td>
</tr>
</tbody>
</table>

$\mu_D = 4.27 \quad \beta \sim 0^*$

TABLE 3.2 (b)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for FCH-5.

<table>
<thead>
<tr>
<th>T C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>9.93</td>
<td>.65</td>
<td>.32</td>
</tr>
<tr>
<td>35</td>
<td>9.54</td>
<td>.63</td>
<td>.31</td>
</tr>
<tr>
<td>39</td>
<td>9.18</td>
<td>.61</td>
<td>.30</td>
</tr>
<tr>
<td>43</td>
<td>8.83</td>
<td>.56</td>
<td>.29</td>
</tr>
<tr>
<td>48</td>
<td>8.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>7.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\mu_D = 4.27 \quad \beta \sim 0^*$
## TABLE 3.2 (c)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for PCH - 7.

<table>
<thead>
<tr>
<th>T.C.</th>
<th>$\Delta \varepsilon$</th>
<th>$S$ from refined</th>
<th>$S$ from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>8.67</td>
<td>.58</td>
<td>.31</td>
</tr>
<tr>
<td>35</td>
<td>8.33</td>
<td>.55</td>
<td>.30</td>
</tr>
<tr>
<td>39</td>
<td>8.12</td>
<td>.50</td>
<td>.29</td>
</tr>
<tr>
<td>43</td>
<td>7.84</td>
<td>.49</td>
<td>.29</td>
</tr>
<tr>
<td>48</td>
<td>7.41</td>
<td>.47</td>
<td>.29</td>
</tr>
<tr>
<td>52</td>
<td>6.92</td>
<td>.45</td>
<td>.29</td>
</tr>
<tr>
<td>56</td>
<td>6.03</td>
<td>.43</td>
<td>.29</td>
</tr>
</tbody>
</table>

$\mu_D = 4.39 \quad \beta \sim 0^\circ$

## TABLE 3.2 (d)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for D - 302.

<table>
<thead>
<tr>
<th>T.C.</th>
<th>$\Delta \varepsilon$</th>
<th>$S$ from refined</th>
<th>$S$ from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>-1.2631</td>
<td>.75</td>
<td>.69</td>
</tr>
<tr>
<td>54.5</td>
<td>-1.2352</td>
<td>.72</td>
<td>.68</td>
</tr>
<tr>
<td>60</td>
<td>-1.1780</td>
<td>.71</td>
<td>.67</td>
</tr>
<tr>
<td>66</td>
<td>-1.1131</td>
<td>.66</td>
<td>.64</td>
</tr>
<tr>
<td>72</td>
<td>-0.9244</td>
<td>.60</td>
<td>.55</td>
</tr>
<tr>
<td>77</td>
<td>-0.8333</td>
<td>.53</td>
<td>.50</td>
</tr>
<tr>
<td>80</td>
<td>-0.5809</td>
<td>.50</td>
<td>.50</td>
</tr>
</tbody>
</table>

$\mu_D = 2.17 \quad \beta \sim 72^\circ$
TABLE 3.2 (a)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for D - 402

<table>
<thead>
<tr>
<th>$^\circ$C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>-1.2227</td>
<td>.73</td>
<td>.74</td>
</tr>
<tr>
<td>52</td>
<td>-1.1252</td>
<td>.67</td>
<td>.72</td>
</tr>
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<td>59.5</td>
<td>-0.9763</td>
<td>.62</td>
<td>.64</td>
</tr>
<tr>
<td>69</td>
<td>-0.7711</td>
<td>.53</td>
<td>.53</td>
</tr>
<tr>
<td>73</td>
<td>-0.6607</td>
<td>.46</td>
<td>.46</td>
</tr>
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</table>

$\mu = 2.08 \quad \beta \sim 72^\circ$

TABLE 3.2 (b)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for D - 501

<table>
<thead>
<tr>
<th>$^\circ$C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>-1.13</td>
<td>.73</td>
<td>.73</td>
</tr>
<tr>
<td>47</td>
<td>-1.008</td>
<td>.72</td>
<td>.72</td>
</tr>
<tr>
<td>51</td>
<td>-1.01</td>
<td>.71</td>
<td>.68</td>
</tr>
<tr>
<td>55</td>
<td>-0.9241</td>
<td>.68</td>
<td>.64</td>
</tr>
<tr>
<td>60.5</td>
<td>-0.8503</td>
<td>.63</td>
<td>.60</td>
</tr>
<tr>
<td>65</td>
<td>-0.7684</td>
<td>.59</td>
<td>.55</td>
</tr>
<tr>
<td>70</td>
<td>-0.5569</td>
<td>.49</td>
<td>.43</td>
</tr>
</tbody>
</table>

$\mu = 2.23 \quad \beta \sim 68^\circ$
### TABLE 3.2 (g)
Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for $D = 55$

<table>
<thead>
<tr>
<th>T°C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.5</td>
<td>-0.479</td>
<td>0.67</td>
<td>0.61</td>
</tr>
<tr>
<td>40</td>
<td>-0.438</td>
<td>0.65</td>
<td>0.57</td>
</tr>
<tr>
<td>42</td>
<td>-0.424</td>
<td>0.61</td>
<td>0.55</td>
</tr>
<tr>
<td>44</td>
<td>-0.367</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>46</td>
<td>-0.317</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\mu_D = 1.99 \quad \beta \sim 65^\circ$

### TABLE 3.2 (h)
Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for CF88.

<table>
<thead>
<tr>
<th>T°C.</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>9.499</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>11.899</td>
<td>0.52</td>
<td>0.32</td>
</tr>
<tr>
<td>38</td>
<td>12.946</td>
<td>0.56</td>
<td>0.34</td>
</tr>
<tr>
<td>36.5</td>
<td>13.354</td>
<td>0.59</td>
<td>0.35</td>
</tr>
<tr>
<td>35</td>
<td>13.959</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>14.120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\mu_D = 5.1 \quad \beta \sim 25^\circ$
TABLE 3.2 (i)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for CFPOB.

<table>
<thead>
<tr>
<th>T°C</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>S from $\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.5</td>
<td>6.627</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75.5</td>
<td>7.551</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>8.321</td>
<td>.49</td>
<td>.28</td>
</tr>
<tr>
<td>70.5</td>
<td>8.911</td>
<td>.52</td>
<td>.30</td>
</tr>
<tr>
<td>67.5</td>
<td>9.533</td>
<td>.56</td>
<td>.32</td>
</tr>
</tbody>
</table>

$\Delta_D = 5.57$  \quad \beta \sim 30$ degree.
TABLE 3.2 (a)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for $E - 4$.

<table>
<thead>
<tr>
<th>T°C</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>12.1589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>11.8791</td>
<td>.65</td>
<td>.23</td>
</tr>
<tr>
<td>40</td>
<td>11.5428</td>
<td>.63</td>
<td>.23</td>
</tr>
<tr>
<td>45</td>
<td>10.9041</td>
<td>.60</td>
<td>.22</td>
</tr>
<tr>
<td>50</td>
<td>10.0976</td>
<td>.57</td>
<td>.21</td>
</tr>
<tr>
<td>55</td>
<td>8.3798</td>
<td>.52</td>
<td>.18</td>
</tr>
</tbody>
</table>

$M = 5.1$ $B \sim 0$ degree.

TABLE 3.2 (b)

Temperature variation of the Dielectric anisotropy $\Delta \varepsilon$ and order parameter $S$ for $E - 7$.

<table>
<thead>
<tr>
<th>T°C</th>
<th>$\Delta \varepsilon$</th>
<th>S from ref.ind.</th>
<th>$\Delta \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>10.2270</td>
<td>.72</td>
<td>.16</td>
</tr>
<tr>
<td>30</td>
<td>10.1403</td>
<td>.69</td>
<td>.15</td>
</tr>
<tr>
<td>35</td>
<td>10.0983</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>10.0769</td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>10.0569</td>
<td>.60</td>
<td>.14</td>
</tr>
<tr>
<td>50</td>
<td>10.0327</td>
<td></td>
<td></td>
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<tr>
<td>55</td>
<td>10.1979</td>
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</tbody>
</table>

$K = 4.5$ $B \sim 0^\circ$
order was completely ignored. Madhusudan in his theory proposed
the existence of antiferroelectric short range order in nematic
phase of strongly polar molecules. Such short range antiparallel
ordering in strongly polar nematic liquid crystals might cause a
large decrease in $\varepsilon_{||}$ resulting in a decrease in the dielectric
anisotropy $\Delta \varepsilon$ and thus a decrease in the order parameter.

From the tables 3.2 (d, e, f, g) it can be seen that the
values of the order parameter calculated from the values of the
dielectric anisotropy $\Delta \varepsilon$ polarizability anisotropy $\Delta \kappa$ and dipole
moment $\mu$ using the Maier and Meier equation for the alkoxyphenyl
trans - 4' alkylcyclohexane carboxylates, compare very well at all
temperatures with those obtained from refractive index methods.
Similarly for alkylphenyl trans - 4' alkylcyclohexane carboxylates
the order parameter $S$ from the Maier and Meier equation also
agree well with those obtained from the refractive index methods
though the former values are only slightly less than the latter.
The slight discrepancy may be due to the estimation of the angle
$\beta$ made by the resultant moment with the long axis of the molecule.
So, it appears that for liquid crystals having dipole moment $\mu$
about 2D or so the Maier and Meier equation with dielectric
anisotropy provides another method for the determination of the
order parameter.

The decrease in $\varepsilon_{||}$ as proposed by Madhusudan and
Chandrasekhar due to short range antiferroelectric dipole
correlation of the permanent dipole moment in less polar nematic
might not affect the dielectric anisotropy and hence the order parameter very effectively.

It is now well known that at the nematic isotropic phase transition the long range nematic ordering vanishes, but short range ordering still persists well into isotropic phase influencing some physical properties such as magnetic birefringence, Kerr constant, light scattering, dielectric permittivity etc. just near the transition temperature. We have observed such pretransitional effect in dielectric permittivity of two monotropic liquid crystals CPBB and CPPOB and three thermotropic liquid crystals E-4, E-5 and E-7.

The pretransitional effects in dielectric permittivity in the liquid crystals are shown in Figure 3.3 (a-1). When temperature dependance of dielectric permittivity $\varepsilon_{\text{iso}}$ over wide range of temperature is illustrated. It can be clearly seen that there is peak in $\varepsilon_{\text{iso}}$ value a little above the transition temperature $T_{\text{NI}}$. Similar pretransitional effects in dielectric constant in nematics with Cyano end groups were reported by Bradshaw, and Raynes and Thoen J and Menu G. Normally the $\varepsilon_{\text{iso}}$ should monotonically increase with decrease of temperature in proportion to $\mu^2/kT$ upto the transition temperature $T_{\text{NI}}$. But instead, a maximum in $\varepsilon_{\text{iso}}$ is observed a little above $T_{\text{NI}}$ and then decreases as $T_{\text{NI}}$ is approached. The reduced contribution to dielectric permittivity $\varepsilon_{\text{iso}}$ from dipole moment $\mu$ is attributed to apparent reduction in $\mu$ value due to the formation of dimers in anti...
parallel local ordering. The pretransitional $\xi_{iso} \sim T_{N_2}$ showing a maximum may be due to appreciable concentration of dimers in a dynamic monomer dimer equilibrium.
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