

Chapter 4

Confinement effects on a highly polar compound

4.1 Introduction

In this chapter we report some measurements on the highly polar compound p-cyanophenyl p-n heptylbenzoate (CP7B). The chemical structure and the transition temperatures of the compound are shown in Figure 4.1. As seen from the chemical structure of the molecule, it has a large dipole moment due to the additive contributions from both the cyano and ester groups. In an earlier investigation, high electric field experiments have been conducted on this compound. Electric field enhances the order parameter. One of the interesting experimental results reported on

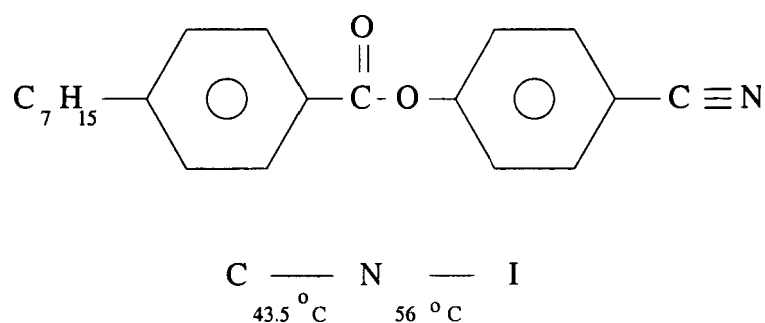


Fig. 4.1: Chemical structure and transition temperatures of CP7B.

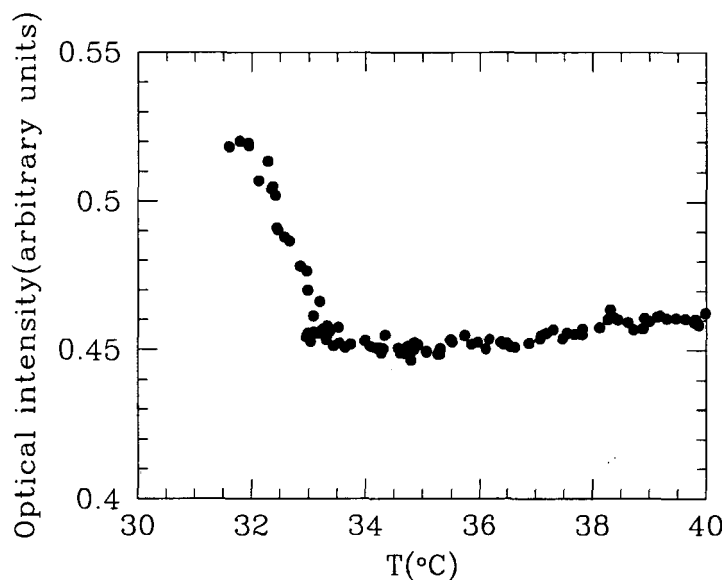


Fig. 4.2: Temperature variation of the light scattered from twist fluctuations in a $10\mu\text{m}$ thick sample of CP7B subjected to 180 V, $f=4111$ Hz.

this compound [35] is the presence of polar short range order in the medium. The authors also report a field induced nematic-nematic phase transition in this compound. They found that the intensity of light scattered from the medium showed a sharp increase at -33°C when the sample was cooled under a field of ~ 600 esu (see Fig. 4.2). The transition probably indicates a jump in the concentration of neighbours with parallel configurations compared to those with antiparallel configurations in the low temperature nematic. The nematic-nematic transition perhaps occurs in this compound at a temperature well below the ambient in the absence of any field. i.e. when the order parameter is sufficiently large. The strong electric fields enhance the order parameter to the required value above the ambient temperature and the transition is seen at -32°C for an electric field of -600 esu. The nematic-nematic transition is a weak first order transition as the macroscopic symmetry of the two nematics is the same.

Highly polar compounds exhibit unusual phenomena like double reentrance of

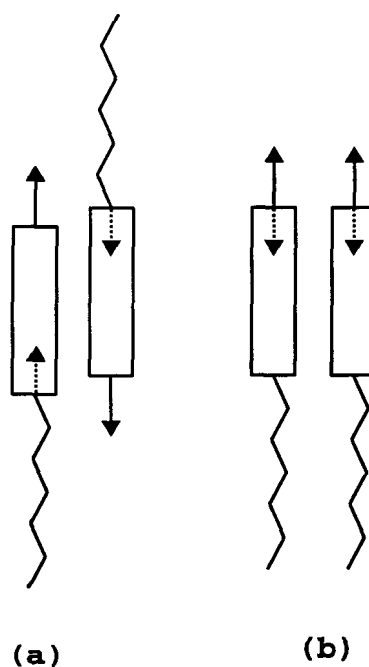


Fig. 4.3: Schematic diagram showing two polar molecules, in antiparallel 'A' configuration at intermediate inter-molecular separations (a) and a parallel 'P' configuration at relatively low values of inter-molecular separation. The arrow head at the end of the solid line indicates the permanent dipole. The one with the dotted line is the dipole induced by the permanent dipole of the neighbouring molecule.

nematic and smectic A liquid crystalline phases and polymorphism of smectic A liquid crystals [1]. At higher temperatures the antiparallel arrangement is such that the aromatic cores overlap and the layer spacing corresponds to a length $\approx a+2c$, where a is the length of the aromatic core and c that of the chain [36, 37] giving rise to a partial bilayer structure (Fig. 4.3). At lower temperatures, the spacing tends towards the molecular length ($\approx a+c$). There is a competition between ordering at these two different lengths. Prost [1, 38] has developed a phenomenological Landau theory which couples the smectic order parameters corresponding to these two lengths. One of the predictions of this model is the occurrence of a nematic-nematic(N-N) transition which is a continuation of a smectic A-smectic A transition in which there is a jump in the layer spacing. Indeed using specific heat measurements such a nematic-nematic transition has been reported earlier in a binary mixture of strongly polar compounds [39].

The physical origin of the monomolecular length at low temperatures has been discussed using different molecular models [40, 41]. In particular, it has been pointed out that at higher densities, there can be a change in intermolecular configuration from an antiparallel to a parallel association [41, 42, 43]. The electrostatic interaction between strong dipoles of neighbouring molecules favours antiparallel orientation between them. The aromatic cores of the molecules have large polarisabilities and the strong dispersion interaction between such cores of neighbouring molecules leads to an antiparallel structure shown in Fig. 4.3a. In this configuration the effective dipole moment of the molecule is enhanced, as the dipole moment induced by permanent dipole of the neighbouring molecule is parallel to the permanent dipole of the given molecule. On the other hand the chains are so far apart that the dispersion interaction between the chains of two neighbours is negligibly small. The interaction energy between permanent dipoles is $\propto 1/r^3$ where r is the intermolecular

separation. When the molecules are in the parallel configuration (see Fig. 4.3b) the dispersion interaction energy between the aromatic cores is $\propto 1/r^6$. The permanent dipolar interaction is now repulsive. The dipole induced in the aromatic core of a given molecule by the neighbouring molecular dipole is opposite to the permanent dipole of the former. Hence the net dipolar repulsive interaction is reduced. At the same time, the chains of neighbouring molecules which now lie next to each other contribute to the attractive interaction. As both the dipole-induced dipole and the dispersion interactions between the chains are $\propto 1/r^6$, at higher densities, the parallel configuration can be favoured, thus producing a polar short range order in the medium [40, 41]. As mentioned above, evidence for such a short range order has been found recently from high electric field experiments on a strongly polar compound [35]. It is clear that highly polar compounds prefer to have antiparallel pairs at higher temperatures and parallel configurations at lower temperatures [41, 42, 43]. The two configurations (see Figure 4.3) naturally account for the two length scales in the Landau theory developed by Prost [44]. The McMillan parameter which is a measure of the layering interaction is larger for the antiparallel type of pairs compared to that for the parallel type of pairs. A molecular statistical theory of the reentrant phases on the basis of the Mcmillan model has been developed using these ideas [41]. This model has been recently extended to account for a nematic-nematic phase transition exhibited by polar compounds [42]. The nematic-nematic transition is due to a jump in the relative concentration of the two types of intermolecular configurations.

It is likely that the electric field increases the N-N transition temperature in CP7B, because of an enhancement in the orientational order parameter rather than inducing that transition. We looked for an evidence for the same in the absence of the electric field. We found that surfaces induce additional order in thin cells

and bring to light the N-N transition. We have also studied the effect of transverse fields on this nematic-nematic transition. In this chapter we describe the following experimental studies on CP7B. a) Transmitted intensity has been measured as a function of temperature for cells of varying thickness. These studies clearly indicate a nematic-nematic transition in thin cells. The transition temperature increases as the thickness of the cell decreases. We interpret this as a nematic-nematic transition due to the change in the short range order of the medium as discussed above. b) Transmitted intensity has been measured with temperature at different magnetic fields applied along the director. The nematic-nematic transition temperature increases by $\sim 4.5^{\circ}\text{C}$ when a field of 5 Tesla is applied. c) Transmitted intensity has also been measured with temperature at different transverse electric fields. When a square wave of 300 volts is applied across a gap of 1mm the transition temperature increases by $\sim 0.5^{\circ}\text{C}$. d) Birefringence has been measured as a function of temperature in cells of different thicknesses. The birefringence and hence the order parameter is enhanced by $\sim 16\%$ in a thin cell compared to a thick cell for both CP7B and another weakly polar compound.

4.2 Experimental setup

The cell was constructed using two flat glass plates which were stuck together using a special glue meant for display devices. The glue did not interact with liquid crystals. The glass plates were treated with polyimide and rubbed unidirectionally for homogeneous alignment of the sample. The thickness of the cell was measured using channel spectrum (section 1.12). The overall accuracy was $\pm 1\%$. The cell was filled with the compound CP7B in the isotropic phase. It was mounted in a HS1 hot stage, which itself was placed on the rotating stage of a Leitz polarising microscope (model ORTHOPLAN). The nematic phase could be supercooled to

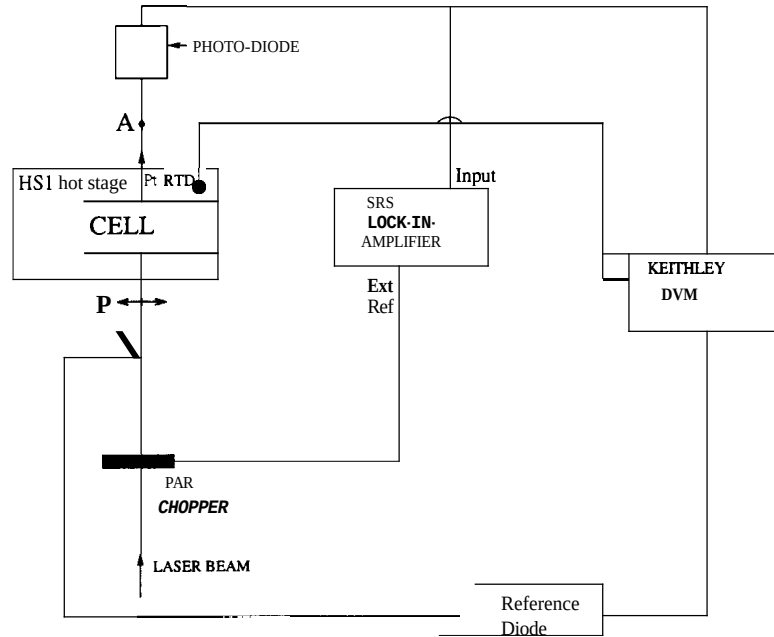


Fig. 4.4: Optical setup for the transmission studies using the polarising microscope.

room temperature. The temperature of the sample was controlled using an Instec MK1 temperature controller. The temperature stability was better than 10mK. A platinum resistance thermometer placed close to the sample was used to measure the sample temperature accurately. The optical setup is shown in Figure 4.4. A helium neon laser (ORIEL 3 mW, $\lambda = 0.6328 \times 10^{-4}$ cm), was mounted on a stand with levelling screws which can be used to adjust the orientation of the laser beam. The stability of the laser beam was monitored by a reference photodiode. The laser beam was passed through a polariser and was allowed to be incident on the sample. Then it was passed through an analyser which was crossed with respect to the polariser. The transmitted intensity was measured by a photodiode. The microscope stage was rotated so that the director makes an angle of 45° with the crossed polarisers. In these experiments we have used a SRS830 lock-in amplifier in

conjunction with the PAR chopper to accurately measure the transmitted intensity. The whole experimental setup was automated using a 486 PC. The transmitted intensity was measured as a function of temperature both in the heating mode as well as in the cooling mode. The readings were taken at temperature intervals of 0.1°C . The experiment was performed for cells of a few different thicknesses.

4.3 Birefringence measurement.

The temperature dependence of the birefringence of this compound was measured for a thick cell as well as for a thin cell. For the thick cell ($\sim 25\mu\text{ m}$) the transmitted intensity I was measured as a function of temperature using the experimental setup described in section 4.2. The birefringence could be measured using the transmitted intensity data. The experiment was performed for maximum intensity setting or in other words the angle made by the optic axis with the plane of polarisation of the incident beam is 45° . The transmitted intensity and $\Delta\phi$ the optical phase difference between the extraordinary and the ordinary rays are given by

$$I = \frac{I_o}{2}(1 - \cos \Delta\phi), \quad (4.1)$$

where

$$\Delta\phi = \frac{2\pi}{\lambda} \Delta n d, \quad (4.2)$$

$\Delta n = n_e - n_o$ where n_e and n_o are the extraordinary and ordinary refractive indices of the nematic, d the thickness of the sample and λ the wavelength of light used ($0.6328\mu\text{m}$). In thick cells the intensity I measured using the above setup showed many maxima and minima as a function of temperature. Hence I_o corresponds to the intensity at the maxima. The order of the maximum was determined from the available refractive index measurements [45]. Using the intensity data Δn was calculated at different temperatures. In the case of a thin cell ($\sim 1.5\mu\text{m}$) the

transmitted intensity measurement in the temperature range from the isotropic to room temperature did not show any maximum or minimum. We found it more accurate to use a quarter wave plate to measure the absolute birefringence of the sample. A quarter wave plate was inserted in the appropriate slot of the polarising microscope and the polariser was adjusted such that the slow axis of the quarter wave plate was perpendicular to the polariser. The analyser was crossed with respect to the polariser. The microscope stage was rotated so that the director made an angle of 45° with the crossed polarisers. At each temperature the analyser was rotated manually to obtain minimum intensity. As this angle corresponds to $2\Delta\phi$ [46], the birefringence A_n can be calculated at different temperatures.

As mentioned above transmitted intensity measurements were performed by applying transverse magnetic and electric fields. We will describe the experimental arrangements used in these measurements in the next two sections.

4.4 **Measurements using a superconducting magnet**

The block diagram of the experimental setup is shown in Fig. 4.5.. We have performed the measurements in a homogeneously aligned CP7B sample of thickness $\sim 1.9 \mu\text{m}$. The cell was placed in a heater specifically constructed for this setup. A platinum resistance thermometer placed close to the sample was used to measure the temperature. The temperature was manually controlled by adjusting the voltage from the power supply to the heater. The heater was mounted in the center of the super conducting magnet consisting of three dewars with fused quartz windows. The specifications of the magnet(Oxford make) are a) maximum central magnetic field of 7Tesla b) field/current ratio is 0.0979T/A. The current flowing through the magnet can be directly measured and hence the corresponding magnetic field can be

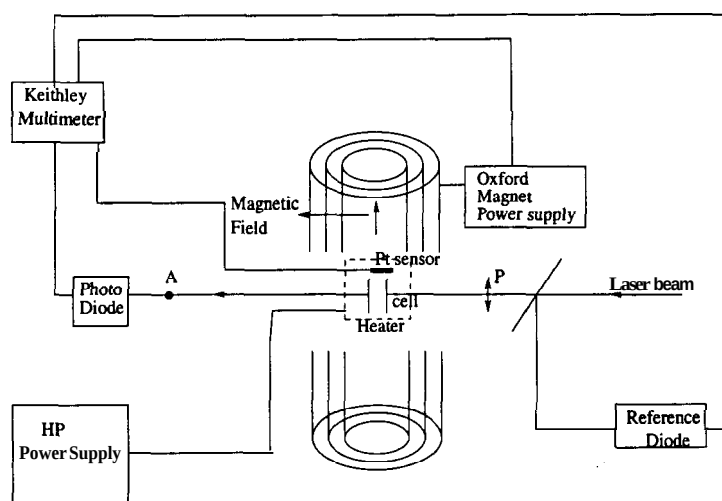


Fig. 4.5: Block diagram of the experimental setup using the super conducting magnet.

calculated. The polariser was crossed with respect to the analyser before mounting the sample. The heater was rotated so that the beam is incident normal to the cell. The polariser and analyser were then rotated in unison so that the polariser is parallel to the director and hence a minimum intensity is obtained. Then the polariser and analyser were rotated through 45° . In this setting the transmitted intensity was measured as a function of temperature at different magnetic fields.

4.5 Measurements using electric fields

A gap of ~ 1 mm was etched on an ITO plate by using dilute hydrochloric acid and zinc dust. The ITO plate and a nonconducting glass plate were coated with polyimide and rubbed along the width of the rectangular glass plates. The cell was constructed using the above mentioned ITO plate and the nonconducting glass plate. The electric field was applied along the director between the two ITO electrodes. Using an experimental setup similar to that described in section 4.2 the transmitted intensity from a planar aligned cell in the gap region was measured as a function

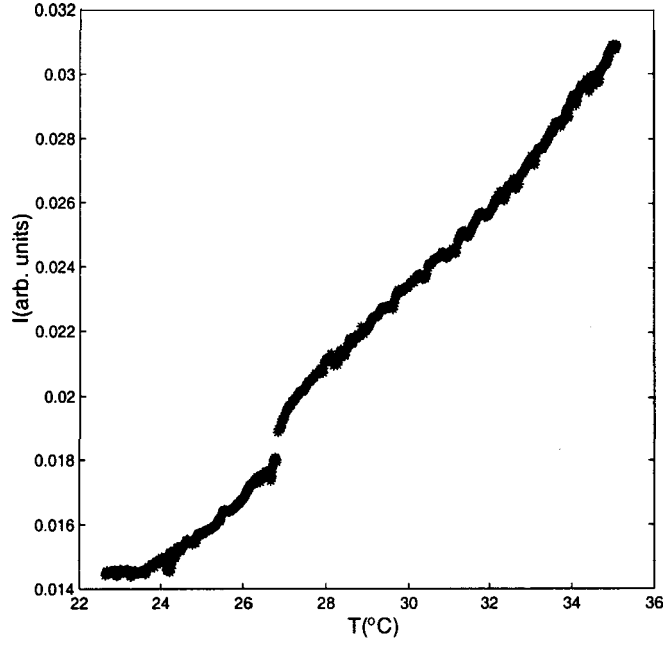


Fig. 4.6: Transmitted intensity profile as a function of temperature for a cell of thickness ($3.0\mu\text{m}$).

of temperature. A HP square wave synthesiser was used to apply the transverse electric field to the cell. The transmitted intensity measurements were performed at various voltages.

4.6 Results

The transmitted intensity profiles for cells of thicknesses $3.0\mu\text{m}$ and $1.9\mu\text{m}$ are shown in Fig. 4.6 and Fig. 4.7 respectively. Note the jump in the transmitted intensity around 27°C and 33°C for the two cells. These jumps in the intensity values correspond to those in A_n which in turn indicate jumps in the orientational order parameter in a weak first order transition. Comparing Fig. 4.6 and Fig. 4.7 the transition temperature *increases* as the thickness *decreases*. If the thickness of the cell in the area illuminated by the laser beam is not very uniform the transition can be smeared out. Indeed in some of the thin cells we could detect only a slope

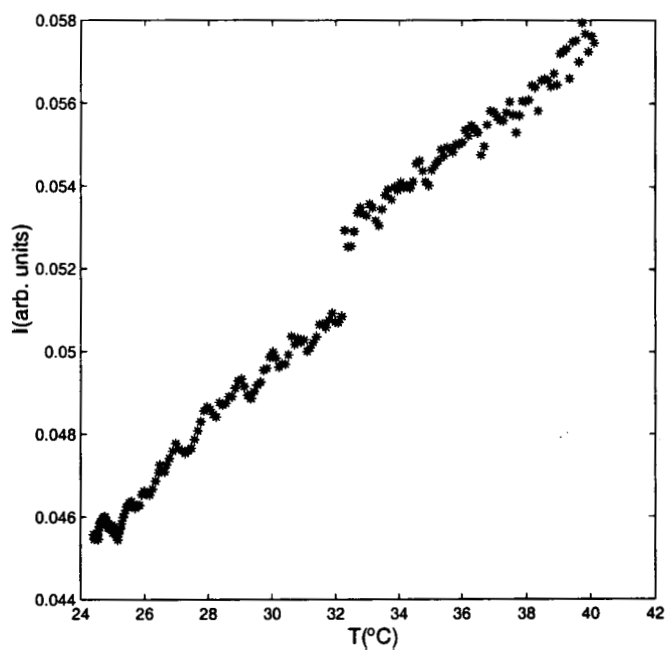


Fig. 4.7: Transmitted intensity profile as a function of temperature for a cell of thickness ($1.9\mu\text{m}$).

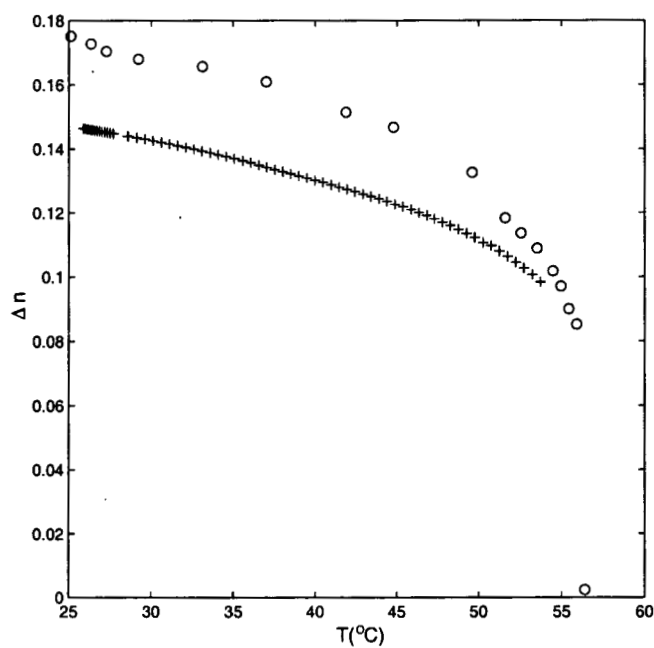


Fig. 4.8: Variation of Δn with temperature for the compound CP7B. The 'o' symbol is for a cell of thickness $\sim 1.5\mu\text{m}$ and '+' symbol for a cell of thickness $\sim 25\mu\text{m}$.

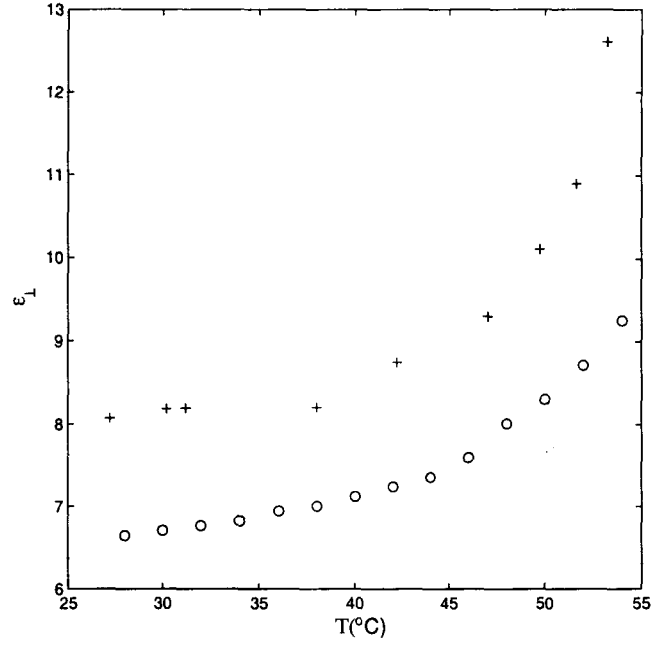


Fig. 4.9: The variation of $\epsilon_{\perp}$ with temperature for the compound CP7B at 1KHz. The '+' symbol is for a cell of thickness $\sim 100\mu\text{m}$ and 'o' symbol for a $\sim 1.5\mu\text{m}$ cell.

change instead of a jump in the intensity (see Fig. 4.8). The variation of A_n as a function of temperature for cells of two different thicknesses is shown in Fig. 4.8. It is clearly seen that the birefringence and hence the order parameter is enhanced in the thin cell compared to that in the thick cell at lower temperatures. The values are practically the same near the nematic isotropic transition temperature (T_{NI}) and the enhancement in the thin cell grows to $\sim 16\%$ at $T - T_{NI} \simeq 6^\circ$ and remains roughly constant at lower temperatures. Hence it is clear that the weak first order transition is associated with the enhancement in the order parameter in the thin cells and in the thick cell such a transition perhaps occurs at a temperature well below the ambient.

Dielectric measurements were performed in order to independently check the enhancement of order parameter in thin cells. The dielectric constant was measured for a cell treated for homogeneous alignment using a HP4192A impedance analyser as

will be described in more detail in the chapter 6. A rectangular pattern is etched on the conducting indium tin oxide (ITO) coated plate which is treated with polyimide and unidirectionally rubbed. As the electric field is applied perpendicular to the director, we measure $\epsilon_{\perp}$. From the dielectric measurements we obtain a lower value for $\epsilon_{\perp}$ for a cell of thickness $1.5\mu\text{m}$ compared to that measured by Titov et al [47] for a $100\mu\text{m}$ thick cell (see Fig. 4.9). As $\epsilon_{\perp} \approx \bar{\epsilon} - (\Delta\epsilon_o S)/3$ where $\bar{\epsilon}$ is the average dielectric constant, $\Delta\epsilon_o$ is the dielectric anisotropy for the fully aligned state, a lower value of $\epsilon_{\perp}$ indicates an enhancement in the order parameter S . This is another independent evidence for the enhancement of the order parameter in thin cells. We could not detect any transition in thin cells using dielectric measurements as the area sensed ($\sim 1\text{cm}^2$) is quite large compared to that in the optical technique ($\sim 0.0015\text{cm}^2$). It is difficult to obtain a very uniform thickness in such large regions and the transition can be expected to be completely smeared out.

In order to check whether enhancement of the order parameter with the reduction in thickness depends on the strong dipole moment of the cyano group, a similar experiment was performed for the compound 4-Ethoxy phenyl-trans-4-butyl cyclohexyl carboxylate (S1563 (from E.Merck)). The transition temperatures are K-37°C-N-75°C-I. The birefringence was measured as a function of temperature for two different thicknesses ($\sim 1.6\mu\text{m}$ and $\sim 18.5\mu\text{m}$). As seen from Fig. 4.10 the birefringence and hence the order parameter is enhanced (-19%) in a thin cell compared to the thick cell for this compound also.

The transmitted intensity profiles for the compound CP7B, without and with a magnetic field are shown in Fig. 4.11 and 4.12. As mentioned above, in these measurements using the superconducting magnet setup, the temperature was controlled manually. In these experiments we could detect only a slope change corresponding to the N-N transition (see Fig. 4.11 and 4.12). The N-N transition temperature

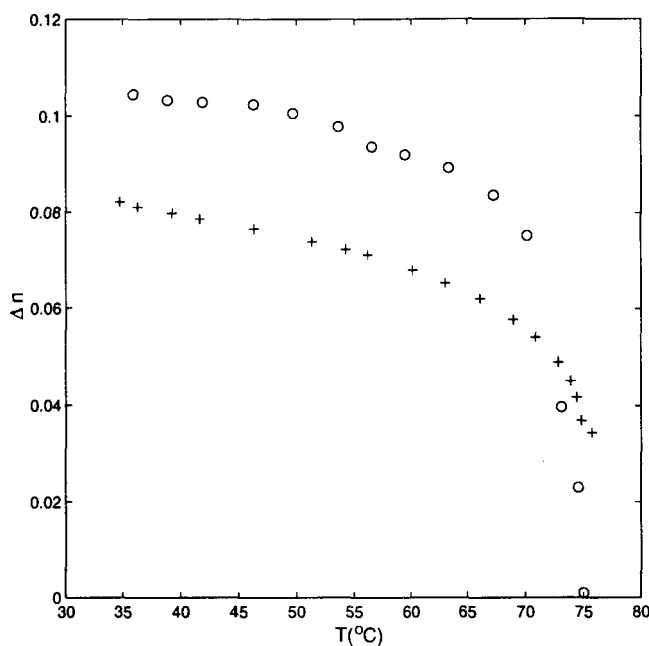


Fig. 4.10: Variation of Δn with temperature for the compound 4-Ethoxy phenyl-trans-4-butyl cyclohexyl carboxylate(S1563). The 'o' symbol is for a cell of thickness $\sim 1.6\mu\text{m}$ and '+' symbol for a cell of thickness $\sim 18.5\mu\text{m}$.

in a thin cell of thickness $1.9\mu\text{m}$ increased roughly quadratically with the applied magnetic field. In Fig. 4.11, the slope change corresponding to the N-N transition occurs at $\sim 31^\circ\text{C}$ which increases to $\sim 35^\circ\text{C}$, when a magnetic field of 4 Tesla is applied. Such a large shift in the transition temperature for such a magnetic field is quite unusual for liquid crystalline transitions. The transmitted intensity profiles, without and with a transverse electric field are shown in Fig. 4.13 and 4.14. When a square wave of 300 volts was applied across a gap of 1mm the transition temperature increased by $\sim 0.5^\circ\text{C}$.

4.7 Conclusions

The compound CP7B has a very large longitudinal dipole moment due to the additive contributions from both the cyano and ester groups. This compound exhibits

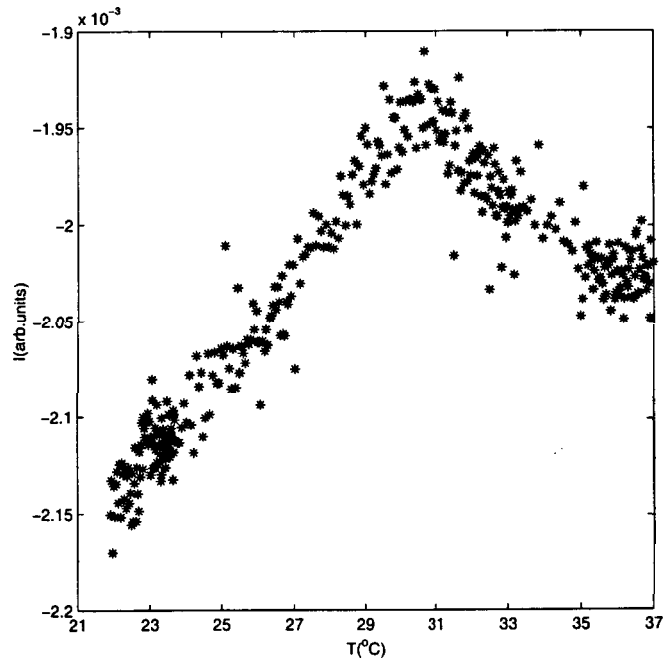


Fig. 4.11: Transmitted intensity profile as a function of temperature for a cell of thickness ($1.9\mu\text{m}$).

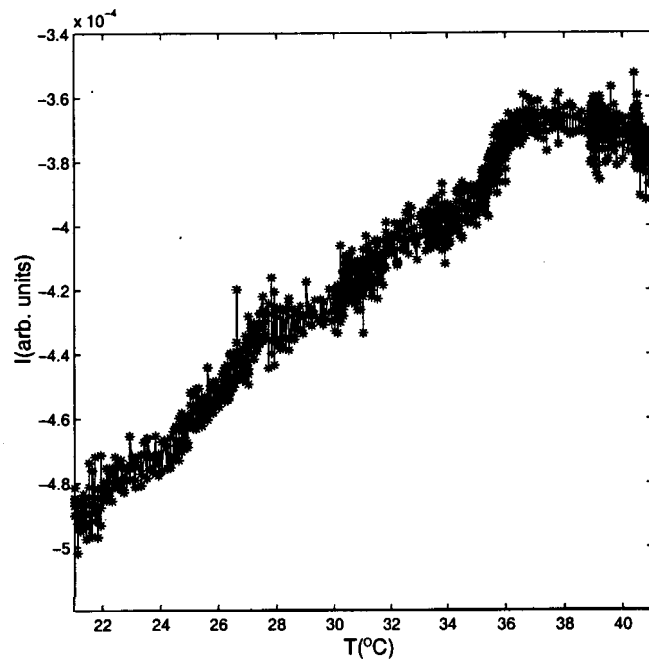


Fig. 4.12: Transmitted intensity profile as a function of temperature for the same cell mentioned in Fig. 4.11 when a magnetic field of 4 Tesla is applied.

Chapter 4

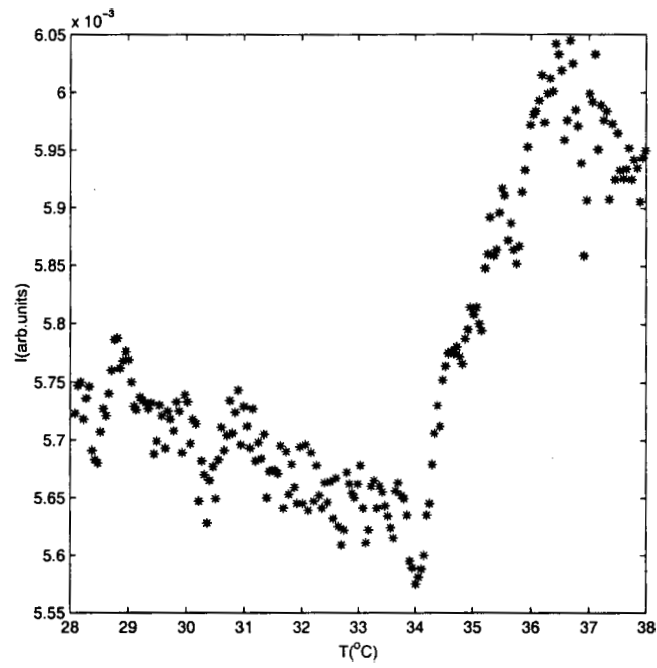


Fig. 4.13: Transmitted intensity profile as a function of temperature for a cell of thickness ($1.5\mu\text{m}$).

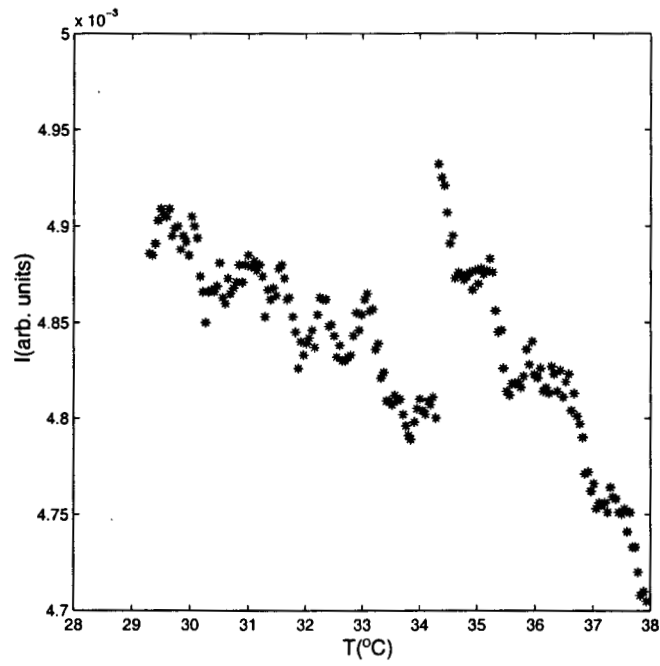


Fig. 4.14: Transmitted intensity profile as a function of temperature for same cell mentioned in Fig. 4.13 when a voltage of 300 volts is applied.

a weak first order transition with a jump $\sim 1\%$ in the orientational order parameter when the latter has a sufficiently large value. As was discussed in the beginning of the chapter, a strong electric field enhances the order parameter to the required value above the ambient temperature and the transition is seen at $\sim 32^\circ\text{C}$ for an electric field of -600 esu [35]. In thick cells, the order parameter does not reach this high value down to the ambient temperature and the transition is not seen in the absence of the field. Our experiments show that the effective order parameter is also enhanced considerably (by $\sim 16\%$) when the thickness of the cell is reduced to $\sim 1.5\mu\text{m}$. In turn the weak first order transition manifests itself in thin cells for the compound CP7B. As has been discussed in reference [35] conoscopic observations on thick cells which exhibit the transition under a strong electric field (~ 600 esu) clearly shows that the lower temperature phase is a uniaxial phase. Textural observations under a similar field applied in the lateral direction of a homogeneously aligned sample showed that the lower temperature phase was not a smectic but a nematic liquid crystal. Hence both the phases involved in this transition are uniaxial nematic phases. We interpret this to be a nematic-nematic phase transition in which the fraction of molecules with antiparallel near neighbour correlation increases as the temperature is raised across the transition point [42].

It is not easy to understand the enhancement in the order parameter in thin cells. As has been discussed in Ref [48] the increase in the order parameter due to quenching of thermal fluctuations because of the finite size of the sample is too small ($\sim 1\%$). Marcerou *et al* [48] have argued that the increase in the order parameter arises from a biaxial nematic phase induced in a relatively thick boundary layer ($\sim 0.8\mu\text{m}$) even though the medium is uniaxial in the bulk. The large increase in the N-N transition temperature in thin cells for the compound CP7B under the action of moderate electric and magnetic fields is also noteworthy. For comparison

the nematic-isotropic transition temperature is shifted only by $\sim 1\text{mK}$ for the fields used in the present experiment [35]. We believe that the above two results are related. Surfaces can induce a higher order parameter due to interactions between the liquid crystal molecules and those of the surface coating. Indeed even when the bulk is in the isotropic phase, there can be a finite orientational order near the surface [49]. The bulk medium undergoes isotropic to nematic transition at $\sim 56^\circ\text{C}$ in both the thick and thin cells (see also Ref [49]) for the compound CP7B. Indeed the large increase in A_n corresponding to this transition in the thin cell is clearly seen in Fig. 4.8. Thus the weak first order jumps at temperatures below 34°C in Fig. 4.6 and Fig. 4.7 correspond to jumps in the bulk order parameter. The order parameter which can be expected to be somewhat higher near the surfaces decreases to the bulk value in a length which corresponds to the correlation length ξ which is $\sim 100\text{\AA}$ according to the usual Landau-DeGennes theory of uniaxial nematics [50]. One possible origin of the the enhancement in the order parameter in thin cells as well as the increase in the N-N transition temperature for the compound CP7B under the action of moderate fields could be that the correlation length is considerably larger in the present system. As we will discuss in the next chapter, the biaxiality of the molecules can be a possible reason for understanding the observed trends.