CHAPTER-VI

SUMMARY AND CONCLUSION

In the present dissertation I have reported the X-ray diffraction, magnetic anisotropy and optical birefringence studies on different liquid crystalline samples.

Keeping in mind that all anisotropic properties of liquid crystals are related to the orientational order parameter $\langle P_2 \rangle$ in a more or less complicated way, I determined $\langle P_2 \rangle$ values of four liquid crystalline materials of a homologous series by three different techniques, viz. X-ray diffraction, magnetic anisotropy and optical birefringence measurements. The apparatus for X-ray diffraction and optical studies were already set-up in our liquid crystal laboratory by previous workers. To determine $\langle P_2 \rangle$ values from magnetic anisotropy measurement I have designed and fabricated a sensitive apparatus for measuring diamagnetic susceptibility, which has been described in chapter II.

The four homologous compounds studied by the three techniques are the four members of alkoxy (or cyano) phenyl trans alkyl cyclohexane carboxylate, namely, MPPCC, PPPCC EPBCC and CPPCC in short. Optical microscopic studies were also done on these compounds. I observed the textures of the four compounds by using a hot stage (Metler FP 80/82) with a polarizing microscope. The transition temperatures, identification of the nematic phase of the four compounds have been observed and noted by me from the texture studies.

A high temperature X-ray camera for taking flat plate photographs of aligned sample of liquid crystal in

magnetic field has been designed and fabricated in our laboratory[1]. Utilising this camera, I took the X-ray photographs of aligned samples of the four compounds over the entire temperature range of the nematic phases[2].

X-ray photographs of these compounds were also analysed to calculate the apparent molecular length (l) and average intermolecular distance (D). The compound EPBCC shows anomalous behaviour from 25°C to 44°C. In this temperature range the D value decreases with the increase of temperature and thereafter increases in the conventional way. This anomalous behaviour in D values of EPBCC was also supported by the anomalous density and ordinary refractive index (n_o) measurements[3] by me in the same temperature range. Average intermolecular distances within a few percent of 5 Å were found for these four compounds. The measurements of l values of these compounds revealed that the compounds form bimolecular association due to partial or, in one case, full overlapping of neighbouring molecules in antiparallel manner. The fact that the presence of cyano group generally increases the apparent molecular length[4-7] has also been confirmed by me for the compound CPPCC.

The orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been calculated for these four compounds following the procedures given by Vainshtein[8] and by Leadbetter and Norris[9]. I found that the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values obtained from Vainshtein approximation is lower than those obtained

from the latter procedure, as expected. The $\langle P_2 \rangle$ values obtained from Leadbetter's approximation agreed reasonably well with the theoretical predictions by Maier and Saupe. But the $\langle P_4 \rangle$ values are significantly lower than their theoretical $\langle P_4 \rangle$ values. I have not been able to explain this discrepancy, which has been reported by other workers as well.

Magnetic susceptibility measurements were also performed on the above four compounds, all having positive diamagnetic anisotropy. As I mentioned earlier that to accomplish these measurements I designed and fabricated a Curie torsion type electromagnetic balance with Suksmith form of magnetic pole pieces. I measured the diamagnetic susceptibility values, $\chi_{\parallel}$ along the director and also $\bar{\chi}$, the mean diamagnetic susceptibility values. From these values I have calculated the magnetic anisotropy ($\Delta\chi$) and the orientational order parameters[10] $\langle P_2 \rangle$ which are close to the Maier-Saupe theoretical values except near the clearing point where the experimental $\langle P_2 \rangle$ values are lower.

Using the experimental set-up of Zeminder et al[11] I measured the refractive indices (n_o , n_e) and densities at different temperatures of the above four compounds. Then I have calculated the principal molecular polarizabilities (α_o , α_e) using both Vuks' and Neugebauer's approaches from these values. Finally I have calculated polarizability anisotropy and the $\langle P_2 \rangle$ values for these compounds. In this case also, I found that the experimental $\langle P_2 \rangle$ values are

in good agreement with the Maier-Saupe theoretical values except near the nematic-isotropic transition temperature where the experimental $\langle P_2 \rangle$ values are significantly lower.

It is found that the orientational order parameter values from refractive index and magnetic susceptibility measurements agree very well with one another, while those obtained from X-ray data are somewhat higher. This is due to different approximations used in these calculations and has been discussed in the relevant chapter.

Optical birefringence studies were also done on three Schiff's base compounds, viz. BBBA[12], PBBA[13] and APAPA[14]. X-ray diffraction studies have already been done by my coworkers in our laboratory. From the refractive index measurements on BBBA, different phase transitions in the mesomorphic state were observed. I failed to observe the transition from cybotactic nematic (N_c) to ordinary nematic (N_o) at 59°C in this compounds from optical birefringence studies. Optical anisotropies ($\Delta n = n_e - n_o$) for the compounds BBBA and PBBA were found to be a function of wavelength, Δn being much larger for blue ray than the other rays. This observation supports the same findings by Blinov et al[15]. My calculated $\langle P_2 \rangle$ values on these three compounds have been compared with the values obtained from X-ray data by coresearchers in our laboratory and with Maier-Saupe theoretical values. My calculated $\langle P_2 \rangle$ values for these compounds agree very well with the theoretical and X-ray

values. It is also found that the $\langle P_2 \rangle$ values got from the anisotropic local field model (Neugebauer's approach) is slightly higher than those obtained from isotropic local field model (Vuks' approach). The possible reasons for such disagreement is explained in the relevant chapter. Near clearing temperature (T_c) the $\langle P_2 \rangle$ values obtained from refractive index measurements are slightly lower than those obtained from X-ray data and from Maier-Saupe theory. The probable reasons of this difference have been discussed in chapter III.

In case of MPPCC, PPPCC, EPBCC and CPPCC the lowering effect near T_c is greater than in the case of Schiff's base compounds. In my opinion the strong dipole moment present in the Schiff's base compounds are responsible for maintaining a short range order near T_c. Only the thermal fluctuation of the director near this temperature causes perturbation of the short range ordering in the Schiff's base compounds.

Lastly I have reported the X-ray diffraction studies on (-)-2-methylbutyl p-(N-(p-methoxy benzylidene) amino) cinnamate (MBAC). In trying to determine the orientational order parameters in the smectic B phase of MBAC, an enthalphyless transition from smectic B (polylayer) to smectic B (monolayer) was observed around 50°C which was designated as second order phase transition[16]. From the orientational distribution function $f(\beta)$ I also calculated the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values of this compound in the smectic B phase. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for MBAC in smectic B phase are

almost constant, being 0.85 ± 0.03 and 0.60 ± 0.03 respectively. There is a discontinuity in $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values at the temperature where the second order phase change takes place, thereby confirming our observation of smectic B (polylayer) to smectic B (monolayer) transition.

References

1. Ref. no.37, chap.II.
2. M.Mitra, R.Paul and S.Paul, communicated for publication in 'Liquid Crystals' (1987).
3. Ref. no.7, chap.III.
4. Ref. no.8, chap.III.
5. Ref. no.9, chap.III.
6. Ref. no.13, chap.III.
7. Ref. no.15, chap.III.
8. Ref. no.23, chap.II.
9. Ref. no.28, chap.II.
10. Ref. no.2, chap.III.
11. Ref. no.97, chap.II.
12. Ref. no.1, chap.IV.
13. Ref. no.2, chap.IV.
14. Ref. no.3, chap.IV.
15. Ref. no.24, chap.IV.
16. Ref. no.6, chap.V.

1. Estimation of Order Parameter of APAPA in Nematic Phase Both From X-ray Diffraction Studies And Refractive Index Measurement

LIST OF PUBLICATIONS

1. X-ray Diffraction And Optical Studies of Oriented Schiff's Base Liquid Crystal

   P.Mandal, M.Mitra, S.Paul and R.Paul

   'Liquid Crystals', 1987 ~~(in press)~~, 2, 183.

2. Neamtic Order of APAPA From X-ray Diffraction and Optical Studies

   P.Mandal, M.Mitra, K.Bhattacharjee,

   S.Paul and R.Paul

   Mol.Cryst.Liq.Cryst., 1987 ~~(in press)~~ 149, 203.

3. Orientational Order Parameters of (-)-2-Methylbutyl -p-(N-(p-Methoxy Benzylidene) Amino) Cinnamate in Smectic B Phase From X-ray Diffraction Measurements

   M.Mitra, K.Bhattacharjee, S.Paul and R.Paul

   'Phase Transitions', 1987 ~~(in press)~~, 9, 337.

4. Order Parameters From Magnetic Susceptibility Measurements on Some Nematogens

   M.Mitra and R.Paul

   Mol.Cryst.Liq.Cryst., 1987 ~~(in press)~~. 148, 185

5. Anomalous Density and Refractive Index of a Nematic Liquid Crystal

   M.Mitra, S.Paul and R.Paul

   'Liquid Crystals', 1987 (in press).

6. Optical Birefringence Study on PBBA

M.Mitra, S.Paul and R.Paul

To be published in the proceeding of 4th National Seminar on Ferroelectrics and Dielectrics, I.I.T., Kharagpur, India, December, 1986.

7. Optical Birefringence Studies on Some Nematogens

M.Mitra, S.Paul and R.Paul

~~Communicated to~~ 'Pramana', J. Phys, 29, 409 (1987) ~~for publication (1987)~~.

8. X-ray Diffraction From a Homologous Series of Nematic Liquid Crystal

M.Mitra, R.Paul and S.Paul

Communicated to 'Liquid Crystals' for publication (1987).

Some of the above works have also been reported in the following Seminars/Conferences

1. Estimation of Order Parameter of APAPA in Nematic Phase Both From X-ray Diffraction Studies And Refractive Index Measurement

K.Bhattacharjee, P.Mandal, M.Mitra, R.Paul and S.Paul

Abstract of the 10th International Liq.Cryst.Conf., New York, July 15-21, 1984, no.A17.

2. Order Parameter of MBAC in Smectic B Phase

   M.Mitra, K.Bhattacharjee, S.Paul and R.Paul

   Abstract of the Solid State Physics Symposium, Bombay, India, December, 1984, no.S1A9.

3. Magnetic Anisotropy and Order Parameter of a Nematic Liquid Crystal

   M.Mitra and R.Paul

   Abstract of the Solid State Physics Symposium, Nagpur, India, December, 1985, no. B33.

4. Magnetic Susceptibility Anisotropy and Orientational Order Parameter of Nematogens

   M.Mitra, R.Paul and S.Paul

   Abstract of the Seminar on Physics of Positionally Disordered Materials, B.H.U., Varánasi, February, 1986, no.LCP-10.

5. X-Ray Diffraction Studies and Birefringence Measurement of a Nematic Liquid Crystal

   M.Mitra, B.Majumdar, R.Paul and S.Paul

   Abstract of the Seminar on Physics of Positionally Disordered Materials, B.H.U., Varanasi, February, 1986, no.LCP-11.

6. X-Ray Diffraction Studies and Optical Birefringence Measurements of Some Nematogens

   M.Mitra, S.Paul and R.Paul

   Abstract of the 11th. International Liquid Crystal Conference, Barkley, U.S.A., June, 1986, no. T-016-ST.

7. X-Ray Diffraction and Optical Studies of Oriented Liquid Crystal (BBBA)

P.Mandal, M.Mitra, S.Paul and R.Paul

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