

## **CHAPTER 9**

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**Summary and conclusion.**

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In the present dissertation I have discussed the crystal structures of one polar and one non-polar liquid crystalline compounds. X-ray diffraction, optical birefringence study of some alkenyl liquid crystalline compounds and determination of dipole moments of polar liquid crystalline samples dissolved in non-polar p-xylene at different concentrations have also been undertaken by me.

In chapter 1, I have given a brief introduction to liquid crystals and in chapter 2 I have described in somewhat detail the theoretical background and experimental technique of crystal structure analysis.

The molecular arrangement in the crystalline state is one of the factors which sometimes predetermines the properties in the liquid crystalline state. Of the six compounds studied by me, single crystal structures for only two compounds such as PCBCH or 1d(3)CC and PEBCH or 1d(3)CCO<sub>2</sub> could be determined. These structures are described in chapter 3 and chapter 4. For other compounds I could not grow good quality single crystal.

The crystal of the compound PCBCH belongs to the monoclinic system with space group  $P2_1/n$  with four molecules in the unit cell. The structure has been solved by direct method program SIMPEL. Least squares refinement produced a R-value of .065 for 2326 observed reflections. The bond lengths and angles in the molecule are found to be consistent with previous observations. Molecules related through the centre of symmetry are bound together by weak dipole induced dipole interaction between the chain part and polar cyano groups. The length of the pair is 30.03 Å. Apparent molecular length in the nematic phase shows the presence of this association. At C-N transition temperature these molecules gain sufficient energy to move within the layers and undergo rotation about axes other than the long molecular axis.

The second compound PEBCH crystallizes in non-centrosymmetric

orthorhombic space group  $P2_12_12_1$  and four molecules in the unit cell. The structure was solved by direct method program GENTAN. Least squares refinement produced a R-value of .077 for 1855 observed reflections. The double bond length in the pentenyl chain differ from normal value to a large extent. Thermal parameters of the two carbon atoms of the double bond are also very large compared to other atoms. So there may be some conformational disorder in the molecular structure around the double bond. Parallel imbricated type of molecular arrangement is observed in the crystalline state as a precursor to the nematic phase. Molecular packing and phase structures have been compared with two related mesogenic compounds.

Chapter 5 deals with the theoretical back-ground and experimental technique of optical birefringence and x-ray diffraction study and dipole moment determination.

In chapter 6 and chapter 7 I have reported the x-ray diffraction and optical birefringence study of some alkenyl liquid crystalline compounds. The physical properties e.g. density, optical anisotropy and molecular parameters are strongly affected by the positional changes of the double bond. I have measured the refractive indices ( $n_o, n_e$ ) of all the compounds, for three different wave-lengths and calculated the molecular polarizability values ( $\alpha_o, \alpha_e$ ) at different temperatures. Optical birefringence  $\Delta n$  are found to be very low for all the alkenyl compounds. Polarizability anisotropy ( $\Delta\alpha$ ) and molecular polarizability ( $\alpha_o, \alpha_e$ ) are also calculated from bond additivity scheme and compared with our experimental values.

The compound 3CPOd(3)1 and 5CPOd(3)1, beyond the temperatures  $45^\circ\text{C}$  and  $52^\circ\text{C}$  respectively, birefringence could not be measured, because the ordinary rays ( $n_o$ ) were not visible. The orientational order parameter  $\langle P_2 \rangle$  at these temperatures drops to a very low value. It seems that there might be a phase transition at this temperature. Density versus temperature graphs also show a somewhat first order phase transition at this particular temperatures. But no

such transition could be observed in the texture and x-ray photographs.

X-ray diffraction photographs were analysed to obtain apparent molecular length ( $l$ ) and average intermolecular distance ( $D$ ) in the mesophase. The apparent molecular length ( $l$ ) of the polar cyano compounds are found to increase in the mesophase, due to dipole - dipole or dipole - induced dipole interactions forming dimers. On the other hand, the molecular length ( $l$ ) of the non-polar compounds are almost same in both solid and mesomorphic phases. Van der waal's type of interactions are responsible for the mesophase stability of these compounds.

The compound 1d(3)CC exhibits a monotropic smecticA phase with two colinear but incommensurate density modulation of periodicity  $14.94 \text{ \AA}$ , which is almost same as the molecular length and the other periodicity is  $24.01 \text{ \AA}$  which is between 1 and 21. The existence of this type of smecticA phase could not be explained from the structural studies in the solid phase. Different kinds of intermolecular interactions are responsible for this phase formation.

Order parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  values are calculated by analysing x-ray diffraction photographs. Temperature variation of order parameters calculated from x-ray and optical data have been compared with Maier-Saupe theoretical values. Sometimes the  $\langle P_2 \rangle$  values determined experimentally are found to be higher than Maier-Saupe values. The orientational behaviour of the nematic phase may be distinguished in two parts : a long range order and a short range order. Whereas Maier-Saupe model reflects only long range ordering in the liquid crystalline phase, but a short range local ordering due to intermolecular interactions also exists. This short range interaction causes an increase in the orientational order parameter  $\langle P_2 \rangle$ .

$\langle P_2 \rangle$  values obtained from optical birefringence differ

considerably with  $\langle P_2 \rangle$  values obtained from x-ray data. This anomaly may be due to the errors inherent in determining  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  in the solid phase by extrapolation procedure and rules of bond additivity. Moreover order parameter values obtained from x-ray data involve different types of approximations and averaging than those obtained from refractive index data.

Molecular dipole moments of five polar liquid crystalline compounds have been determined by measuring the dielectric constants and refractive indices of solutions of the compounds in a non-polar solvent p-xylene. Dipole moment of an isolated molecule is evaluated by extrapolation to infinite dilution. Molecular parameters such as mean polarizability and polarizability anisotropy were also calculated from bond additivity rule. From the crystal structure data, atomic charge distributions for two of the five compounds were calculated by different empirical methods using molecular orbital theory. The calculated values of dipole moments were compared with our experimental data. This is described in detail in chapter 8.

## LIST OF PUBLICATION

1. Study of mesomorphic properties of a number of alkenyl liquid crystalline compounds.  
A. Nath, B. Chaudhury and S. Paul, Mol. Cryst. Liq. Cryst., 265, page, 699 - 711, (1995).
2. Structure and properties of an alkenyl liquid crystalline compound.  
S. Gupta, A. Nath, S. Paul, H. Schenk and K. Goubitz, Mol. Cryst. Liq. Cryst., 1994. [ In Press ].
3. Structural analysis by x-ray diffraction of a non-polar alkenyl liquid crystalline compound.  
A. Nath, S. Gupta, P. Mandal, S. Paul and H. Schenk, Communicated to Liquid Crystals.
4. Determination of molecular properties of some polar mesogenic compounds.  
A. Nath, P. Mandal, B. Chaudhury and S. Paul, communicated to Mol. Cryst. Liq. Cryst.

The following papers have been presented at the National Solid State Physics Symposium and International Conferences.

1. Structure and properties of an alkenyl liquid crystalline compound.  
S. Gupta, A. Nath, S. Paul, Solid State Physics Sym., S.V.U., Tirupati (INDIA) Dec.28, 1992 - Jan.1, 1993.
2. Structure and properties of an alkenyl liquid crystalline compound.  
S. Gupta, A. Nath, S. Paul, presented at IUC, XVI, Beijing. 21 - 29 August, 1993.
3. Study of mesomorphic properties of an alkenyl cyano compound.  
A. Nath, S. Gupta, B. Chaudhury and S. Paul, Indian Liquid Crystal Conference, Mysore, 18 - 20 Oct. 1993.
4. Study of mesomorphic properties of a number of alkenyl liquid

crystalline compounds.

A. Nath, B. Chaudhury and S. Paul, 15<sup>th</sup> International Liquid Crystal Conference, 3 - 8 July. Budapest. 1994.

5. Optical studies of two mesogenic phenyl cyclohexane alkenyls.

S.Gupta, A. Nath and S. Paul, 15<sup>th</sup> ILCC, 3-8 July.1994, Budapest.