

CHAPTER-V

ORDER DISORDER PHENOMENA FROM X-RAY DIFFRACTION STUDY OF MONOLIQUID  
CRYSTAL

## 4.1 Order Disorder Phenomena from X-ray Diffraction Study of Monoliquid Crystal

### 4.1.1 Introduction

A monoliquid crystal is a fairly homogeneous and well oriented sample of liquid crystal which is achieved by melting a single crystal of liquid crystalline compound to the mesomorphic state without an external field. It is a disordered crystal.

If we take a crystal disordered in one or more ways and cool it down, in principle, one or two things can happen. Either the disorder becomes frozen in or else the crystal undergoes some kind of transition and becomes ordered<sup>1</sup>. Some times the crystal may have to pass through more than one transition to reach a completely ordered state.

The thorough study of order-disorder involves a number of experimental techniques. The technique most widely employed is that of X-ray diffraction.

I have undertaken the diffraction study of monoliquid crystals of compounds belonging to the series  $R_1 - O - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{CN}$  with  $R_1 = \text{C}_n\text{H}_{2n+1}$  where  $n = 9$  to  $12$ , ( $n$ -OCB in short). These compounds have been studied extensively in liquid crystalline state in our laboratory using different experimental techniques. Detailed experimental procedure for determining refractive indices and orientational order parameters in the mesomorphic range is given in chapter III. The results of this study has been published<sup>2</sup>.

X-ray diffraction study of these samples in the mesogenic state, aligned by magnetic field was carried out by Das et al<sup>3</sup>. X-ray diffraction photographs show interesting patterns indicating the presence of incommensurate structures which poses difficulty in

characterisation. Structural analysis of 110CB and 120CB have been undertaken by Mandal et al<sup>4</sup>. Both the structures are highly disordered.

In this chapter I present X-ray diffraction study of these compounds in solid phase obtained by slowly cooling the monoliquid crystal. Our purpose of this work is to study how these solid phases are structurally different from the highly ordered single crystals. The transition temperatures of all the four compounds are given in chapter III. Except 90CB each of these compounds under study exhibits a single mesophase of smectic A type.

#### 4.1.2 Experimental Procedure

In this study, the flat film method has been used. To raise the temperature of the sample a high temperature attachment is used which was designed and fabricated by us in our laboratory and it was oriented on a Carl Zeiss Universal camera (model 90486). Plate like thin crystals were grown from solvent evaporation technique using acetone. Ni filtered X-ray beam is collimated and passes through the sample. The crystals were placed in the capillary with their longest directions perpendicular to X-ray beam. The capillary is placed in a brass block which serves as a temperature controlled oven. The temperature is controlled by a temperature controller (Indotherm model 401). The capillary is parallel to the film and they are both perpendicular to the direction of the incident beam. The exact distance between the film and the sample is calculated using aluminium powder. The whole set up was covered with plywood enclosure having one side open, to protect it from draught.

By raising the temperature gradually the crystal was melted to smectic phase. Since it started as a single crystal, the molecular

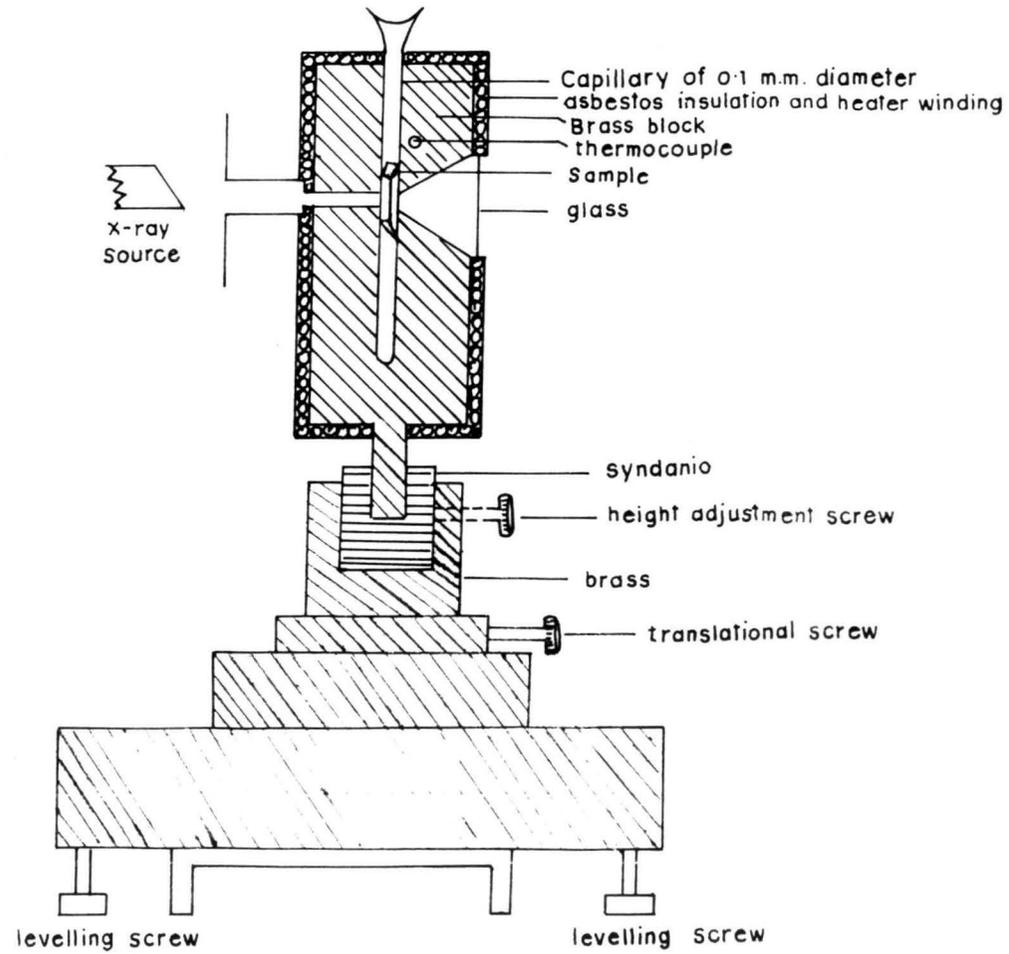


Fig. 5.1. Sectional diagram of the high temperature attachment.

orientation in the monoliquid crystal is expected to be the same as that of mesophase aligned by the magnetic field. Curiously enough, the photograph at this temperature did not show any preferred orientation or alignment of the molecules. This is the observation for all the compounds. The smectic melt was now cooled down to the room temperature at the rate of  $0.1^{\circ}/\text{minute}$  and diffraction photograph was taken. In our set up, the capillary could be rotated around its long axis so that various alignments of the sample with respect to the X-ray beam were possible. Another photograph of the solid phase was taken by rotating the capillary through  $90^{\circ}$ . The same procedure was followed for all the compounds and diffraction photographs of the solid phases for two different orientations are shown in Figs. 5.2-5.9. It should be noted here that we could not get good quality single crystals for 90CB and 100CB.

#### 4.1.3 Results and Discussions

The photographs can be divided into two groups according to the characteristic of their X-ray pattern. One group shows random orientations of the domains with respect to the X-ray beam and the other group shows preferred orientations. We shall deal only with those photographs belonging to the second group. The main results are reported here.

(i) X-ray patterns show some odd-even effect in their appearance at low angles. For the even members of the series several sharp diffraction maxima in the form of arcs are observed in the meridional direction. For odd members only one pair of broad arcs is observed.

(ii) At large diffraction angles two equatorial diffuse streaks appear on each photograph.

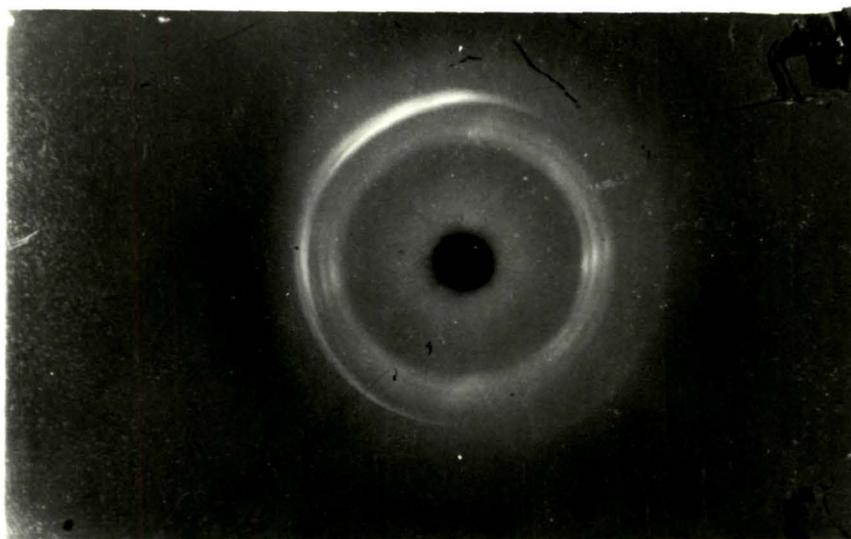


Fig.5.2

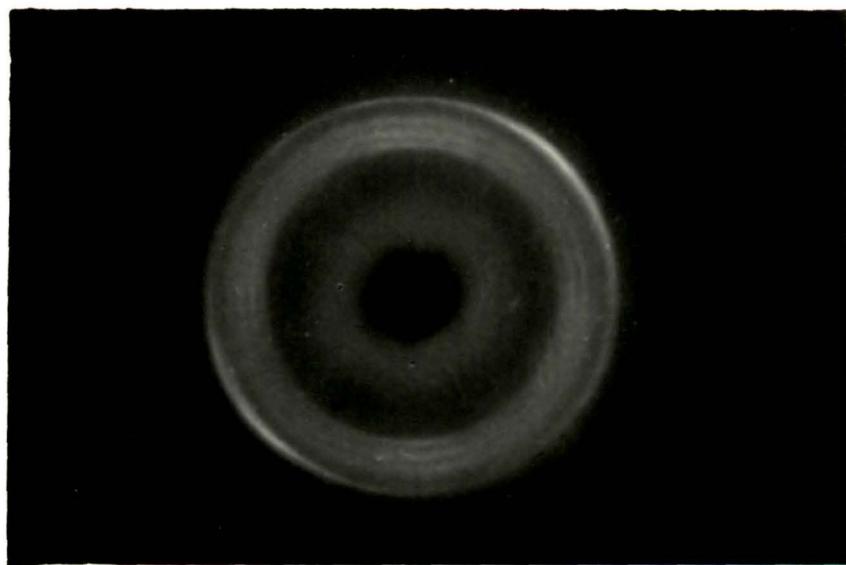


Fig.5.3

X-ray diffraction photographs of the samples 90CB (Fig.5.2) and 100CB (Fig.5.3) for random orientations of the domains with respect to the X-ray beam.

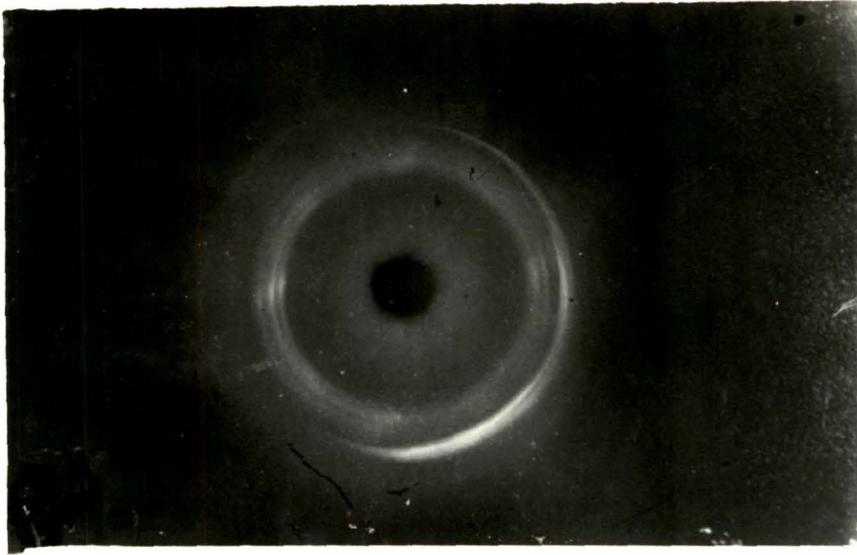


Fig.5.4

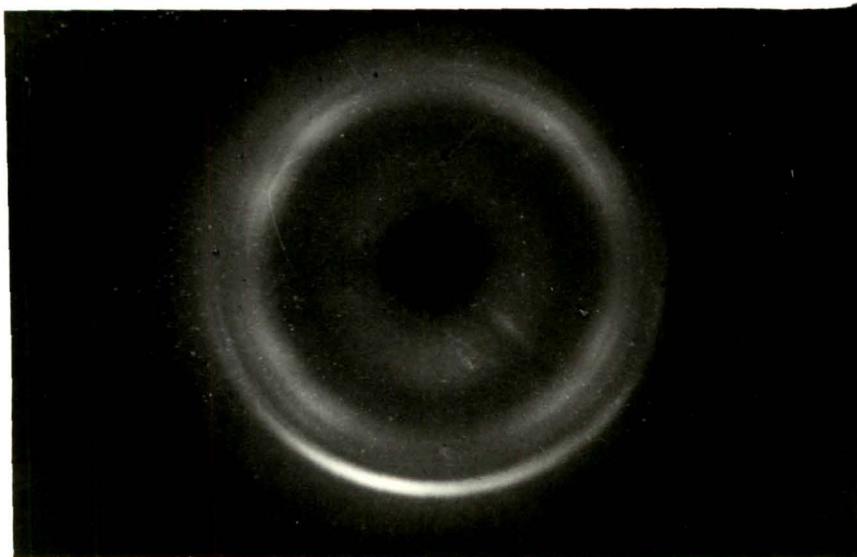


Fig.5.5

X-ray diffraction photographs of the samples 110CB (Fig.5.4) and 120CB (Fig.5.5) for random orientations of the domains with respect to the X-ray beam.

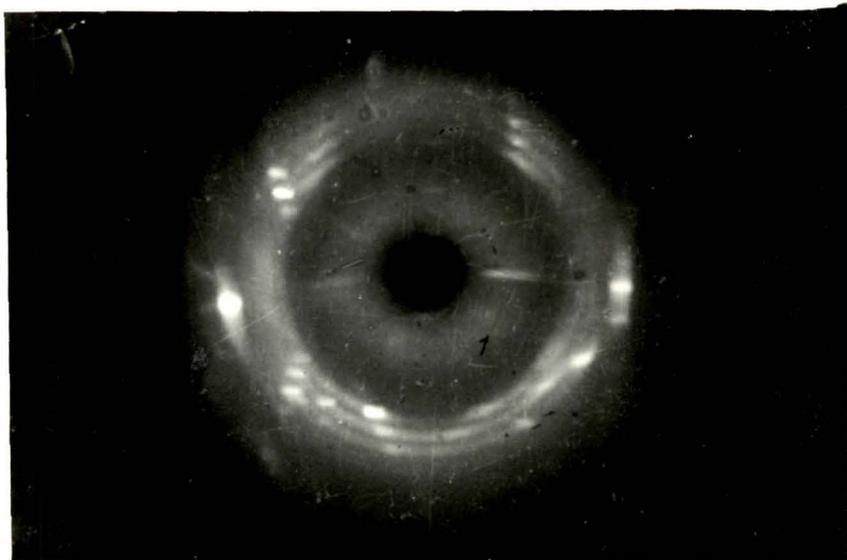


Fig.5.6

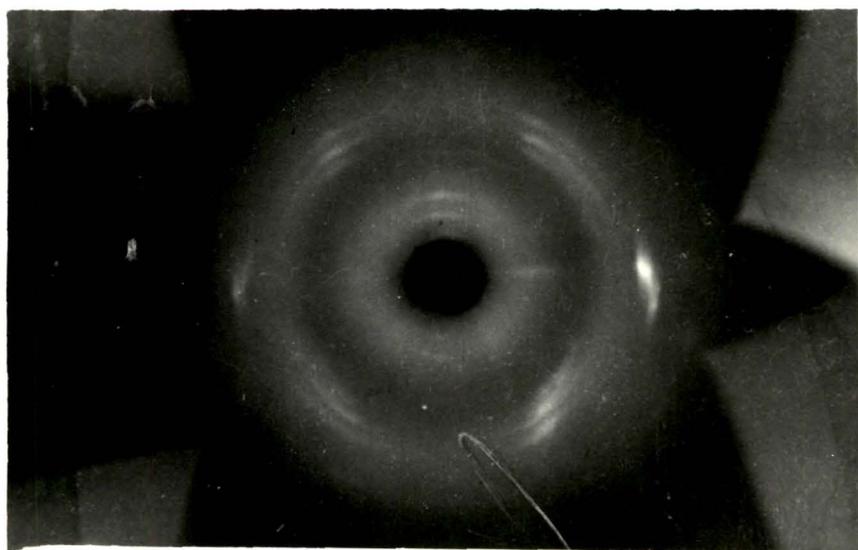


Fig.5.7

X-ray diffraction photographs of the samples 90CB (Fig.5.6) and 100CB (Fig.5.7) for preferred orientation.

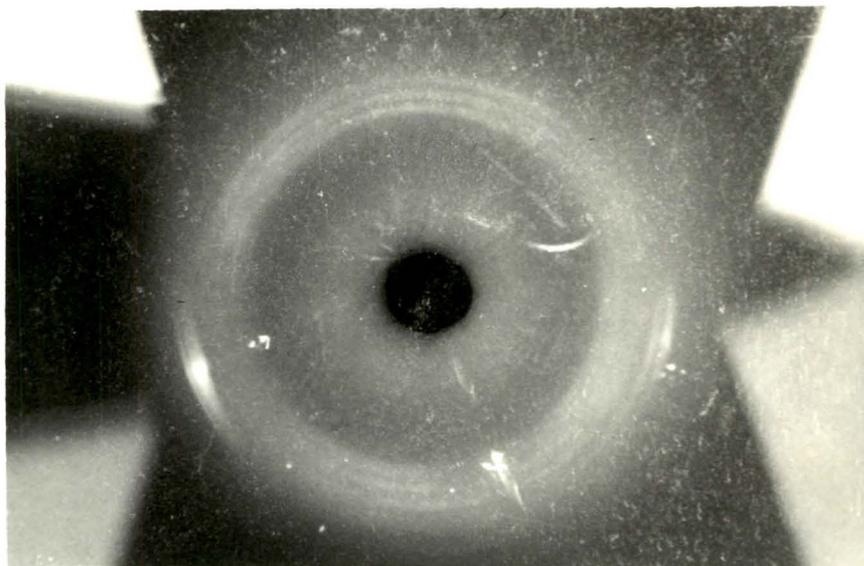


Fig.5.8

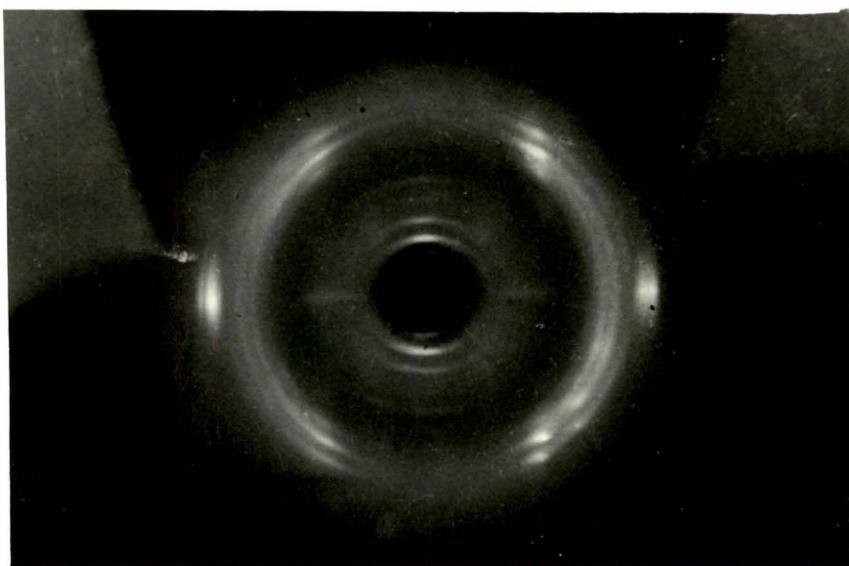


Fig.5.9

X-ray diffraction photographs of the samples 110CB (Fig.5.8) and 120CB (Fig.5.9) for preferred orientation.

Table-5.1

Bragg angles ( $\theta$ ) and d spacings of diffraction photographs

Sample	Inner diffraction pattern				Outer diffraction pattern			
	Serial no.	dia (cm.)	$\theta$ (degree)	d <sub>o</sub> (Å)	Serial no.	dia (cm.)	$\theta$ (degree)	d <sub>o</sub> (Å)
90CB	could not be measured				1	2.20	9.78	4.54
					2	2.42	10.68	4.16
					3	2.58	11.31	3.93
					*4	3.01	12.97	3.44
					*5	3.08	13.23	3.37
100CB	1	0.66	3.04	14.52	1	2.40	10.60	4.19
	2	0.81	3.73	11.86	2	2.41	10.64	4.18
	3	0.88	4.05	10.93	3	2.42	10.68	4.16
					*4	2.84	12.32	3.61
					*5	2.99	12.89	3.46
110CB	could not be measured				1	2.22	9.87	4.50
					2	2.38	10.52	4.22
					3	2.56	11.23	3.96
					*4	2.95	12.74	3.50
					*5	3.08	13.23	3.37
120CB	1	0.58	2.68	16.51	1	2.30	10.19	4.36
	2	0.80	3.68	12.00	2	2.44	10.76	4.13
	3	1.06	4.86	9.10	3	2.57	11.27	3.94
	4	1.39	6.33	6.99	*4	2.95	12.74	3.50
	5	1.62	7.33	6.04	*5	3.10	13.30	3.35

\* indicates diffuse spots along the equator.

(iii) Each compound is characterised by a large number of diffraction rings at large angles.

(iv) Meridional streaks forming layer like patterns are superimposed on well defined rings at large angles, indicating the coexistence of large single domain and polycrystalline powder.

Bragg angles of the rings and the corresponding  $d$  values are given in the Table 5.1.

We are not able to interpret the X-ray diffraction pattern, especially the low angle diffraction rings and thereby characterise the structure. It is evident from the Table 5.1 that none of the  $d$  values at low angles correspond to molecular length or layer spacings. From the sharpness of the diffraction rings we may conclude that there are long range order in the molecular directions but we can't explain the molecular arrangement. Occurrence of sharp outer ring,  $d$  value of which corresponds to intermolecular spacing, indicates the existence of lateral order of the parallel molecules. The absence of sharp diffraction spots shows that long range order of the single crystal does not exist. Diffuse spots and streaks are indications of imperfections, disorder of the lattice and also of large thermal vibrations. It is clear that this phase is significantly different from either the smectic phase or the crystalline phase. The molecular packing is quite complex and requires further experiments, to be solved. Existence of the incommensurate modulated structures in the aligned liquid crystalline phase suggests that the crystal structures of these compounds may be aperiodic. Structural models of 110CB and 120CB, based on standard methods, do not agree with the experimental results. Structure determination of these two compounds still remains a difficult challenge. When these are

solved we may get some idea about the molecular arrangement in these solid phases.

### References

1. N.G.Parsonage L.A.K.Staveley, Disorder in crystals, Clarendon Press, Oxford, (1978).
2. M.Mitra, S.Gupta, R.Paul and S.Paul, Mol.Cryst.Liq.Cryst., 199, 257(1991).
3. M.Das and R.Paul, Private communication.
4. P.Mandal and S.Paul, Private communication.

In the present dissertation the results of X-ray diffraction and optical studies of some liquid crystalline compounds belonging to the two homologous series of alkoxy cyanobiphenyl alkyl ether and alkyl cyclohexyl cyanophenyl pyrimidine have been reported.

A high temperature X-ray camera was designed and fabricated in our laboratory<sup>1</sup> for taking flat plate photographs of liquid crystal compounds in presence of magnetic field. Temperature was controlled with temperature controller (Indotherm model 401).

From the X-ray diffraction photographs of the two members (ECCPP and HCCPP) of the homologous series of alkyl cyclohexyl cyanophenyl pyrimidine orientational order parameters  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  at different temperatures are calculated with Vainshtein's and Leadbetter's approximation. Leadbetter's calculation fits better to the theoretical values given by Maier-Saupe<sup>2-4</sup>, Humphries et al<sup>5</sup> and McMillan<sup>6,7</sup>. The same compounds are studied by optical method using thin prism technique<sup>8</sup>. These results are discussed in chapter III. Orientational order parameters  $\langle P_2 \rangle$  at different temperatures are calculated from molecular polarizabilities. Order parameters from these two experimental techniques differ considerably as temperature increases. This may be due to the fact that two different types of averaging are involved in the two cases<sup>9</sup>.

From the X-ray diffraction photographs of these two compounds (ECCPP and HCCPP) apparent molecular length  $l$  (in case of nematic), layer spacing  $d$  (in case of smectic) and intermolecular distance  $D$  at different temperatures are measured.  $D$  values are found to be 5 Å approximately throughout the mesomorphic range for both the compounds and are almost temperature independent.  $l$  and  $d$  values measured from both aligned and non aligned samples. It is found