

## **Chapter - 7**

**ON THE TEMPERATURE DEPENDENCE OF CRYSTAL  
STRUCTURE OF TWO MESOGENIC COMPOUNDS**

## 7.1 INTRODUCTION

The structure determination of mesogens in the crystalline state may provide correlation between crystal structures and mesophase behaviour<sup>[140,141]</sup>. Under this context the structural investigation of a number of mesogenic compounds<sup>[121,142-146]</sup> were undertaken in our laboratory. In the last twenty years many such studies on structural analysis have been reported, but the available data cannot predict the existence of definite phase. Certain trends can be concluded from the knowledge of the conformation and packing of the mesogenic molecules in crystalline state. In most cases it has been found that smectic precursors form layered structure while the nematic precursors possess imbricated structure. Disorder is frequently observed in the crystal structure of mesogenic compounds<sup>[142,174]</sup>. It seemed promising to determine the crystal structures at low temperatures. It may provide more detailed information about the thermal behaviour of the molecule.

This chapter describes the crystal structures of 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl) pyrimidine (ECCPP) at 246K and 5-(trans-4-heptylcyclohexyl)-2-(4-cyanophenyl) pyrimidine (HCCPP) at 243K. Structures of these two compounds at room temperature were determined earlier in our laboratory<sup>[142,144]</sup>. The compound ECCPP, lower member of the series, shows nematic phase (124°C) when heated to isotropic phase and HCCPP shows smectic (82°C) as well as nematic phase (158°C)<sup>[175]</sup>.

## 7.2 EXPERIMENTAL

### 7.2.1 Crystal Data

Plate - shaped transparent crystals of suitable size for x-ray diffraction were obtained from a solution of acetone for both the compounds. Intensity data were collected at low temperature using an Enraf Nonius CAD - 4 diffractometer with graphite monochromated  $\text{CuK}_\alpha$  radiation in the  $\omega - 2\theta$  scan mode. A total of 5287 reflections for ECCPP and 3612 reflections for HCCPP were taken. Reflections having intensity below  $2.5\sigma(I)$  level were treated as unobserved. Both the crystals belong to monoclinic system. The space group of HCCPP is  $P2_1/c$

having systematic absences  $h0l$  for  $l$  odd ( $2n + 1$ ) and  $0k0$  for  $k$  odd and the space group of ECCPP is  $P2_1/n$  having  $h0l$  absent for  $h + 1$  odd and  $0k0$  with  $k$  odd.

The reflections were corrected for Lorentz and polarisation factors but no absorption correction was made. Basic crystallographic data both at room temperature and low temperature are given in Table - 7.1. There was no indication of phase transformation on cooling the crystal. The contraction in volume at low temperature is by 2% for ECCPP and 1% for HCCPP.

**Table - 7.1**

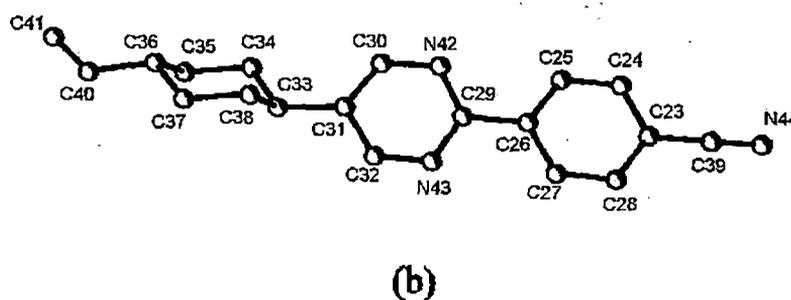
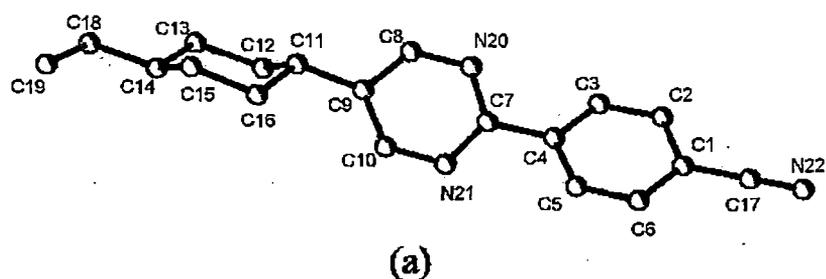
**Crystallographic data**

	Room Temp. (for ECCPP)	Low Temp. (246 K) (for ECCPP)	Room Temp. (for HCCPP)	Low Temp. (243 K) (for HCCPP)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
$a / \text{Å}$	15.959	15.6149	13.0422	13.0171
$b / \text{Å}$	33.469	33.4043	17.7464	17.7024
$c / \text{Å}$	6.210	6.2376	9.5950	9.5620
$\beta / \text{deg}$	90.335	91.4622	107.170	107.5498
$Z$	8	8	4	4
$V / \text{Å}^3$	3316.90	3252.50	2121.81	2100.85
$d_{\text{cal}} / \text{gm-cm}^{-3}$	1.17	1.19	1.13	1.14

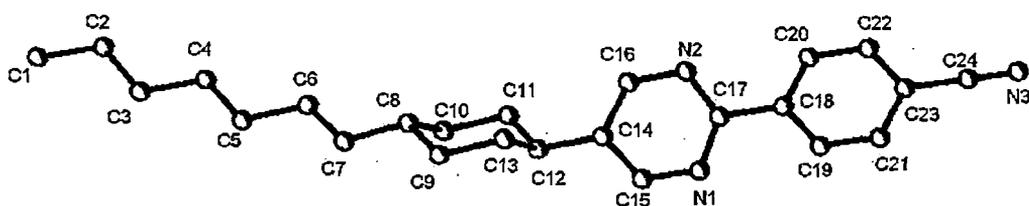
**7.2.2 Structure determination and refinement**

The structures were solved by direct method using the PC version of program Multan-80 of NRCVAX package<sup>[176]</sup>. 450 structure amplitudes were selected for initial phase determination for ECCPP with  $E \geq 1.83$  and for HCCPP with  $E \geq 1.53$ . E-map with the highest figure of merit showed fragments of the molecules. Remaining carbon atoms were located by successive Fourier synthesis. I had great difficulty in locating the positions of atoms of one of the two molecules of ECCPP but for HCCPP atomic position are located easily. Successive Fourier

and difference Fourier were applied several times to arrive at the trial structure. The positions of the hydrogen atoms were determined from the known geometry around carbon atoms and also with the help of difference Fourier map. The structures were refined by full matrix least squares method. The final  $R_w$ -value for ECCPP and HCCPP were found to be 0.096 ( $R = 0.099$ ) and 0.061 ( $R = 0.62$ ) respectively. I could not get crystals of very good quality and the  $R$  values are therefore somewhat high.



### EPPCC Molecule



### HCCPP Molecule

Fig. 7.1 Molecular structure of ECCPP and HCCPP

## 7.3 RESULTS AND DISCUSSION

### 7.3.1 Molecular structure

Molecular structure of ECCPP and HCCPP are shown in Fig.-7.1 with the atom numbering scheme. Final positions and thermal parameters of the non hydrogen atoms at low temperature are listed in Table - 7.2 – 7.3 and the bond lengths and bond angles at both temperatures in Table - 7.4 – 7.7. In both the cases values of bond lengths and bond angles are comparable with the structures determined at room temperature<sup>[142,144]</sup> except the cyclohexane ring of the molecule B of the compound ECCPP. In the room temperature structure, the cyclohexane ring of the molecule A has a normal chair conformation, however in the molecule B, it is approximately planar — this was the result of disorder, in which two mirrored chair conformations of about equal weight are involved. This disorder is also manifested in anomalous bond distances and angles involving the cyclohexane atoms and abnormally large temperature parameters for some of these atoms. The most remarkable feature of the low temperature structure is the conformational change of the cyclohexane ring of molecule B from planar to chair form. Its bond lengths and bond angles agree with reported values for cyclohexane rings<sup>[144,146,174,177]</sup>. The cyclohexane rings for HCCPP are in chair conformation at both the temperatures. The relative positions of the successive rings within the molecules are shown in the Newman's projections of Fig.-7.2 and 7.3.

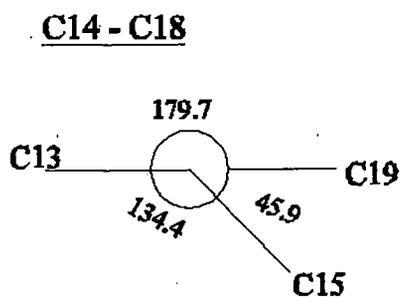
For ECCPP, the dihedral angle between the phenyl and the pyrimidine rings are  $16.3^\circ$  (A molecule) and  $7.8^\circ$  (B molecule), the room temperature values being  $15.2^\circ$  and  $6.9^\circ$  respectively. For HCCPP this angle is  $15^\circ$  in both the cases.

### 7.3.2 Molecular Packing

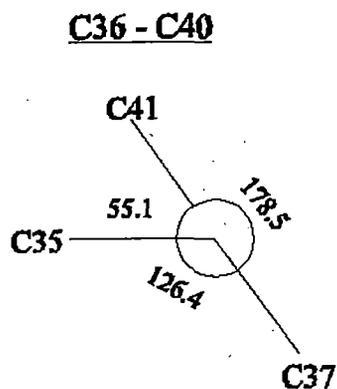
Projections of the structure along [ 001] and [010] for ECCPP are shown in Fig.-7.4. Intermolecular distances smaller than the sum of the Van der Waal's radii of the atoms involved have been calculated. There were short contacts between AA and AB molecules as have been found in room temperature analysis. At low temperature the shortest distance of approach between AA molecules is  $3.41\text{\AA}$

### ECCPP Molecule

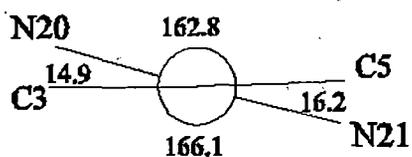
Molecule - A



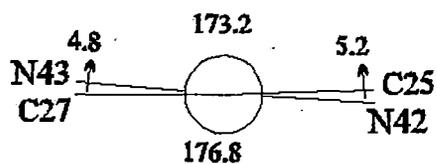
Molecule - B



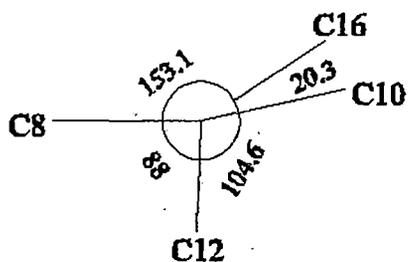
C4 - C7



C26 - C29



C9 - C11



C31 - C33

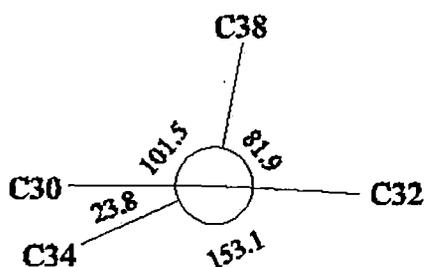
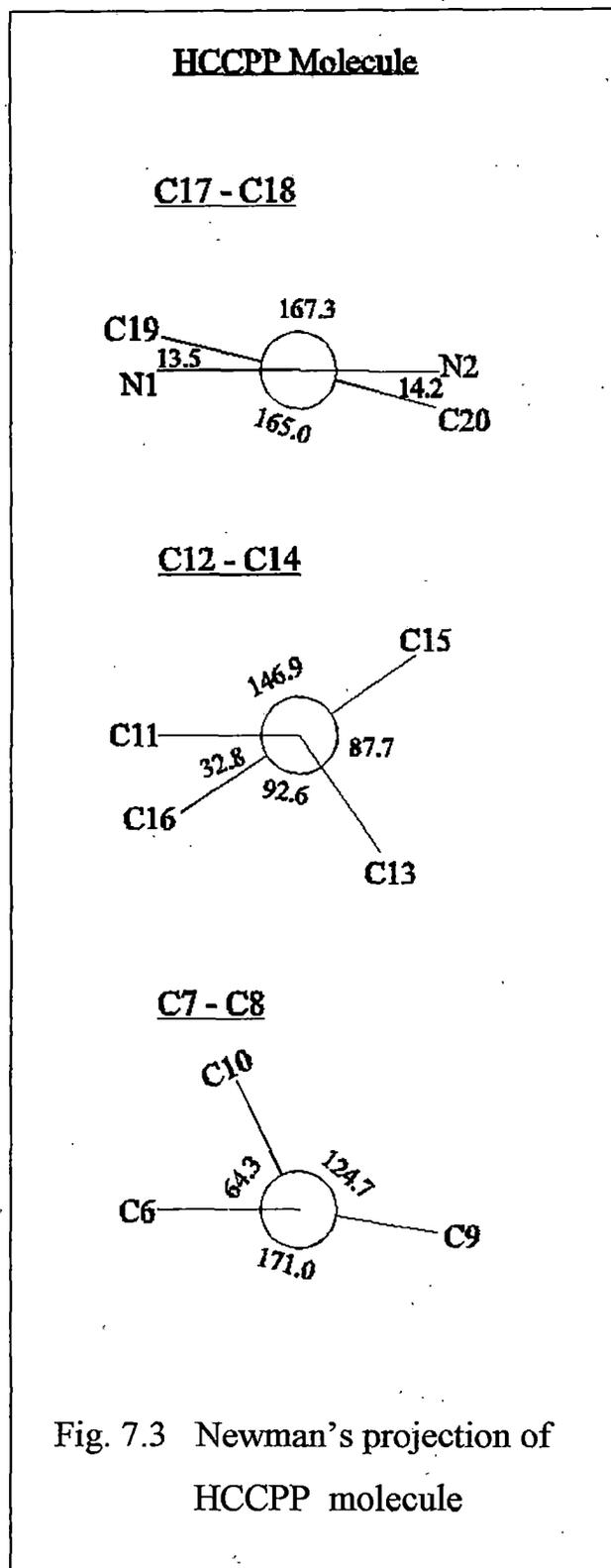


Fig. 7.2 Newman's projection of ECCPP molecule



and that of AB molecules is  $3.31\text{\AA}$ . These are about  $0.04\text{\AA}$  less than those found at room temperature. The interaction of AA and AB are both of dipolar nature. The associated pair lengths of AA is  $23.1\text{\AA}$  and that of AB is  $30.9\text{\AA}$ . From x-ray diffraction photographs of nematic phase, the apparent length of pairs of associated molecule is found to be about  $25.0\text{\AA}$ . I, therefore, conclude that AA type association plays a crucial role in mesophase formation. Pairs of molecules related by a centre of symmetry give rise to a sheet of parallel molecule in the plane (100) and these sheets are stacked in an imbricated fashion along the c-axis.

The projections of the structures of HCCPP along [001] and [010] are shown in the Fig.-7.5. Intermolecular short contacts occur between molecules related through a centre of symmetry ( $\frac{1}{2}, 0, \frac{1}{2}$ ). These short contacts suggest that associated pairs of molecules are bound

together by weak interactions between benzenes, pyrimidines and cyano groups. Total length of this pair is  $32\text{\AA}$  which becomes  $33.7\text{\AA}$  in smectic phase and  $37\text{\AA}$  in nematic phase. The molecules are arranged in layers in (101) planes and the layers

are stacked along [010]. The molecular packing therefore fulfils the geometrical prerequisite for smectic phase formation on melting as was found in the room temperature structure.

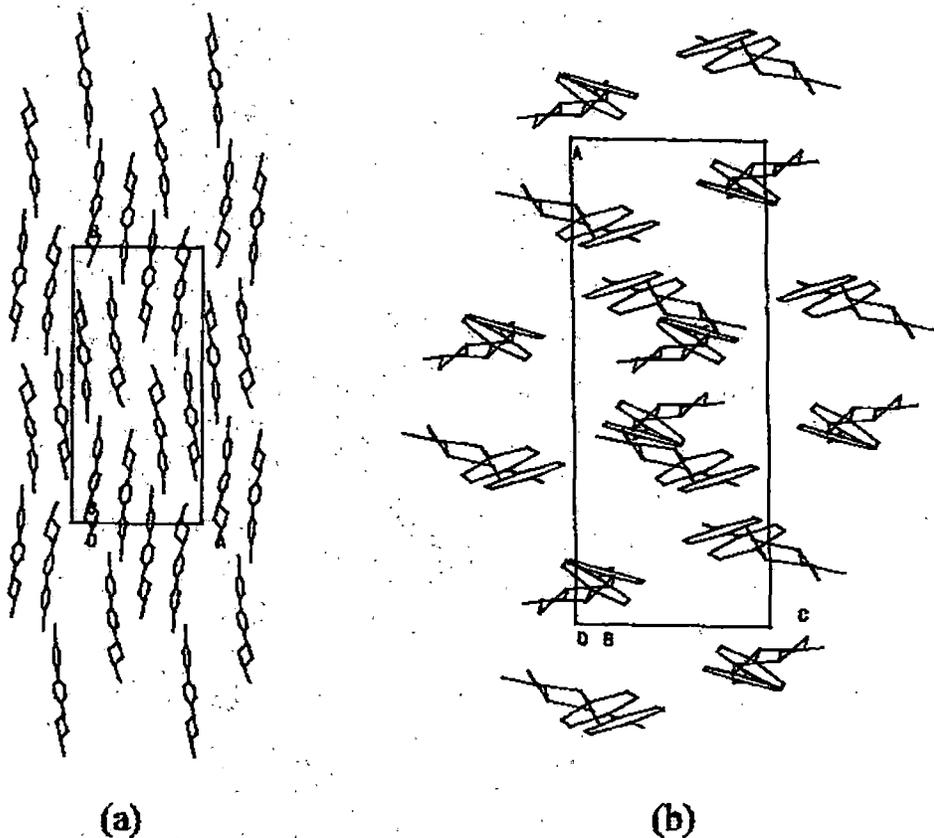


Fig. 7.4 Projection of the structure of ECCPP along a) [001] and b) [010]

### 7.3.3 Molecular thermal vibrations

Thermal ellipsoid plot of the molecules using the program ORTEP<sup>[178]</sup> for both the compounds at low and at room temperatures are shown in Fig.-7.6 and Fig.-7.7. Thermal ellipsoids are at 50% probability level. I find that ellipsoids enclosing hydrogen atoms are consistently larger than those for the C and N atoms. For ECCPP molecules ORTEP drawing at low and room temperatures differ significantly, specially in the molecule B, which is highly disordered at room temperature.

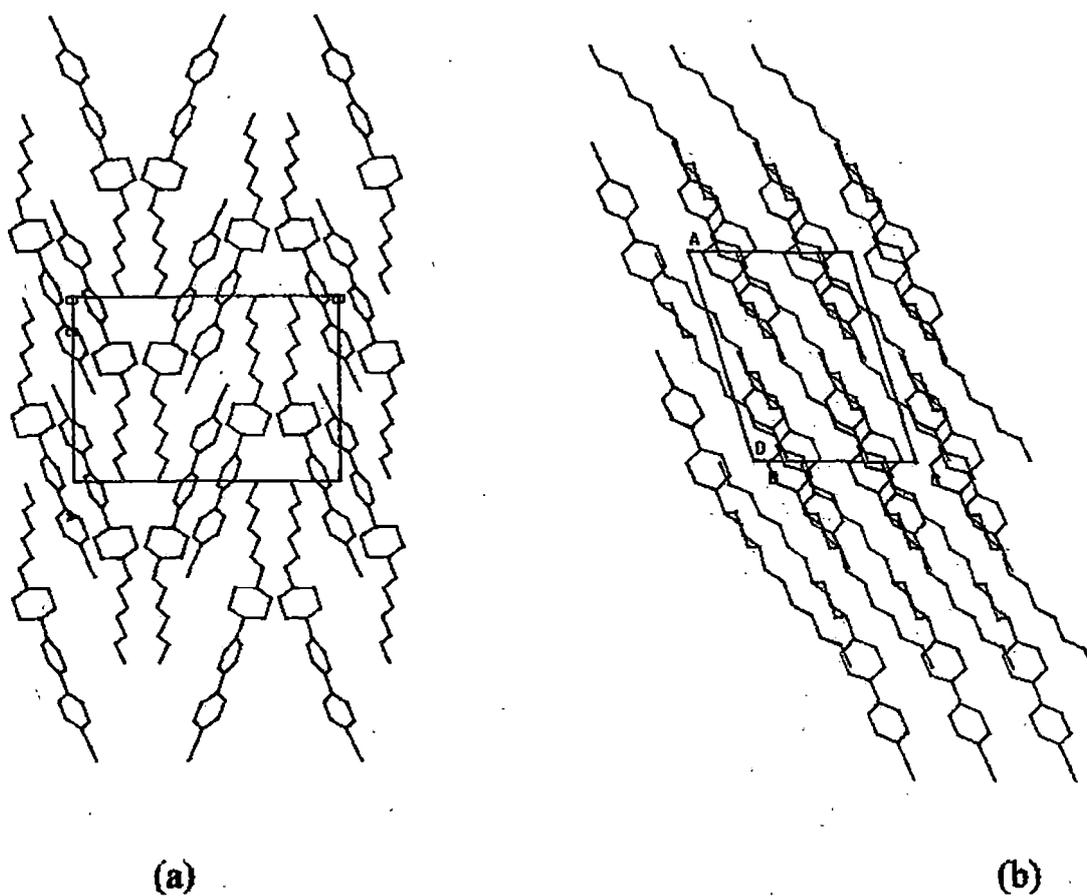


Fig. 7.5 Projection of the structure of HCCPP along a) [001] and b) [010]

It was shown by Cruickshank<sup>[179]</sup> and Schoemaker and Trueblood<sup>[180]</sup>, that a linear least square analysis of the anisotropic displacement parameters of the individual atoms in a molecule that might be assumed to behave as a rigid body, could provide librational (L) and translational (T) tensors describing the overall motion of the molecules. The anisotropic displacement parameters of the two compounds were fitted to the rigid body model. A computer program was written in our laboratory. The analysis was carried out at low and room temperatures treating the entire molecule as a rigid body and the molecular fragment consisting of the cyanophenyl pyrimidine as rigid body. The mean square amplitudes of

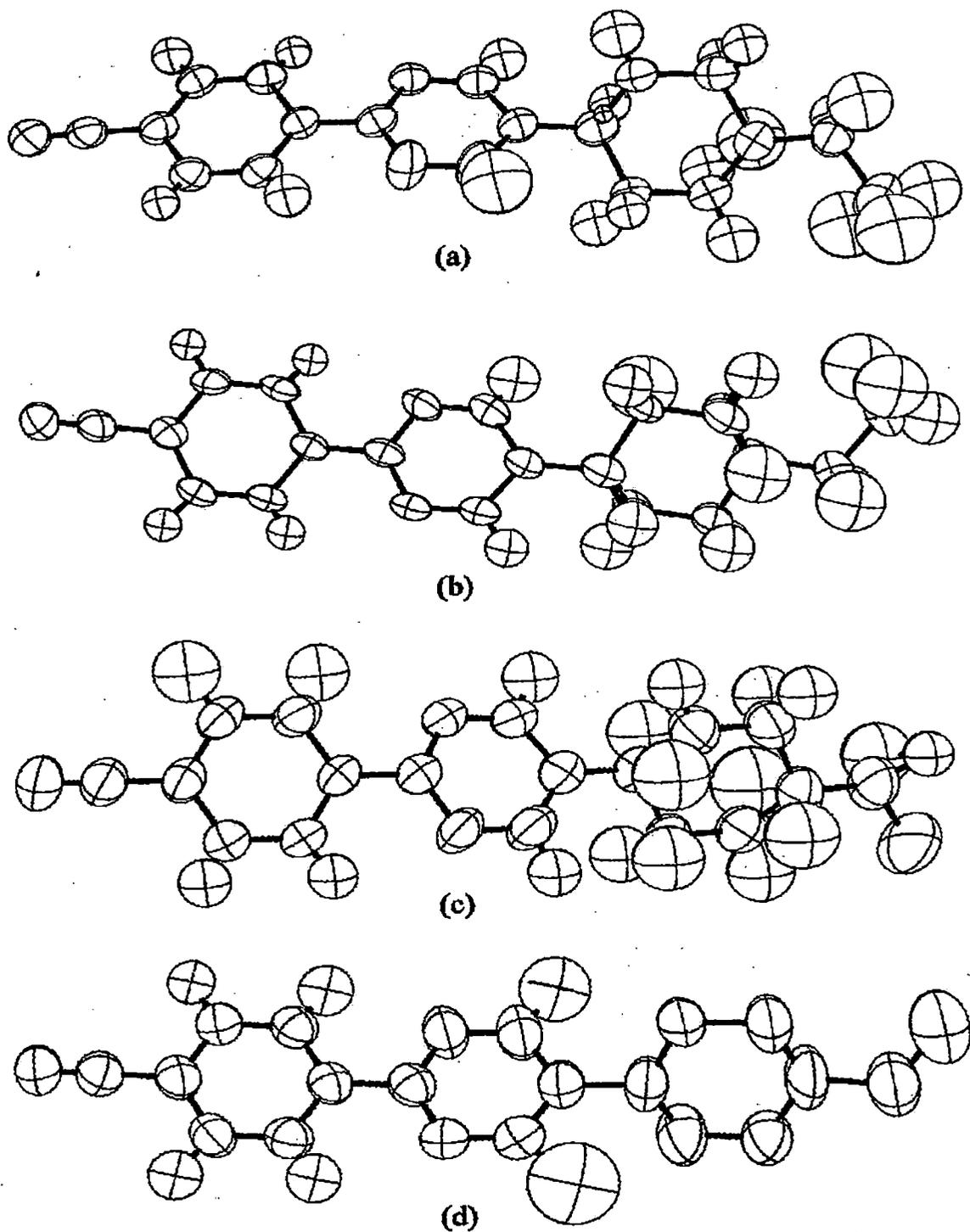
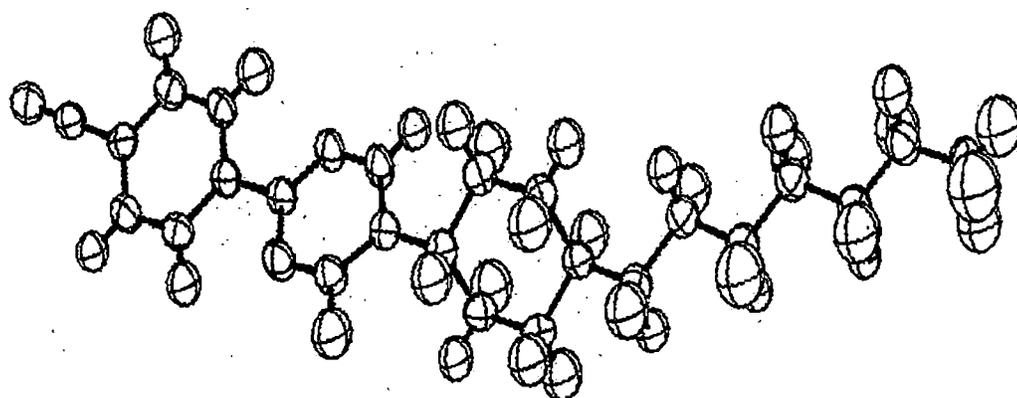
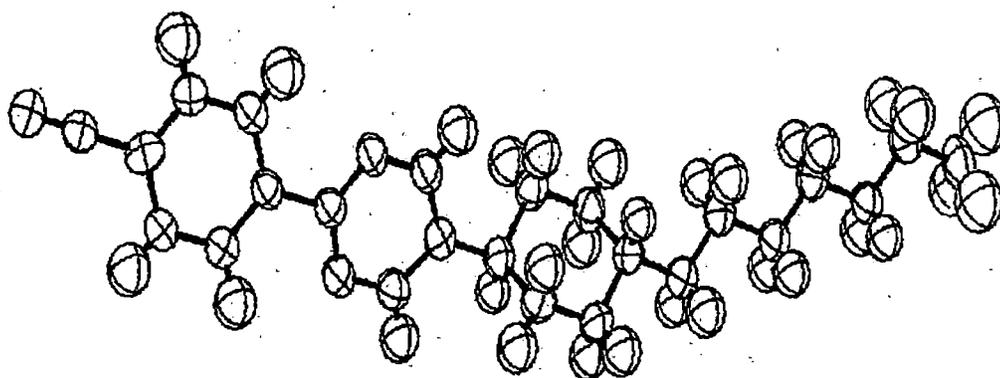


Fig. 7.6 ORTEP drawing for ECCPP a) molecule A at low temperature, b) molecule B at low temperature, c) molecule A at room temperature and d) molecule B at room temperature



(a)



(b)

Fig. 7.7 ORTEP drawing for HCCPP a) at low temperature and b) at room temperature

translational motion and angular libration corresponding to three principal axes of T and L ellipsoids are given in the Table - 7.8. These motions are referred to cartesian axes with molecular centre of mass as origin. The X-axis is taken to the best fitted line in the least square plane of the cyano phenyl pyrimidine group and passing through the para position of the molecules. Y-axis is in this plane perpendicular to X-axis and Z-axis is perpendicular to the plane. I have also

calculated the moment of inertia (M.I) of the molecules. The principal axes about which eigen value of M.I tensor is minimum, is the long axis of the molecule.  $L_3$  is the libration about the long molecular axis. From the table it is found that for the compound HCCPP values of the librational motions are very low at both the temperatures when the whole molecule is concerned. When the ring system is considered it is found that  $L_3$  is rather large. At low temperature this  $L_3$  value is about 0.6 times of that of high temperature value. For ECCPP molecules (A and B)  $L_3$  values are comparatively large for both the ring system and when the whole molecule is considered. At low temperature this  $L_3$  values is smaller than that at room temperature. In all cases the mean squares amplitudes of translational motions have the smallest values along the stacking directions and largest along the molecular axes. At low temperatures these values are much smaller than those at room temperature. The translational vibration is much larger at room temperature in the case of molecule B when the whole molecule is considered. This is consistent with the disorder in the crystal structure.

Since the molecules considered in these analyses are not strictly rigid, I cannot have a simple interpretation of motion in terms of translation and libration. However the results indicate that the molecular motion is anisotropic and is mainly translational in character.

To investigate the orientational behaviour of the two compounds at different temperatures the orientational order parameters for the principal molecular axes have been calculated. The order parameter in principle could be evaluated using

$$S = \frac{1}{N} \left\langle \sum_{i=1}^N \left( \frac{3}{2} \cos^2 \theta_i - \frac{1}{2} \right) \right\rangle$$

where  $\theta_i$  is the angle of the axis of the  $i^{\text{th}}$  molecule with the director. The director,  $\mathbf{n}$  is found by diagonalisation of the ordering tensor  $Q$ , for the principal molecular axis.  $Q$  is defined as<sup>[181]</sup>

$$Q_{\alpha\beta} = \frac{1}{N} \sum_i \left( 3a_{i\alpha} a_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} \right)$$

where  $N$  is the number of molecules,  $a_\alpha$  and  $a_\beta$  are the components of a unit vector  $a_i$  associated with the long axes of the individual molecule. Calculations were carried out for 108 molecules. For ECCPP at room temperature molecules A and B have  $S$  values of 0.980 and 0.978 respectively. At low temperature the values increase to 0.991 and 0.986.  $S$  values for HCCPP at low temperature is 0.940 and at room temperature it is 0.926. For long range ordered crystalline state  $S$  should be 1. However,  $S$  is only unambiguously defined for rigid molecules. In reality, typical mesogenic molecules are neither rigid nor highly symmetric. The flexible chain part at the end often has low symmetry and more degrees of freedom and as a result it can take different conformations. As the chain becomes larger, the flexibility increases. This causes a lowering of order parameter of HCCPP molecule.

I calculated the correction to the order parameter for the libration about the axis transverse to the long molecular axis, using the following equation for the average value of  $\langle \text{Cos}^2\theta \rangle$ .

$$\langle \text{Cos}^2\theta \rangle = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \text{Cos}^2(\theta_0 + \theta_1 \text{Cos}(\omega t)) dt$$

where  $\theta_0$  is the angle between the molecule and the director,  $\theta_1$  is the mean square librational amplitude perpendicular to the long molecular axes. When  $\theta_1$  is very small above equation can be written as

$$\langle \text{Cos}^2\theta \rangle = \text{Cos}^2\theta_0 - \frac{\theta_1^2}{2} \text{Cos}^2 2\theta_0$$

The correction to the order parameters at both the temperatures were of the order of  $10^{-3}$ .

## 7.4 CONCLUSIONS

A systematic study of the molecular and crystalline structure of mesogenic material is of considerable interest in the interpretation of the physical properties of liquid crystalline phases. The molecular arrangement in any liquid crystalline

phase is specific and is quite often related to the packing in the respective crystal phase.

It is often found that molecules of these mesomorphic compounds have certain translatory movements which eventually lead to disorder in the structure. In the compound ECCPP such disordering have been observed in the cyclohexane ring of the molecule B. Thermal motions are at 273K and 323K show significant difference. It is expected that if the crystal is further heated the molecule will have increased thermal and conformational disorder.

Crystal structure for a number of mesogenic compounds have been determined to establish rules concerning the relation between solid phase and mesomorphic phases. But the structural studies of mesomorphic compounds at different temperatures in the solid phase are few.

I do not have experimental set-up for collecting diffraction data at high temperatures. Single crystal structural analysis near the melting point could have given us more insight into the fluctuations of the physical properties at solid – mesophasic transition.

**Table -7.2**

Fractional co-ordinates of the non-hydrogen atoms for the HCCPP molecule at low temp.

	x	y	z	Biso
C1	0.0139(3)	0.8159(3)	0.7082(4)	5.92(20)
C2	0.1158(3)	0.8485(2)	0.6907(4)	4.65(14)
C3	0.8105(2)	0.1572(2)	0.5762(3)	3.96(12)
C4	0.2594(2)	0.8454(2)	0.5623(3)	4.04(12)
C5	0.3093(2)	0.8045(2)	0.4594(3)	3.97(12)
C6	0.4150(2)	0.8386(7)	0.4541(3)	3.88(12)
C7	0.4718(2)	0.7925(2)	0.3650(3)	3.94(12)
C8	0.5840(2)	0.8202(1)	0.3706(3)	3.28(11)
C9	0.6406(2)	0.7645(2)	0.2969(3)	4.09(13)
C10	0.5822(2)	0.8981(2)	0.3030(3)	3.85(12)
C11	0.6932(2)	0.9245(2)	0.3020(3)	3.96(13)
C12	0.7467(2)	0.8687(2)	0.2253(3)	3.28(11)
C13	0.7518(2)	0.7907(2)	0.2960(3)	3.92(12)
C14	0.8549(2)	0.8943(1)	0.2170(3)	3.12(10)
C15	0.8915(2)	0.8759(2)	0.0989(3)	3.72(12)
C16	0.9271(2)	0.9382(2)	0.3241(3)	3.81(12)
C17	1.0479(2)	0.9405(1)	0.1945(2)	3.08(10)
C18	1.1513(2)	0.9672(1)	0.1798(2)	3.12(10)
C19	1.1941(2)	0.9367(2)	0.0754(3)	3.66(11)
C20	1.2073(2)	1.0255(2)	0.2690(3)	3.78(11)
C21	1.2892(2)	0.9628(2)	0.0593(3)	3.70(11)
C22	1.3024(2)	1.0524(2)	0.2540(3)	3.95(12)
C23	1.3439(2)	1.0217(1)	0.1484(3)	3.22(10)
C24	1.4414(2)	1.0522(1)	0.1301(3)	3.45(11)
N1	0.9858(2)	0.8974(1)	0.0852(2)	3.82(10)
N2	1.0221(2)	0.9617(1)	0.3144(2)	3.80(10)
N3	1.5181(2)	1.0784(1)	0.1153(3)	4.30(10)

**Table - 7.3**

Fractional co-ordinates of non-hydrogen atoms for the ECCPP molecule at low temp.

	x	y	z	Biso
C1	0.1118 (2)	0.4435 (1)	0.1663 (6)	3.91(15)
C2	0.0898 (2)	0.4660 (1)	0.3453 (6)	4.12(17)
C3	0.0854 (2)	0.5068 (1)	0.3303 (5)	3.89(17)
C4	0.1030 (2)	0.5266 (1)	0.1390 (5)	3.34(14)
C5	0.1257 (2)	0.5035 (1)	-0.0373 (5)	3.96(16)
C6	0.1306 (2)	0.4628 (1)	-0.0256 (5)	4.08(17)
C7	0.0948 (2)	0.5703 (1)	0.1220 (5)	3.70(15)
C8	0.0413 (3)	0.6283 (1)	0.2502 (6)	5.16(21)
C9	0.0720 (3)	0.6501 (1)	0.0790 (6)	5.22(22)
C10	0.1174 (3)	0.6271 (2)	-0.0647 (7)	6.08(24)
C11	0.0465 (4)	0.6936 (2)	0.0567 (7)	6.6 (3)
C12	0.1009 (4)	0.7195 (2)	0.1957 (7)	7.1 (3)
C13	0.0790 (3)	0.7638 (1)	0.1818 (7)	5.74(23)
C14	0.0698 (4)	0.7791(1)	-0.0479 (7)	6.5 (3)
C15	0.0198 (4)	0.7529 (2)	-0.1861 (8)	7.3 (3)
C16	0.0465 (3)	0.7089 (1)	-0.1731 (6)	5.21(21)
C17	0.1151 (3)	0.4006 (1)	0.1800 (6)	4.73(19)
C18	0.0507 (3)	0.8233 (1)	-0.0528 (8)	5.72(21)
C19	0.0398 (4)	0.8424 (2)	-0.2699(10)	8.3 (3)
N20	0.0522 (2)	0.5895 (1)	0.2740 (5)	4.55(16)
N21	0.1297 (2)	0.5881 (1)	-0.0477 (5)	5.27(17)
N22	0.1173 (3)	0.3665 (1)	0.1922 (6)	6.39(21)
C23	0.2007 (3)	0.3138 (1)	0.7193 (6)	4.21(16)
C24	0.2245 (3)	0.2985 (1)	0.9221 (6)	4.46(17)
C25	0.2199 (3)	0.2580 (1)	0.9579 (6)	4.28(17)
C26	0.1920 (2)	0.2320 (1)	0.7975 (6)	3.80(15)
C27	0.1688 (2)	0.2478 (1)	0.5954 (6)	4.17(17)
C28	0.1733 (3)	0.2882 (1)	0.5590 (6)	4.29(17)
C29	0.1842 (2)	0.1885 (1)	0.8420 (6)	4.12(17)
C30	0.1981 (4)	0.1375 (2)	1.0784 (8)	7.2 (3)
C31	0.1602 (3)	0.1112 (1)	0.9378 (6)	5.24(22)
C32	0.1382 (3)	0.1277 (1)	0.7428 (6)	5.65(24)
C33	0.1379 (3)	0.0680 (1)	0.9819 (7)	5.38(22)
C34	0.1264 (3)	0.0582 (1)	1.2170 (6)	5.32(22)
C35	0.0991 (3)	0.0149 (2)	1.2494 (7)	6.15(25)
C36	0.1594 (3)	-0.0147 (1)	1.1517 (8)	5.93(23)
C37	0.1777 (3)	-0.0039 (1)	0.9196 (7)	5.60(22)
C38	0.2021 (4)	0.0395 (2)	0.8900 (8)	6.7 (3)
C39	0.2059 (3)	0.3562 (1)	0.6846 (6)	4.81(20)
C40	0.1312 (3)	-0.0580 (1)	1.1662 (8)	5.74(22)
C41	0.1129 (5)	-0.0735 (2)	1.3856 (10)	9.1 (4)
N42	0.2118 (3)	0.1762 (1)	1.0349 (6)	6.43(19)
N43	0.1494 (2)	0.1656 (1)	0.6921 (5)	5.13(18)
N44	0.2102 (3)	0.3902 (1)	0.6619 (6)	6.58(23)

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

**Table - 7.4**

Bond distances (Å) of the non-hydrogen atoms with standard deviations in parentheses for molecule HCCPP at low temperature.

C(1)-C(2)	1.502(4)	C(8)-C(10)	1.522(4)	C(14)-C(16)	1.398(3)	C(19)-C(21)	1.375(4)
C(2)-C(3)	1.515(4)	C(9)-C(13)	1.522(4)	C(15)-N(1)	1.328(3)	C(20)-C(22)	1.373(4)
C(3)-C(4)	1.508(4)	C(10)-C(11)	1.522(4)	C(16)-N(2)	1.334(3)	C(21)-C(23)	1.398(3)
C(4)-C(5)	1.516(4)	C(11)-C(12)	1.519(4)	C(17)-C(18)	1.472(3)	C(22)-C(23)	1.391(3)
C(5)-C(6)	1.517(4)	C(12)-C(13)	1.530(4)	C(17)-N(1)	1.349(3)	C(23)-C(24)	1.437(3)
C(6)-C(7)	1.522(4)	C(12)-C(14)	1.505(3)	C(17)-N(2)	1.343(3)	C(24)-N(3)	1.148(3)
C(7)-C(8)	1.526(3)	C(14)-C(15)	1.390(3)	C(18)-C(19)	1.391(3)	C(18)-C(20)	1.396(3)
C(8)-C(9)	1.524(4)						

**Table - 7.5**

Bond angles (deg.) of the non-hydrogen atoms with standard deviations in parentheses for molecule HCCPP at low temperature.

C(1)-C(2)-C(3)	115.39(25)	C(11)-C(12)-C(14)	113.69(20)	C(17)-C(18)-C(20)	120.25(20)
C(2)-C(3)-C(4)	113.43(22)	C(13)-C(12)-C(14)	112.22(19)	C(19)-C(18)-C(20)	118.49(22)
C(3)-C(4)-C(5)	115.08(22)	C(9)-C(13)-C(12)	111.19(21)	C(18)-C(19)-C(21)	121.28(22)
C(4)-C(5)-C(6)	113.74(22)	C(12)-C(14)-C(15)	121.87(21)	C(18)-C(20)-C(22)	120.93(22)
C(5)-C(6)-C(7)	113.85(22)	C(12)-C(14)-C(16)	124.17(21)	C(19)-C(21)-C(23)	119.56(22)
C(6)-C(7)-C(8)	115.47(21)	C(15)-C(14)-C(16)	113.96(21)	C(20)-C(22)-C(23)	120.03(22)
C(7)-C(8)-C(9)	111.58(20)	C(14)-C(15)-N(1)	124.52(22)	C(21)-C(23)-C(22)	119.70(22)
C(7)-C(8)-C(10)	112.56(20)	C(14)-C(16)-N(2)	123.65(21)	C(21)-C(23)-C(24)	120.74(21)
C(9)-C(8)-C(10)	109.72(20)	C(18)-C(17)-N(1)	117.40(20)	C(22)-C(23)-C(24)	119.55(22)
C(8)-C(9)-C(13)	113.53(21)	C(18)-C(17)-N(2)	117.62(20)	C(23)-C(24)-N(3)	178.2(3)
C(8)-C(10)-C(11)	112.82(20)	N(1)-C(17)-N(2)	124.97(21)	C(15)-N(1)-C(17)	116.20(20)
C(10)-C(11)-C(12)	112.20(21)	C(17)-C(18)-C(19)	121.24(21)	C(16)-N(2)-C(17)	116.69(20)
C(11)-C(12)-C(13)	109.83(20)				

**Table - 7.6**

Bond distances (Å) of the non-hydrogen atoms with standard deviations in parentheses for molecule ECCPP at low temperature.

C(1)-C(2)	1.3960(3)	C(11)-C(16)	1.5223(3)	C(29)-N(42)	1.3328(5)
C(1)-C(6)	1.3966(3)	C(12)-C(13)	1.51859(14)	C(29)-N(43)	1.3145(5)
C(1)-C(17)	1.43707(12)	C(13)-C(14)	1.5250(3)	C(30)-C(31)	1.3659(5)
C(2)-C(3)	1.36723(11)	C(14)-C(15)	1.4441(6)	C(30)-N(42)	1.33783(12)
C(3)-C(4)	1.3989(3)	C(14)-C(18)	1.50750(13)	C(31)-C(32)	1.3712(4)
C(4)-C(5)	1.3973(4)	C(15)-C(16)	1.52903(16)	C(31)-C(33)	1.51200(15)
C(4)-C(7)	1.46781(12)	C(17)-N(22)	1.14031(9)	C(32)-N(43)	1.31861(11)
C(5)-C(6)	1.36381(11)	C(18)-C(19)	1.5019(3)	C(33)-C(34)	1.5181(3)
C(7)-N(20)	1.3361(6)	C(23)-C(24)	1.4059(4)	C(33)-C(38)	1.5074(8)
C(7)-N(21)	1.3412(5)	C(23)-C(28)	1.3746(4)	C(34)-C(35)	1.52352(17)
C(8)-C(9)	1.3887(4)	C(23)-C(39)	1.43606(11)	C(35)-C(36)	1.5054(7)
C(8)-N(20)	1.31458(11)	C(24)-C(25)	1.37118(11)	C(36)-C(37)	1.5267(4)
C(9)-C(10)	1.3885(6)	C(25)-C(26)	1.3866(4)	C(36)-C(40)	1.51423(17)
C(9)-C(11)	1.51223(16)	C(26)-C(27)	1.4048(4)	C(37)-C(38)	1.50885(15)
C(10)-N(21)	1.32210(11)	C(26)-C(29)	1.48579(12)	C(39)-N(44)	1.14664(9)
C(11)-C(12)	1.4784(7)	C(27)-C(28)	1.37110(11)	C(40)-C(41)	1.4971(4)

**Table -7.7**

Bond angles (deg.) of the non-hydrogen atoms with standard deviations in parentheses for molecule ECCPP at low temperature.

C(2)-C(1)-C(6)	19.917(17)	C(12)-C(13)-C(14)	113.354(12)	C(26)-C(29)-N(43)	118.036(13)
C(2)-C(1)-C(17)	119.875(8)	C(13)-C(14)-C(15)	113.17(3)	N(42)-C(29)-N(43)	125.534(22)
C(6)-C(1)-C(17)	120.208(9)	C(13)-C(14)-C(18)	111.208(10)	C(31)-C(30)-N(42)	124.009(12)
C(1)-C(2)-C(3)	119.615(8)	C(15)-C(14)-C(18)	118.59(3)	C(30)-C(31)-C(32)	113.991(25)
C(2)-C(3)-C(4)	121.371(9)	C(14)-C(15)-C(16)	114.08(3)	C(30)-C(31)-C(33)	126.536(10)
C(3)-C(4)-C(5)	117.913(17)	C(11)-C(16)-C(15)	111.458(16)	C(32)-C(31)-C(33)	119.408(20)
C(3)-C(4)-C(7)	120.982(11)	C(1)-C(17)-N(22)	179.5	C(31)-C(32)-N(43)	124.504(14)
C(5)-C(4)-C(7)	121.068(7)	C(14)-C(18)-C(19)	116.771(10)	C(31)-C(33)-C(34)	114.553(12)
C(4)-C(5)-C(6)	121.628(8)	C(7)-N(20)-C(8)	117.227(10)	C(31)-C(33)-C(38)	112.12(4)
C(1)-C(6)-C(5)	119.546(10)	C(7)-N(21)-C(10)	116.013(19)	C(34)-C(33)-C(38)	109.10(4)
C(4)-C(7)-N(20)	117.965(11)	C(24)-C(23)-C(28)	119.941(19)	C(33)-C(34)-C(35)	111.945(15)
C(4)-C(7)-N(21)	117.438(16)	C(24)-C(23)-C(39)	118.658(9)	C(34)-C(35)-C(36)	112.98(4)
N(20)-C(7)-N(21)	124.59(3)	C(28)-C(23)-C(39)	121.401(11)	C(35)-C(36)-C(37)	111.20(3)
C(9)-C(8)-N(20)	123.968(18)	C(23)-C(24)-C(25)	119.403(9)	C(35)-C(36)-C(40)	114.64(4)
C(8)-C(9)-C(10)	113.42(3)	C(24)-C(25)-C(26)	121.061(12)	C(37)-C(36)-C(40)	110.228(15)
C(8)-C(9)-C(11)	118.70(3)	C(25)-C(26)-C(27)	118.820(20)	C(36)-C(37)-C(38)	113.476(12)
C(10)-C(9)-C(11)	127.596(9)	C(25)-C(26)-C(29)	120.226(11)	C(33)-C(38)-C(37)	112.80(4)
C(9)-C(10)-N(21)	124.728(11)	C(27)-C(26)-C(29)	120.925(11)	C(23)-C(39)-N(44)	178.4
C(9)-C(11)-C(12)	111.26(3)	C(26)-C(27)-C(28)	120.298(9)	C(36)-C(40)-C(41)	116.527(14)
C(9)-C(11)-C(16)	113.731(16)	C(23)-C(28)-C(27)	120.475(12)	C(29)-N(42)-C(30)	115.572(16)
C(12)-C(11)-C(16)	109.99(3)	C(26)-C(29)-N(42)	116.409(11)	C(29)-N(43)-C(32)	116.299(12)
C(11)-C(12)-C(13)	114.24(3)				

**Table - 7.8**Eigen values and eigen vectors of libration (L in deg.) and translation (T in Å<sup>2</sup>)

<b>Compound ECCPP</b>								
<b>Molecule A</b>								
<i>Whole Molecule</i>								
Room Temperature				Low Temperature				
Eigen value		Direction Cosines			Eigen value		Direction Cosines	
<b>T</b>	0.0783	0.6519	0.7209	-0.2358	0.0706	0.8949	-0.3681	-0.2519
	0.0737	-0.7409	0.5384	-0.4021	0.0650	0.3950	0.9152	-0.0673
	0.0548	-0.1629	0.4367	0.8847	0.0275	0.2057	-0.1603	0.9651
<b>L</b>	1.81	0.9815	-0.1752	0.0767	1.45	0.0751	0.0282	-0.7083
	9.36	0.1649	0.9784	0.1245	7.31	-0.1332	0.9863	-0.0933
	1.90	-0.0969	-0.1096	0.9893	1.40	0.6964	0.1601	0.6993
<i>Cyano phenyl pyrimidine</i>								
<b>T</b>	0.0479	0.6547	-0.5137	-0.5545	0.0359	0.6971	0.2673	-0.6646
	0.0779	0.3623	0.8571	-0.3662	0.0653	-0.1932	0.9631	0.1881
	0.0630	0.6634	0.0389	0.7437	0.0183	0.6891	-0.0008	0.7232
<b>L</b>	1.62	0.9586	-0.2834	0.0268	1.40	0.9790	0.2010	-0.0250
	9.50	0.2774	0.9511	0.1358	8.63	-0.2010	0.9780	-0.0410
	3.19	-0.0640	-0.1228	0.9904	3.13	0.0160	0.0460	0.9990
<b>Molecule B</b>								
<i>Whole Molecule</i>								
<b>T</b>	0.1429	0.9149	0.0013	0.3934	0.0655	0.8290	0.5290	-0.1780
	0.0804	0.2464	0.7776	-0.5784	0.0674	-0.4700	0.8330	0.2880
	0.0717	-0.3067	0.6287	0.7146	0.0364	0.3010	-0.1550	0.9400
<b>L</b>	1.90	0.8687	0.1317	-0.4774	0.8100	0.8042	0.0334	0.5930
	8.323	0.1063	0.9911	0.0800	7.8970	0.1094	0.9729	-0.2031
	1.510	0.4837	-0.0188	0.8750	1.510	-0.5840	0.2283	0.7780
<i>Cyano phenyl pyrimidine</i>								
<b>T</b>	0.0387	0.8954	0.1734	-0.4101	0.0272	0.7949	-0.2062	0.5760
	0.0717	0.1339	0.7735	0.6195	0.0645	0.1970	0.9770	0.0853
	0.0810	0.4247	-0.6096	0.6695	0.0428	-0.5810	0.0436	0.8120
<b>L</b>	1.40	0.9750	0.2094	0.0741	3.992	0.9610	-0.2600	0.0833
	11.47	0.2209	0.9489	0.2255	9.655	0.2710	0.9490	-0.1550
	4.47	-0.0231	-0.2662	0.9714	3.38	-0.0435	0.1729	0.9830
<b>Compound HCCPP</b>								
<i>Whole Molecule</i>								
<b>T</b>	0.0558	0.8274	-0.0325	0.5607	0.0528	0.9980	0.0255	-0.0444
	0.0494	-0.4159	0.6355	0.6505	0.0452	-0.0374	0.9558	-0.2915
	0.0536	-0.3774	-0.7714	0.5123	0.0346	0.0350	0.2920	0.9553
<b>L</b>	5.72	0.9486	0.2374	-0.2094	2.63	0.9860	0.1645	0.0264
	0.628	-0.1994	0.9618	0.1875	0.512	-0.1570	0.8640	0.4770
	0.850	0.2458	-0.1361	0.9597	0.1150	0.0556	-0.4743	0.8785
<i>Cyano phenyl pyrimidine</i>								
<b>T</b>	0.0541	0.8864	0.4177	0.1996	0.0524	0.9678	-0.2482	0.0410
	0.0497	-0.4231	0.9059	-0.0166	0.0467	0.2512	0.9454	-0.2074
	0.0431	-0.1878	-0.0697	0.9797	0.0292	0.0127	0.2110	0.9772
<b>L</b>	8.223	0.9508	0.2991	-0.0877	4.928	0.9912	0.1293	-0.0364
	1.718	-0.2694	0.9270	0.2611	0.4438	-0.0892	0.8171	0.5295
	1.415	0.1553	-0.2264	0.9619	0.2560	0.9872	-0.5617	0.8214