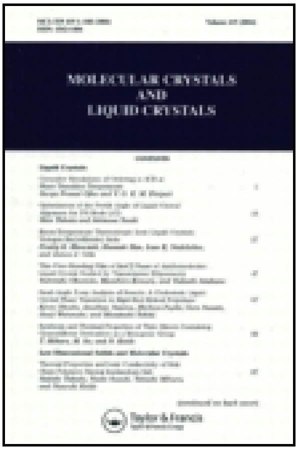

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Anisotropic Atomic Displacement Parameters and Molecular Motions in Mesogenic Crystals

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Anisotropic Atomic Displacement Parameters and Molecular Motions in Mesogenic Crystals

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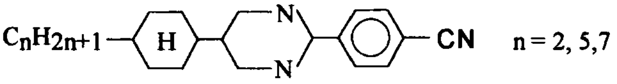
In this paper we describe the results of vibrational analysis of molecules in the crystalline phase of three mesogenic compounds of the series n-alkyl cyclohexyl cyanophenyl pyrimidine from experimental atomic displacement parameters using the rigid body model of Cruickshank. The rigid body model has been applied so far for estimation of corrections in bond lengths arising from the librational modes of motion. We have undertaken this vibrational analysis to find out whether we can get any idea about the transition from crystalline to liquid crystalline phase. Two tensors T (translation) and L (libration) are used to describe the motion. These tensors have been diagonalized to obtain the principal axes and amplitudes of translational and librational motions.

Keywords: Rigid body; molecular motions; mesogenic crystals

INTRODUCTION

Atomic anisotropic displacement parameters (ADPS) are determined routinely together with atomic coordinates during single crystal structure analysis. It was shown by Kruickshank[1] that a linear least square analysis of the ADPs of the individual atoms in a molecules, that might be assumed to behave as a rigid body, could provide tensors describing the overall motion of the molecules. Three tensors are needed to described the motion of rigid molecule T (translation), L (libration)and S (coupled rotation and libration). We have applied the rigid body model for the vibrational analysis of ethyl, pentyl and heptyl members a homologous series (henceforth referred as ECCPP, PCCPP and HCCPP respectively) whose crystal structures have already been published[2-4]. In their liquid crystalline phases the compounds have been studied by different experimental techniques[5]. The structure formula of the series is given below.



These compounds have got mesomorphic phase over a wide range of temperature. Mesomorphic molecules begin to gain rotational and translational degrees of freedom in the process of transformation from from solid to the liquid crystalline phase. So far the rigid body model has been applied for estimation of the correction in bond lengths arising from the librational modes of motion. In this paper our aim is to find whether the information about the overall molecular motion might give some insight into the transition from crystalline to liquid crystalline phase.

CRYSTALLOGRAPHIC DATA

The crystallographic data of the compounds are given in Table 1. From the values of R, the refinement index, it is apparent that the structure determination is accurate enough to analyse the motions of the molecules. In all cases the ADPs are refined independently and used in the linear least square process as described later.

Table 1. Crystallographic data

Compound	ECCPP	PCCPP	HCCPP
a (Å)	15.959(2)	18.437(1)	13.0422(6)
b (Å)	33.469(3)	7.102(5)	17.7464(11)
c (Å)	6.210(3)	13.342(1)	9.5950(5)
β (°)	90.335(7)	106.35(5)	107.170(1)
Space group	$P2_1/n$	P2/a	$P2_1/c$
Z	8	4	4
No of observed reflections	3779	2246	2951
$\sin\theta/\lambda$ ($Å^{-1}$)	≤0.59	≤0.61	≤0.70
R	0.086	0.049	0.041

METHOD OF ANALYSIS

In deriving the model for the analysis of the thermal vibrations it was assumed that the molecular rigid body motions are not correlated with the intra molecular non rigid modes so that the corresponding mean squared displacements are simply additive. Such contributions may be estimated from normal coordinate analysis[6]. We do not have to consider the translation - libration correlation matrix S since in our systems the point group of the crystal site symmetry is 2/m for which the S matrix vanishes[7].

For analysis the crystal axes are transformed to a orthogonal system such that X^O is along [100], Y^O is in the plane (001) and Z^O is perpendicular to X^O and c^*. Using the transformed coordinates and U_{ij}s of each atom the twelve normal equations are solved for the components of T and L, eigen values and eigen vectors are determined by diagonalizing the tensors. Necessary computer program was developed by the authors.

RESULTS AND DISCUSSIONS

The analysis was carried out treating the entire molecule as rigid and also the molecular fragment containing only the cyanophenyl pyrimidine group as rigid. The origin was taken to be the centre of mass. The mean squared amplitudes of translational motion and angular libration corresponding to three principal axes of T and L ellipsoids and the orientations of these axes relative to the orthogonal system are given in Table 2. We observe that in all cases the mean squared amplitudes of librational motions about the molecular long axes are 3 to 4 times larger than those in other two axes. Librational motion of the rigid part is slightly more than the whole molecule but in HCCPP this is about 4 times. Librational motion is also found to decrease with chain length which is very prominent when the entire molecule is considered. For the cyanophenyl pyrimidine groups, however, these values do not differ significantly. For these groups the mean squared amplitudes of translational motions in molecular planes are maximum followed by displacements along the stacking directions. For the entire molecules similar behaviour is observed in ECCPP and PCCPP but in HCCPP the stacking and the in plane displacements are almost same. Rigid part of the molecule B of ECCPP, however, exhibit maximum displacement along stacking direction and in plane maximum displacement is found when entire molecule is considered. The maximum values of the rms discrepancy (RMSD) between the observed and calculated ΔU_{ij} are also given in Table 2. This discrepancy is high for the molecule B of ECCPP since the cyclohexyl group is found to have disordering (Mandal et al, 1990).

We have also calculated the moment of inertia (MI) of the molecules. The principal axes about which the MI is minimum, i.e.

Table 2. Eigen values and eigen vectors of L and T

Compound ECCPP								
Molecule A								
	Whole molecule				Cyanophenyl pyrimidine			
	Eigen Values	Direction cosines			Eigen Values	Direction cosines		
T	.0783	.6519	.7207	-.2358	.0469	.6547	-.5137	-.5545
	.0737	-.7406	.5384	-.4021	.0770	.3623	.8571	-.3662
	.0548	-.1629	.4369	.8847	.0603	.6634	.0389	.7473
L	1.8120	.9815	-.1752	.0767	1.6210	.9586	-.2834	.0268
	9.3620	.1649	.9784	.1245	9.5010	.2774	.9511	.1358
	1.9000	-.0969	-.1096	.9893	3.1900	-.0640	-.1228	.9904
RMSD		.0264					.0080	
Molecule B								
T	.1429	.9194	.0013	.3934	.0378	.8954	.1734	-.4107
	.0804	.2464	.7776	-.5784	.0717	.1339	.7735	.6195
	.0717	-.3067	.6287	.7146	.0810	.4247	-.6096	.6694
L	1.9000	.8687	.1317	-.4774	1.4030	.9750	.2094	.0741
	8.3230	-.1063	.9914	.0800	11.473	-.2209	.9489	.2255
	1.5160	.4837	-.0188	.8750	4.4750	-.0231	-.2364	.9714
RMSD		.0890					.0214	
Compound PCCPP								
T	.0467	.9673	-.1711	-.1874	.0402	.7464	-.6558	-.1129
	.0646	.1262	.9650	-.2298	.0497	.6575	.7530	-.0272
	.0714	.2202	.1968	.9550	.0684	.1029	-.0539	.9932
L	6.4820	.8931	.0173	-.4496	8.7650	.8582	.0410	-.5117
	1.1460	.1122	.9591	.2598	2.1140	-.1303	.9816	-.1398
	.8100	.4357	-.2825	.8546	2.2190	.4966	.1867	.8477
RMSD		.0072					.0088	

Continued ......

Continued .....

	Compound HCCPP							
	.0558	.8274	-.0325	.5607	.0541	.8864	.4177	.1996
T	.0494	-.4159	.6355	.6505	.0497	-.4231	.9059	-.0166
	.0536	-.3774	-.7714	.5123	.0431	-.1878	-.0697	.9797
	1.8120	.9486	.2374	-.2093	8.2230	.9508	.2991	-.0811
L	.6280	-.1994	.9618	.1875	1.7190	-.2694	.9270	.2611
	.8500	.2458	-.1361	.9597	1.1460	.1553	-.2264	.9619
RMSD		.0106					.0058	

long axis of the molecule, almost coincides with the maximum librational axis. Only exception is molecule B of ECCPP where the angle between them is 8.7 which implies the precession of the molecular long axis about the librational axis.

From the above discussion we may infer that for these compounds the displacive type of transition is more likely in liquid crystal formation than reconstructive type[8]. Atomic displacements do increase significantly with temperatures. Studies of given structures near the crystal-mesophase transition will therefore give more information about the nature of transition.

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