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Minimum Energy Configuration of Dimers of Ethyl, Pentyl and Heptyl Members of 5-(trans-4-Alkylcyclo-Hexyl)-2-(4-Cyanophenyl) Pyrimidine

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Interaction between two rigid molecules for three mesogenic compounds are calculated by atom-atom potential method taking into account Van der Walls' and electrostatic interactions. Stacking, in-plane and overall minimum energy configurations are studied and the most favourable arrangements for the dimers are found. The Van der Waals' interactions are found to be determinant in the dimer stabilization. The stable configurations are compared with the previous data obtained from crystal structure analysis and from X-ray scattering studies in mesophases.

Keywords: Mesomorphism; Intermolecular interactions; Dimers; Atom-atom potential

INTRODUCTION

Intermolecular interactions are extremely important to understand the mesogenic behaviour of liquid crystals. It is the anisotropy in molecular interaction that is responsible for the existence of the liquid crystalline phases. An atomic scale analysis of intra- and intermolecular forces acting on molecules in mesophases is extremely difficult because

of the complicated averaging effects due to intra- and intermolecular motions. On the contrary such an analysis seems quite possible in crystal structures of mesogenic compounds assuming the constituent molecules as rigid bodies and this analysis can be used as precursors of liquid crystal structures[1-9]. Based on interaction calculations classically used in conformational analysis this paper reports the nature of molecular interactions for ethyl, pentyl and heptyl members of a mesogenic homologous series 5-(trans-4-alkylcyclohexyl)-2-(4-cyanophenyl) pyrimidine [ECCPP, PCCPP and HCCPP respectively in short] all of which exhibit nematic phase but HCCPP also shows Sm A phase.

METHOD OF CALCULATION

The total interaction energy for a pair of molecules, whose centre of masses are separated by the distance R, is given by

$$U(R) = - \sum_{i,j} C_{ij}/r_{ij}^{6} + \sum_{i,j} A_{ij} \exp(-B_{ij} r_{ij}) + D \sum_{i,j} q_i q_j/(\varepsilon r_{ij})$$

where r_{ij} is the distance of the ith atom of the first molecule from the jth atom of the second molecule. The molecules, as obtained from crystal structure analysis [10-12], are assumed to be rigid. A Buckingham type potential has been used for Van der Waals' interaction. The coefficients are taken from Cotrait et. al.[13]. Partial atomic charges are used to calculate electrostatic interaction. The constant D takes care of the unit used and the value of the dielectric permittivity is taken as 1.

Partial atomic charges are calculated using MNDO method[14]. Energy minimization for a pair of molecules has been carried out by keeping one molecule fixed, moving the other one along three orthogonal axes and also rotating around them with a resolution of 0.1Å for translation and 1° for rotation. Both parallel (↑↑) and antiparallel (↑↓) combinations of molecules are considered. Since the molecules are flat, stacking and in-plane interaction energies have been minimized separately and then search has been made for the overall minimum energy configurations.

To facilitate the above calculation an orthogonal coordinate system is defined by taking the origin at the centre of the mass of the molecule, Z-axis as the molecular long axis along the least-squares fitted line through all the non-hydrogen atoms; Y-axis is so chosen that YZ-plane is the plane of the molecule and X-axis is taken as the stacking direction. All the calculations are done on a Pentium PC, necessary codes are written in FORTRAN.

RESULTS AND DISCUSSION

Stacking, in-plane and overall minimum energy values and the relative configurations of both the (↑↑) and (↑↓) pairs are given in Table1. θ denotes the angular separation of R from X-axis in XY-plane and Rx, Ry and Rz represent rotations about the subscripted axes. It is observed that in all cases (stacking, in-plane and overall minimum) main contribution to the total interaction energy comes from Van der

Waals' interaction, the contribution of the electrostatic interaction is in no case greater than 4%. The configurations of the dimers corresponding to the overall minimum interaction energy are shown in

TABLE 1. Interaction energy values (Kcal/mol)

Compound	Vdw	Elec	Total
ECCPP (↑↑)			
Stacking(R=3.9,θ=180,Z=-3.9,Rz=-166)	-12.67	0.12	-12.55
In-plane(R=5.8,θ=90,Z=-3.3,Rx=4,Ry=1,Rz=-1)	-5.88	-0.17	-6.05
Overall(R=3.9,θ=180,Z=-3.9,Rz=-166)	-12.67	0.12	-12.55
ECCPP (↑↓)			
Stacking(R=4.2,θ=0,Z=1,Ry=-2,Rz=26)	-12.67	-0.22	-12.89
In-plane (R=5.8,θ=90,Z=-1.3,Ry=6)	-5.96	-0.32	-6.29
Overall(R=4.2,θ=345,Z=-0.9,Rx=-1,Ry=-1,Rz=14)	-13.11	-0.30	-13.41
PCCPP (↑↑)			
Stacking (R=4.9,θ=0,Z=-6.0,Rx=-4,Rz=45)	-9.06	0.18	-8.88
In-plane (R=5.6,θ=90,Z=-5.6,Ry=-1,Rz=-27)	-6.18	0.00	-6.18
Overall (R=5.0,θ=15,Z=3.9,Ry=-10,Rz=-7)	-11.19	-0.04	-11.23
PCCPP (↑↓)			
Stacking (R=4.7,θ=0,Z=2.6,Rz=-15)	-11.53	-0.32	-11.85
In-plane (R=5.5,θ=90,Z=5.4,Ry=3)	-6.82	-0.14	-6.96
Overall (R=4.6,θ=165,Z=2.5,Rx=-7,Ry=-1,Rz=-31)	-12.54	-0.31	-12.85
HCCPP (↑↑)			
Stacking (R=5.5,θ=180,Z=4.0,Ry=-9)	-8.34	-0.31	-8.65
In-plane (R=4.7,θ=90,Z=-2.4,Rz=-7)	-11.21	-0.27	-11.48
Overall (R=4.3,θ=285,Z=1.1,Rx=-4,Ry=1,Rz=-1)	-15.24	0.68	-14.56
HCCPP (↑↓)			
Stacking (R=5.5,θ=180,Z=-4.3,Rz=-27)	-9.06	-0.02	-9.08
In-plane (R=4.8,θ=90,Z=-5.6,Rx=1,Ry=86)	-9.58	-0.17	-9.75
Overall (R=4.8,θ=150,Z=1.8,Rx=-3)	-12.02	0.08	-11.94

R, Z in Å and θ, Rx, Ry, Rz in degrees

Figure 1 and are used to compare with the crystallographic data and also with mesophase data obtained from X-ray scattering studies[15].

The lengths of ECCPP, PCCPP and HCCPP molecules, obtained from stereo model in most extended conformations, are

respectively 17.25, 21.2 and 23.5 Å. For ECCPP molecules, we find that (↑↑) and (↑↓) pairs have minimum energy values -12.55 and -13.41 Kcal/mol at a stacking distance of 3.9 and 4.1 Å respectively, the length of the respective dimers being 20.5 and 18.1 Å. Thus the (↑↓) pair is energetically more favourable. Crystal structure of ECCPP contains two molecules per asymmetric unit and association of different types between the molecules have been observed. However, bimolecular associations between two same type of molecules across the centre of symmetry with associated pair length of 25 Å is assumed to play key role in mesophase formation since this pair length is closer, than the other possible pairs, to the apparent length of the molecule in nematic phase (23.5Å). The average intermolecular distances between neighbouring molecules in ECCPP is found to be 4.0 Å in solid state and 5.0 Å in nematic state. We thus find that calculated stacking distance agrees well with the solid state data. The length of the dimer differs considerably from its values in crystalline and nematic states. But, it is observed that when the second molecule is translated 2.5 Å further along the molecular axis from the minimum energy configuration the increase in total energy is only ~3 Kcal/mol. Length of the dimer then becomes reasonably close to the nematic phase value.

In PCCPP, the (↑↑) pair have minimum energy -11.23 Kcal/mol with associated length of 25.31 Å and stacking distance is 4.83 Å. The respective values for the (↑↓) dimer are -12.85 Kcal/mol, 21.7 Å and 4.44 Å. Thus the (↑↓) dimer is also favourable in this case. A bimolecular association across the centre of symmetry is observed in

the crystalline state, the length of the pair being 27.8 Å. The apparent length of the molecules in nematic phase is 25.8 Å. Average intermolecular distance in crystal state is 3.8 Å and in nematic state it is

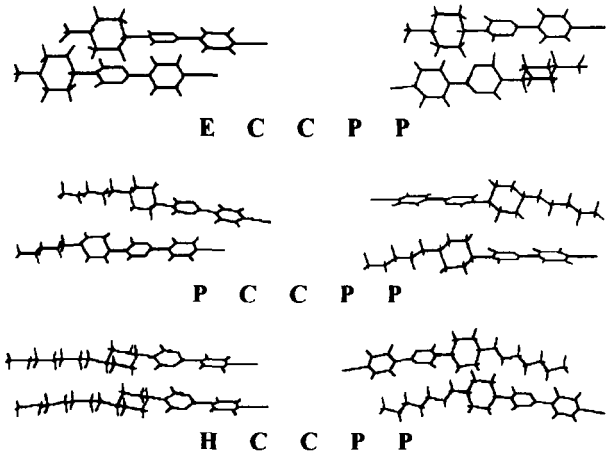

Figure 1. Configurations of the (↑↑) and the (↑↓) dimers at the overall minimum interaction energies.

about 5 Å. Thus we find that calculated stacking distance lies midway between the values in solid and nematic states. It is also observed that when the second molecule is shifted by 2 Å along molecular axis from the minimum energy configuration the total energy increases by about 2 Kcal/mol and then the dimer length becomes equal to the associated length in nematic phase.

In HCCPP, the (↑↑) dimer has energy (-14.56 Kcal/mol) at a stacking distance of 1.11 Å and lateral displacement of 4.15 Å and the

(↑↓) dimer possesses energy -11.94 Kcal/mol at a stacking distance of 4.16 Å with lateral displacement of 2.4 Å. The length of the respective dimers are 24.4 and 27.0 Å. Thus the (↑↑) dimer, in this case, has lower energy than the (↑↓) dimer but it essentially stabilizes due to in-plane interaction. In the crystal structure of HCCPP bimolecular association across the centre of symmetry is found and the length of the pair is 32 Å, which becomes 33.7 Å in Sm phase and 37 Å in nematic phase. The average intermolecular distance in crystal and mesogenic states are 4.6 Å and 5 Å respectively. Thus the calculated (↑↓) stacking distance is slightly less than the crystal state data but the difference in dimer length is quite large. However, if we increase the dimer length by reducing the overlap region by about 3 Å energy of both the dimers becomes ~9.0 Kcal/mol. In all cases we also observe that if we make stacking distance of the dimers around 5 Å and if we further slide one molecule of the dimer along the molecular axis by 2 to 3 Å, the interaction energy at best increases by 5 Kcal/mol from the value at the overall minimum energy configurations.

We may thus conclude that the dispersion forces play the key role in stabilizing both the stacking and in-plane interactions. That the dimer energy do not change drastically when the stacking distance is increased by ~ 1 Å and molecular overlap is decreased by ~ 3 Å, indicate that the compounds are capable of retaining molecular order up to a considerable extent against thermal agitations. Thus the compounds exhibit mesogenic behaviour instead of directly going from crystalline state to a completely random and disorganized

isotropic melt. In case of HCCPP in-plane interaction energy is much stronger compared to other two compounds. The stacking energy plays a major role in mesophase stability, the significant contribution of in-plane interaction may, however, favour the smectic phase.

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