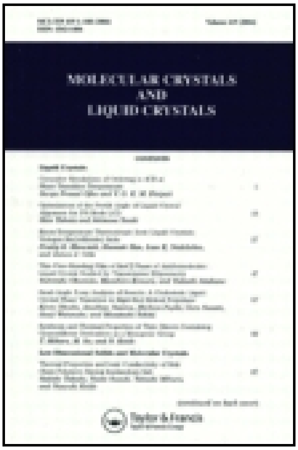

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Order of a Thermotropic Mesogen: HCCPP-A Statistical Study Based on Quantum Mechanics and Computer Simulation

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Order of a Thermotropic Mesogen: HCCPP-A Statistical Study Based on Quantum Mechanics and Computer Simulation

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A computational analysis has been carried out to determine the configurational preference of a pair of 5-(*trans*-4-heptylcyclohexyl)-2-(4-cyanophenyl) pyrimidine **(HCCPP)** molecules with respect to translatory and orientational motions. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole components at each atomic centre of the molecule. Configuration energy has been computed using Rayleigh-Schrodinger perturbation method. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration at phase transition temperature using Maxwell-Boltzmann formula. An attempt has been made to identify the most probable configuration at phase transition temperature. Further, the flexibility of various configuration has been studied in terms of variation of probability due to small departures from the most probable configuration. On the basis of stacking, in-plane, and terminal interaction energy calculations, all possible geometrical arrangements of a molecular pair have been considered. An attempt has been made to identify the most probable configuration at phase transition temperature.

Keywords: HCCPP, statistical study, computer simulation

INTRODUCTION

Liquid crystals are becoming an increasingly important class of molecules due to their wide range of applications [1–3]. The majority of mesogenic molecules are composed of an aromatic core to which one or two alkyl chains [4] are attached. The liquid crystal properties, such as the nematic-isotropic

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transition temperature and the entropy of transitions, are influenced by the presence of the alkyl chain. In recent years there has been increasing interest in the stable phases mediating the transition between different liquid crystalline phases [5–8]. Further, computer speed has led to the use of computer simulation as a tool for understanding liquid crystal phases [9–11]. However, it is essential to study simple models in some depth in order to understand the forces responsible for mesophase formation. The possibility also exists of extending these simple models by building in realistic features such as molecular flexibility, complicated structural anisotropy, and electrostatic forces.

The role of intermolecular forces in the mesomorphic behavior has attracted attention of many workers [12–14]. The characteristics of mesomorphic behavior, which occur at phase transitions, are primarily governed by the intermolecular interactions acting between sides, planes, and ends of a pair of molecules [15]. The melting point, the temperature at which an ordered geometrical arrangement collapses and gives rise to the disordered isotropic melt, depends to a very large extent on the nature of intermolecular interaction existing within the system [16,17]. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on interaction energy result will provide information regarding the most probable molecular aggregation. It therefore seems important to investigate the relative freedom of the molecules to depart from the minimum energy configuration in terms of (1) variation in orientation and (2) translation along the long molecular axis. Through these computations one is able to obtain information of dimer complex, the relative freedom of a molecule in terms of variations in inclination, separation, or sliding of one molecule over the other, etc.

In the present paper, an attempt has been made to identify the characteristic features of liquid crystalline in terms of pair energy of configuration probabilities between a molecular pair of **HCCPP** at an intermediate distance of 4.8 Å for stacking and 4.7 Å for in-plane interactions. Similarly, a distance 21.4 Å has been kept for terminal interactions. The distances chosen for these computations are such that the possible van der Waals contacts are avoided.

The thermodynamic data has revealed that **HCCPP** shows solid to smectic phase at 355 K, nematic phase at 431 K, and isotropic melt at 496 K [18].

METHOD OF COMPUTATIONS

The molecular geometry of **HCCPP** has been constructed on the basis of the published crystallographic data with standard values of bond lengths and bond angles. The **CNDO/2** method [19] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. The computations have been carried out in two parts, as shown below.

Part 1: Computation of Interaction Energy at Various Configurations

A computer program based on the simplified formula for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. According to the second order perturbation theory as modified for intermediate range interactions [20], the total interaction energy (E_{total}) between a pair molecule is given by

$$E_{total} = E_{el} + E_{pol} + E_{disp} + E_{rep},$$

where E_{el}, E_{pol}, E_{disp}, and E_{rep} represent the electrostatic, polarization, dispersion, and repulsion components, respectively.

Again, electrostatic term is expressed as

$$E_{el} = E_{QQ} + E_{QMI} + E_{MIMI} + \cdots,$$

where E_{QQ}, E_{QMI}, and E_{MIMI}, etc. are monopole-monopole, monopole-dipole, and dipole-dipole, etc. terms, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the eletrostatic interaction energy, and the calculation only up to dipole-dipole term gives satisfactory result [21]. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term. The necessary formulae may be found elsewhere [22].

In this case, the origin on an atom has been chosen close to the center of mass of the molecule. The X-axis has been chosen along the long molecular axis, while the Y-axis lies in the plane of the molecule and Z-axis lies perpendicular to the molecular plane.

Part 2: Computation of Configurational Probabilities

The total interaction energy values obtained through the interaction energy calculation were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell-Boltzmann formula [22]:

$$P_i = \exp(-\beta\varepsilon_i) / \sum_i \exp(-\beta\varepsilon_i); \quad \beta = 1/kT,$$

where P_i is the probability of a particular configuration, ε_i is the energy of configuration i relative to the minimum energy configuration, k is the Boltzmann Constant, and T is the absolute temperature.

RESULTS AND DISCUSSION

The molecular geometry of **HCCPP** is shown in Figure 1. The results of probability distribution (based on intermolecular interaction energy) corresponding to different modes of interactions are discussed below.

Stacking Interactions

In the molecular pair, one of the interacting molecules is fixed in X-Y plane, while the second molecule has been kept at separation of 4.8 Å along the Z-axis with respect to the fixed one. The choice of the distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the range of short- and medium-range interactions.

The variation of stacking interaction energy with respect to rotation about Z-axis has been carried out at an interval of 2° and probability at each point has been calculated (Figure 2). The flexibility of rotation is sufficiently small at 355 K, which accounts for the smectic character of the molecule. Futhermore, this indicates a finite probability for alignment at low temperature exists when the thermal vibration does not drastically disturb the molecular alignments. Having refined the interacting configuration with respect to translation along Y-axis at equilibrium position, the energy is brought down and the probability is further investigated with respect to rotation about X-axis (Figure 3).

It has been observed that the sharp maxima corresponding to the minimum energy point occurs at an equilibrium position at nematic-isotropic transition temperature (496 K). Further, the translational freedom along the long molecular axis has been allowed at intervals of 0.2 Å as well as a corresponding change in probabilities distribution (Figure 4). The variation of probability is almost constant in the region of $-1.6\,\text{Å} \pm 0.2\,\text{Å}$, which may

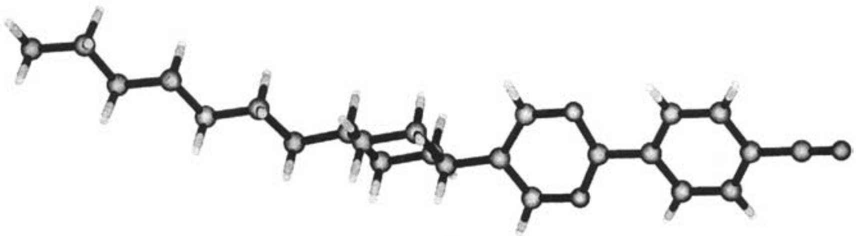

FIGURE 1 Molecular geometry of HCCPP molecule.

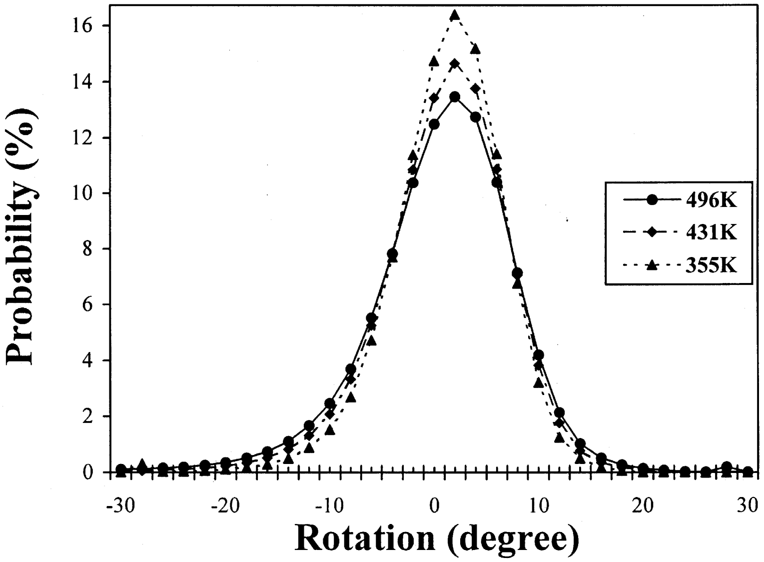

FIGURE 2 Variation of probability with respect to rotation about Z-axis during stacking interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

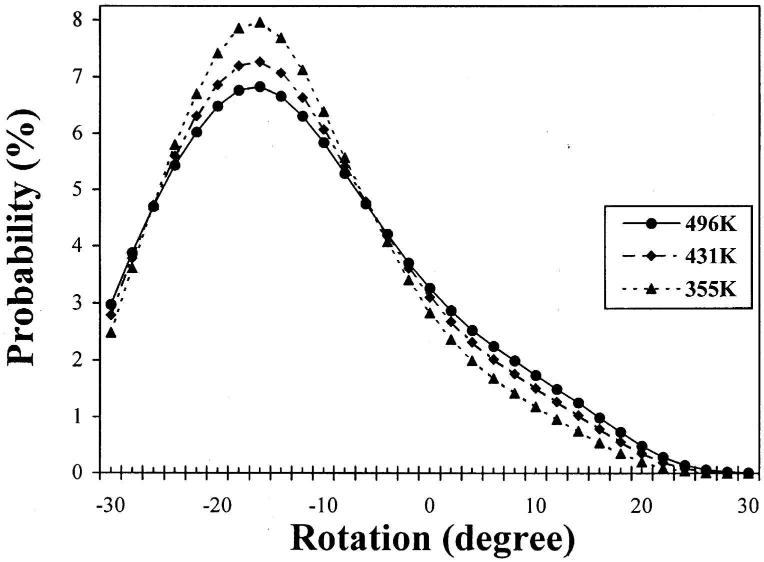

FIGURE 3 Variation of probability with respect to rotation about X-axis during stacking interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

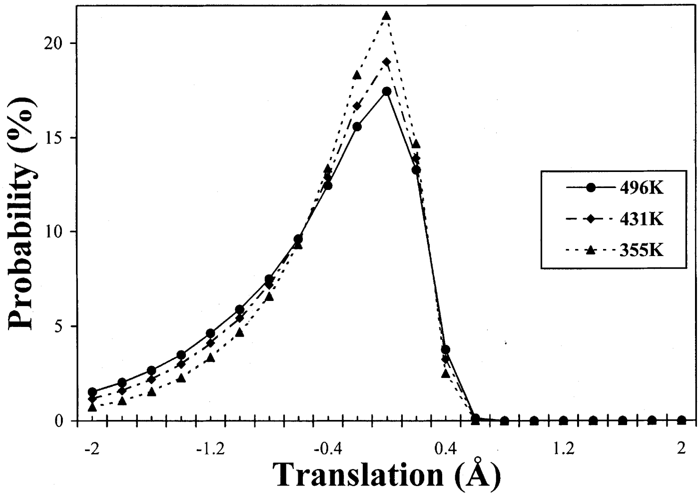

FIGURE 4 Variation of probability with respect to translation along X-axis during stacking interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

be correlated with the fluidity of compounds maintaining their alignment in mesophase at nematic-isotropic transition temperature (496 K).

In-plane Interactions

Similar calculations have been performed for in-plane interactions. To avoid the possibility of van der Waals contacts, the interacting molecule has been kept at separation of 7 Å along Y-axis with respect to the fixed one to avoid the possibility of van der Waals contacts. Again, rotations about Y- and X-axis have been given, and corresponding energy has been calculated. The energy has been minimized with respect to translation and rotation about all axes.

Figure 5 shows the variation of probability with respect to rotation about X-axis during in-plane interactions. Generally the molecules may be assumed to be capable of free rotations, except at lower temperatures where the two molecules prefer being in the same plane. Further, it is clear that the smooth rise near the equilibrium position indicates the existence of an aligned structure at low temperature when thermal agitation does not drastically disturb the molecular alignment.

The variation of probability with respect to translation along X-axis during in-plane interactions is shown in Figure 6. Since the in-plane

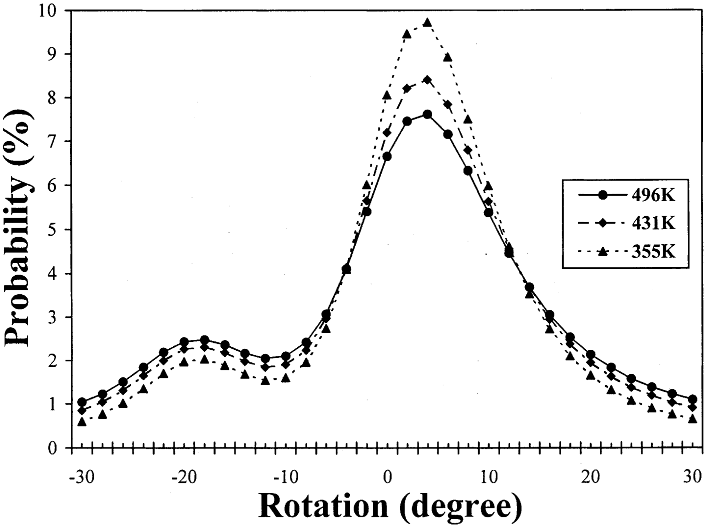

FIGURE 5 Variation of probability with respect to rotation about X-axis during in-plane interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

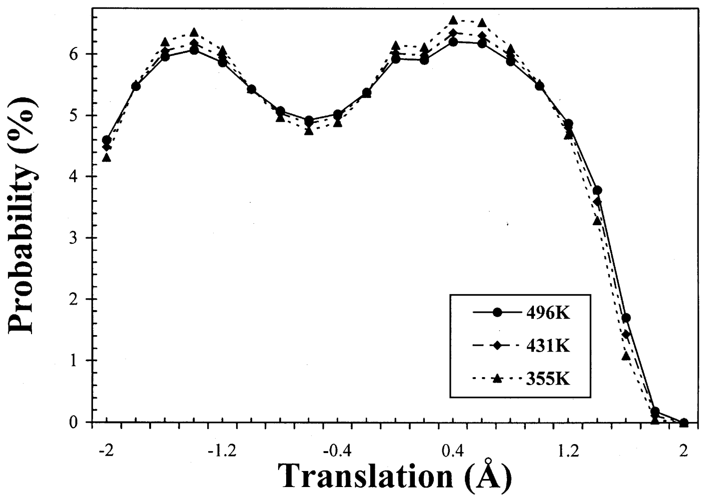

FIGURE 6 Variation of probability with respect to translation along X-axis during in-plane interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. The maximum probability occurs at an equilibrium position. It is evident that the stacked pair of molecules can slide one above the other in the range of −0.8 Å ± 0.2 Å near the equilibrium position at nematic-isotropic transition temperature (496 K) without any significant change in the energy, and hence it is capable of retaining molecular order up to 1.2 Å against increased thermal agitation.

Terminal Interactions

Terminal interactions are much weaker as compared to stacking or in-plane interactions. To investigate the terminal interactions apart from van der Waals contacts, the interacting molecule has shifted along X-axis by 21.4 Å with respect to the fixed one and allowed rotation about X-axis. The variation of probability with respect to rotation about X-axis (Figure 7) shows no preference for any angle, i.e., molecules are completely free to rotate about their long molecular axis. The minimum energy so obtained is then taken as the starting point, and the entire process is repeated at smaller intervals. The energy has been minimized with respect to translation and

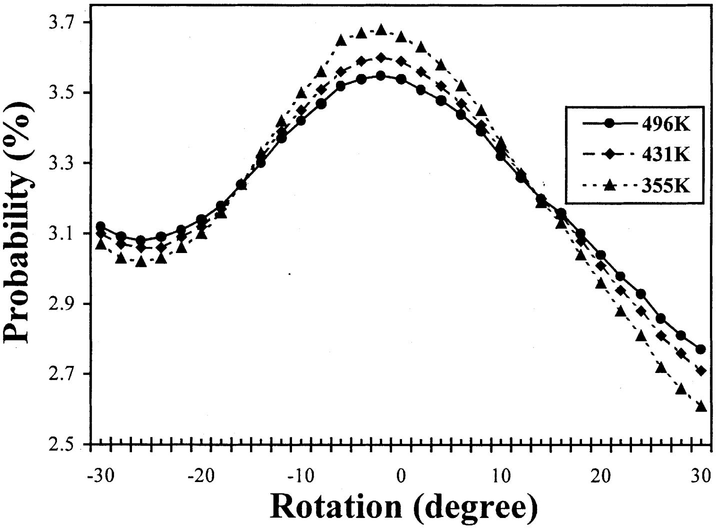

FIGURE 7 Variation of probability with respect to rotation about X-axis during terminal interactions at solid-smectic (355 K), smectic-nematic (431 K), and nematic-isotropic (496 K) transition temperatures.

rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved.

The refined interaction energy values corresponding to one minimum energy configuration in each type, i.e., stacking, in-plane, and terminal interactions are reported in Table 1 with all the contributory terms to enable comparison. It seems important to note here that the largest attractive contribution in stabilizing the stacked, in-plane, and terminal interacting pair of **HCCPP** molecules comes from the dispersion forces. Further, all possible geometrical arrangements between a molecular pair of **HCCPP** have been considered during stacking; in-plane and terminal interactions provide an insight of molecular arrangements inside bulk materials. The most favorable stacked configuration of pairing has been obtained at an interplaner separation of 3.4 Å with energy −13.89 kcal/mole (Figure 8).

CORRELATION OF THE RESULTS

The present calculation may be reasonably correlated with the mesomorphic behavior of the system. The nematic character of liquid crystal is generally manifested by its translational freedom along the long molecular axis. Therefore, for stacking and in-plane interactions, translations have been allowed at an interval of 0.2 Å and corresponding change in probabilities has been reported.

Figure 4 shows the results for stacking interactions. It may be observed that stacking interaction has lesser translational freedom. Table 2 shows that the ratio of probability of being at maximum probable point, having ± 0.2 Å displacement along the long molecular axis, is 0.60 at nematic-isotropic transition temperature. However, at room temperature the value is

TABLE 1 Stacking, in-plane, and terminal interaction energy values between a pair of **HCCPP** molecules after refinement

Energy terms	*Stacking interactions*	*In-plane interactions*	*Terminal interactions*
E_{QQ}	0.107	0.076	−0.194
E_{QMI}	−0.136	−0.024	−0.371
E_{MIMI}	−0.269	−0.004	0.031
E_{el}	−0.298	0.048	−0.534
E_{pol}	−0.486	−0.191	−0.521
E_{disp}	−22.081	−9.858	−3.688
E_{rep}	8.973	3.095	2.134
E_{total}	−13.892	−6.905	2.610

Energy is expressed in kcal/mole.

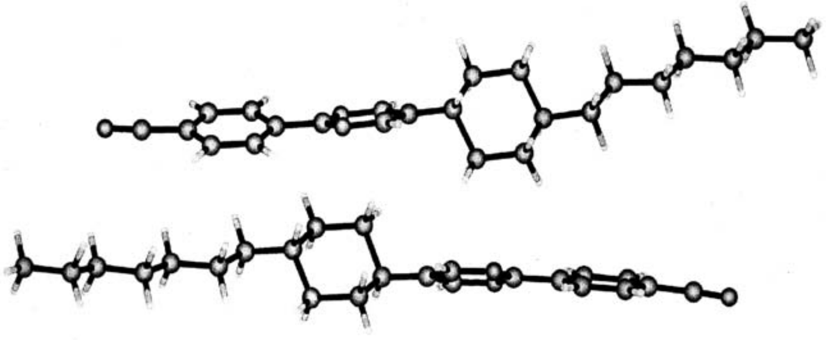

FIGURE 8 The most favorable stacked configuration obtained among the different modes of interactions at an interplaner separation of 3.4 Å with energy −13.89 kcal/mole.

0.68, indicating a strong binding at lower temperature. However, with an increase of temperature the molecule obtains sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planner interaction. Thus, even at room temperature this value is 0.53, which is reduced to 0.51 at transition temperature. It may be noted that (Figure 6) although the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus in the mesomorphic range, small movements of the molecules are only possible.

It is clear from the above discussion that an isolated consideration for any particular degree of freedom manifests; in general, a preference for aligned structure with some allowance of deviation from its minimum energy (or maximum probability) configuration. Also, each configuration has its own minimum energy structure for every degree of freedom. Thus in a molecular assembly, a number of local minimum energy configurations exist. All of

TABLE 2 Translational rigidities* along the long molecular axis (X-axis) during stacking and in-plane interactions between a pair of **HCCPP** molecules

	Probability ratio	
Temperature (K)	*Stacking interactions*	*In-plane interactions*
300	0.68	0.53
355	0.65	0.52
431	0.62	0.52
496 N−I	0.60	0.51

*This has been defined as the ratio of probability being at maximum probable point to having ± 0.2 Å displacement along the long molecular axis. N-I = nematic-isotropic them have their own importance, as in the case of closed molecular packing where any molecule, depending on its own spatial position, may be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance because while coming down from a very high temperature, when the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy. The others have a sequential preference depending on their individual relative probabilities.

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