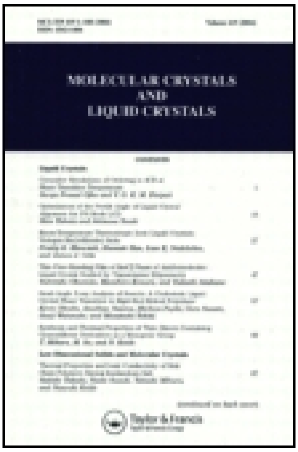

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Effect of Non-Mesogenic Solvent on Molecular Conformations and Interactions of a Nematogen: A Probabilistic Approach

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A probabilistic approach has been carried out on molecular conformations and interactions of a monotropic nematogen 4-n-hexyl-N-(4-cyanophenyl) piperidine with respect to translational and orientational motions. The atomic net charge and dipole moment components at each atomic center have been evaluated using the complete neglect differential overlap method. The modified Rayleigh–Schrodinger perturbation theory along with the multicentered–multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while a "6-exp" potential function has been assumed for short-range interactions. The interaction energy values obtained during the different modes of molecular interactions have been taken as input to calculate the configurational probability at room temperature (300 K). On the basis of stacking, in-plane, and terminal interaction energy calculations, all possible geometrical arrangements between the molecular pairs have been considered. Furthermore, the effect of a non-mesogenic solvent (benzene) on molecular conformations during different modes of interactions has been analyzed. The adopted framework provides valuable information on configurational freedom of a molecule that may be useful in understanding the mesomorphic behavior/transitions.

Keywords Molecular conformations; configurational probability; nematogen

Introduction

Research on liquid crystals (LCs) is an interdisciplinary and international pursuit [1]. The correlation between structure and mesomorphic properties of molecular systems can be determined by molecular interactions. In general, these interactions are non-central, i.e., they are dependent on the relative orientation/translation of molecules [2, 3]. The differences between the nematic behavior of simple conventional mesogens (monomers) and dimers are thought to stem entirely from the configurational correlations that the spacers impose on mesogenic units [4]. Thus, the inclusion of such correlations constitutes the major step in the formulation of a molecular theory that goes from the description of aggregation behavior of single mesogen to dimer, and to multi-mesogen phases.

It is well known that liquid crystallinity can be affected by molecular shape [5], conformation [6], and intermolecular interaction [7]. The exact nature of the configurational

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*Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada-520 008, A.P., India. E-mail: durga_ojha@hotmail.com freedom or degree of molecular motion of flexible end chains in condensed phases needs special considerations in order to understand a two-fold notion: one that assumes that the chains are liquid-like and highly disordered, and another that the chains are extended and ordered. The degree of fluidity of the chains is significant in understanding the properties of mesophases. This aspect also has great biological relevance because of the analogy of these structures to biological membranes. It is generally accepted that the existence of LC phases is determined by the anisotropy [8] of pair molecular interaction [9].

Although in consideration of thermotropic phase transition the orientation-dependent energy should be taken into account, the anisotropic steric repulsion and attractive forces play a dominant role. These are responsible for packing, intermolecular distances, and alignment of molecules to form mesophases [10]. The structure of the nematic phase near the transition can, therefore, be approximated as a calculable perturbation of the structure of the coexisting isotropic liquid. The short-range angular correlation, which develops either due to hindered rotation [11] or anisotropy in intermolecular interactions or both, is already present in the isotropic phase.

Based on the Rayleigh–Schrodinger perturbation method, the role of molecular interactions in mesomorphic compounds has engrossed the attention of several researchers [12–14]. These studies have intended to establish the anisotropic nature of the pair potential, and subsequently find out the minimum energy configuration of a pair of liquid crystalline molecules. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over the other. These values, however, do not replicate the actual relative preference, which can only be obtained through their probabilities corresponding to each configuration. Hence, in order to obtain a quantitative measure for the relative preference, the authors have evaluated the relative probability of occurrence of each configuration based on interaction energy results. These computations provide valuable information regarding the most probable molecular aggregation.

The molecule 4-*n*-hexyl-*N*-(4-cyanophenyl) piperidine (HCPP) is of meticulous interest, since it is the only mesogen in a series of 4-*n*-alkyl-*N*-(4-cyanophenyl) piperidines ($n = 4$–8) showing monotropic nematic phase. A detailed knowledge of structural features of LC substances in their crystal phase is of considerable importance in understanding their structure and properties in the mesophase. Hence, in the present paper, the author reports the molecular conformations and interactions of a nematogen HCPP at room temperature (300 K) because the phase transition temperature has not been reported by crystallographers [15]. Configurational probabilities of a molecular pair have been computed at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. Hence, the choice of distance has been made to eliminate the possibility of the van der Waals contacts completely and to keep the molecule within the short- and medium-range interactions.

Computational Methodology

The molecular geometry of HCPP has been constructed on the basis of published crystallographic data with the standard values of bond angles and bond lengths [15]. The following computations have been carried out.

Computation of Atomic Net Charge and Dipole Moments

The simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic center through an all-valance electron method. In the present computation, the complete neglect differential overlap (CNDO/2) method [16] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [17] 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 for intermediate range interactions [18], the total pair interaction energy of molecules (U_{pair}) is represented as the sum of various terms contributing to the total energy:

$$U_{\mathrm{pair}} = U_{\mathrm{el}} + U_{\mathrm{pol}} + U_{\mathrm{disp}} + U_{\mathrm{rep}},$$

where U_{el}, U_{pol}, U_{disp}, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively.

Again, electrostatic term is expressed as

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

where U_{QQ}, U_{QMI}, and U_{MIMI} are monopole–monopole, monopole–dipole and dipole–dipole terms, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy and the calculation only up to dipole–dipole term gives satisfactory result [12–14, 19]. The computation of electrostatic term has, therefore, been restricted only up to the dipole–dipole energy term.

In the present computation, the dispersion and short-range repulsion terms are considered together because several semi-empirical approaches, viz. the Lennard–Jones or the Buckingham-type approach, actually proceed in this way. Kitaygorodsky [20] introduced the Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskaya [21] for hydrocarbon and several other molecules and finally gave the following expression:

$$U_{\mathrm{disp}} + U_{\mathrm{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda,\ \nu),$$

$$U(\lambda,\ \nu) = K_{\lambda}\, K_{\nu}\, (-A/Z^6 + B\, e^{-\gamma Z}),$$

where $Z = R_{\lambda\nu}/R^0{}_{\lambda\nu}$; $R^0{}_{\lambda\nu} = [(2R^w{}_{\lambda})\ (2R^w{}_{\nu})]^{1/2}$, and $R^w{}_{\lambda}$ and $R^w{}_{\nu}$ are the van der Waals radii of atoms λ and ν, respectively. The parameters A, B, and γ do not depend on atomic species. But $R^0{}_{\lambda\nu}$ and factor $K_{\lambda}K_{\nu}$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [22].

Computation of Configurational Probabilities

The total interaction energy values obtained through these computations have been used as an input to calculate the probability of occurrence of a particular configuration i using the Maxwell–Boltzmann formula [19] to obtain a better insight:

$$P_i = \exp(-ß\varepsilon_i) \Big/ \sum\nolimits_i \exp(-ß\varepsilon_i),$$

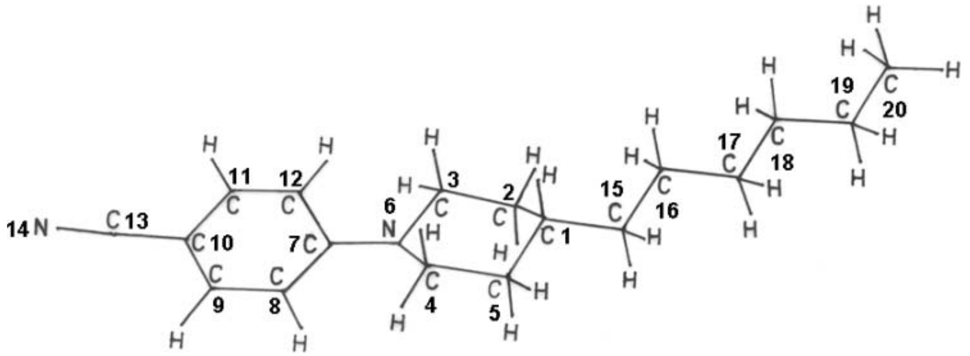


Figure 1. Molecular geometry of HCPP with various atoms.

where P_i stands for probability. $\beta = 1/kT$, where k is the Boltzmann constant, T is the absolute temperature, and ε_i represents the energy of configuration i to the minimum energy value in a particular set for which the probability distribution is computed.

An orthogonal coordinate system has been considered to facilitate the above calculation. The origin has been chosen at almost the midpoint of the molecule. The x-axis has been chosen along a bond parallel to the long molecular axis, while the y-axis lies in the plane of the molecule and the z-axis is perpendicular to the x–y plane.

Results and Discussion

The molecular geometry of HCPP is shown in Fig. 1. The atom-based partial charges on heavy atoms of HCPP have been reported in Fig. 2 to understand the molecular charge distribution that enables to study the different modes of intermolecular interactions and probability distribution.

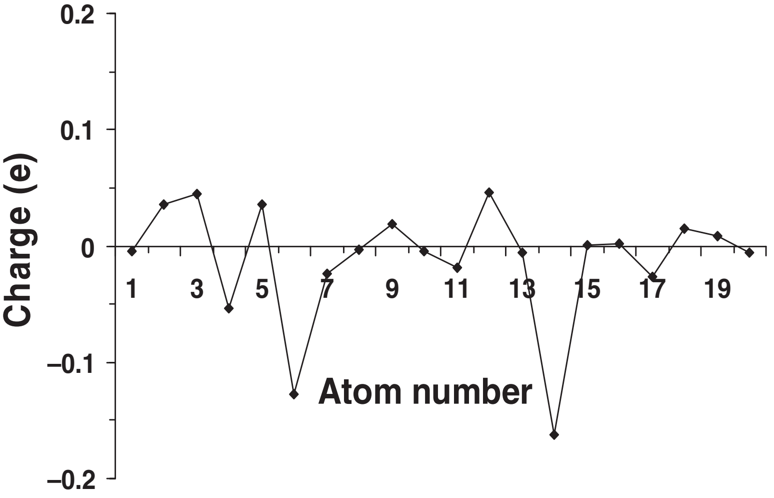


Figure 2. Partial charges on heavy atoms of HCPP.

Molecular Charge Distribution

The electrostatic interactions between a pair of molecules represent a significant contribution to the total pair energy. It is expected that the specific charge distributions and electrostatic interactions in LC molecules play a decisive role in the formation of various mesophases. To parameterize the intermolecular interactions for computer simulation studies, atom-positioned partial charges are helpful, which are not quantum mechanical observables.

It can be observed in Fig. 2 that even when the magnitude of the partial charge is restrained, it varies very much from atom to atom. These charges represent the electrostatic molecular interactions very well, but they do not show the real charge distribution in the molecule. Due to the shielding of carbon charges by adjacent hydrogens, the correct electrostatic potential might be reproduced by different partial distributions. Furthermore, strong alternation of charges results in a small variation of electrostatic potential around the molecule. In spite of these uncertainties, the full set of partial charges is very useful, as it can provide a detailed insight into the molecular arrangement in mesophases. Furthermore, they reproduce the electrostatic potential very well and provide valuable information regarding molecular multipole properties that are associated with the multipole expansion of the electronic charge distribution.

Configurational Probability Distribution

The role of different modes of interactions and configurational probability distribution during the different molecular motions is discussed below.

Role of Stacking Interactions

In a molecular pair, one of the interacting molecules has been kept at a separation of 6 Å along the z-axis with respect to the fixed molecule. The variation of probability with respect to translation along the long molecular axis (x-axis) corresponding to configuration y (0^0) z (0^0) in crystal phase (300 K) has been reported in Fig. 3. The configuration shows a sharp preference toward the minimum energy point and the maximum probability has been obtained at the equilibrium position. The variation of probability is almost constant in the region of 16 Å + 4 Å. It shows that the sliding of one molecule over the other is energetically allowed in a small range, which may be correlated with fluidity of the compound maintaining its alignment in mesophase. Having refined the interacting configuration with respect to translation along the x-axis at the equilibrium condition, the energy is brought down and the configurational probability is further investigated with respect to rotation about the x-axis.

The variation of probability with respect to rotation about the x-axis at room temperature (300 K) corresponding to configuration y (180^0) z (0^0) has been reported in Fig. 4. The maximum probability has been achieved at -4^0 rotations indicating a slight preference for the aligned structure of this configuration. The variation of probability with respect to rotation about the z-axis has also been carried out corresponding to configuration x (0^0) y (0^0). It has been observed that the configuration shows a sharp preference toward the minimum-energy point. The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for small intervals. The energy has been minimized with respect to translations and rotations about the x, y, and z-axes. Accuracy of 0.1 Å in translation and 1^0 in rotation of one molecule with respect to the other has been

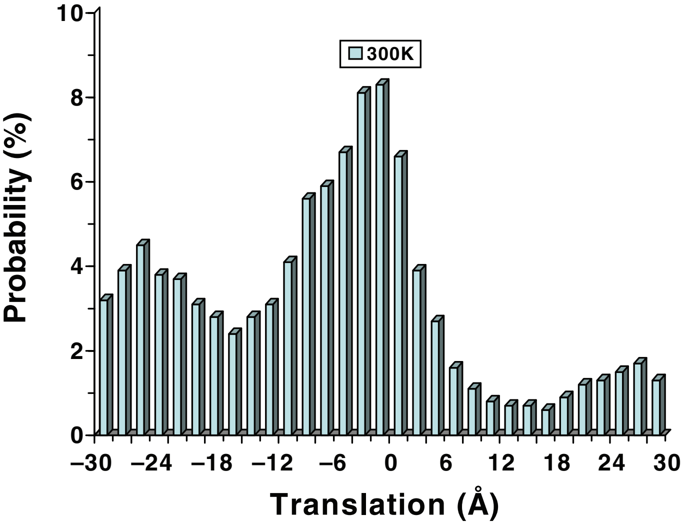


Figure 3. Variation of probability with respect to translation along the *x*-axis during stacking interactions corresponding to configuration *y* (0^0) *z* (0^0) at room temperature (300 K) (Color figure available online).

achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for the minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route.

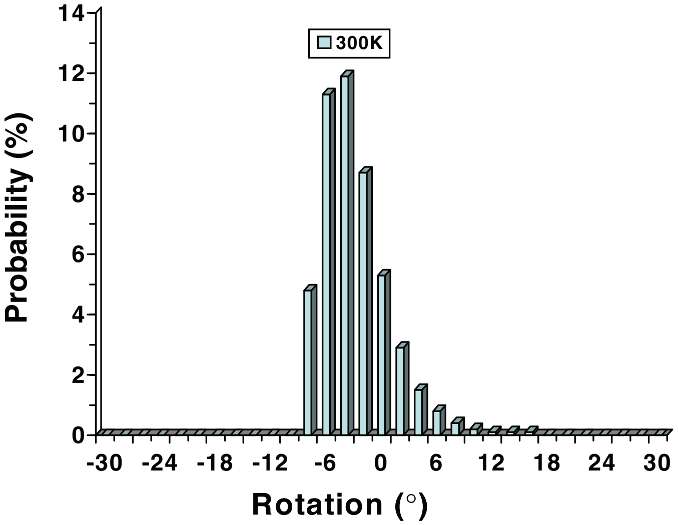


Figure 4. Variation of probability with respect to rotation about the *x*-axis during stacking interactions corresponding to configuration *y* (180^0) *z* (0^0) at room temperature (300 K) (Color figure available online).

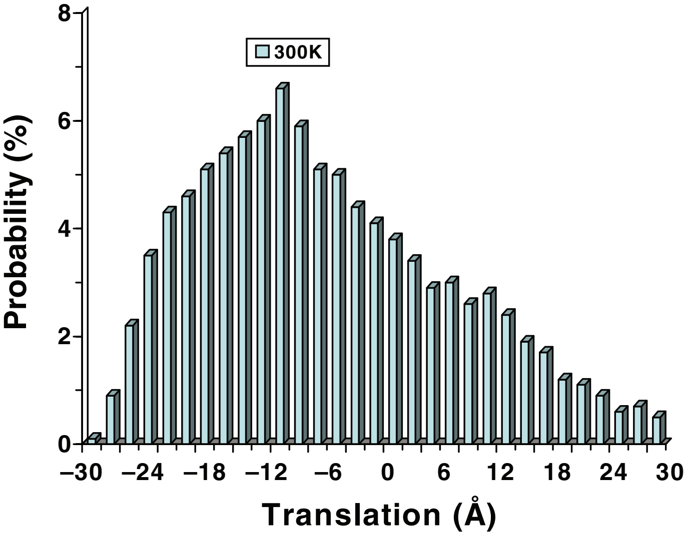


Figure 5. Variation of probability with respect to translation along the *x*-axis during in-plane interactions corresponding to configuration *y* (180^0) at room temperature (300 K) (Color figure available online).

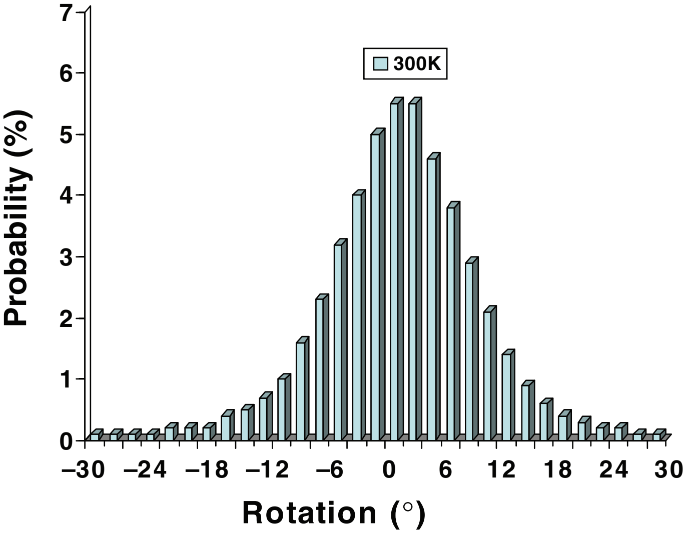
Role of In-Plane Interactions

The interacting molecule has been kept at a separation of 8 Å along the *y*-axis with respect to the fixed one. The electrostatic energy during in-plane interactions is more effective than that in stacking, since the anti-parallel orientation of molecular rings provides a more effective dipole–dipole attraction. In addition, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped anti-parallel molecular ring orientation. These factors ultimately cause large variation in total interaction energy and, thereby, in probability of the configuration. The variation of probability with respect to translation along the *x*-axis corresponding to the configuration *y* (180^0) at room temperature (300 K) has been plotted in Fig. 5. Since in-plane interactions are weaker than stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at −10 Å. The interacting configurations have been refined with respect to translation along the *x*-axis at the equilibrium condition, and the energy is brought down and the probability is further investigated with respect to rotation about the *x*-axis.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration *y* (0^0) has also been carried out as shown in Fig. 6. Evidently, a pronounced peak exists at 4^0 rotation point, and there is no drastic preference for the aligned structure. Furthermore, it is observed that the rotational freedom is much more pronounced as compared to the stacking interactions. The variation of probability with respect to rotation about the *y*-axis corresponding to the configuration *x* (0^0) has been carried out, and it has been observed that the rotation about the *y*-axis does not alter the configurational probability drastically.

Role of Terminal Interactions

In order to investigate terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the *x*-axis by 22 Å. The terminal interactions



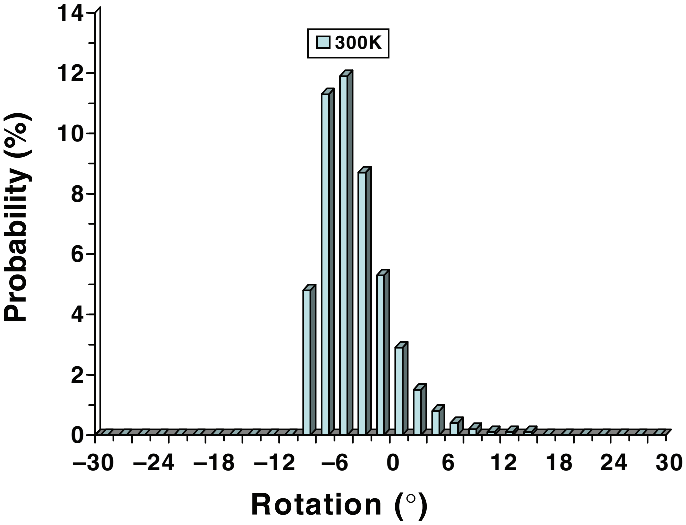


Figure 6. Variation of probability with respect to rotation about the x-axis during in-plane interactions corresponding to configuration y (0^0) at room temperature (300 K) (Color figure available online).

are much weaker as compared to stacking or in-plane interactions. The rotations about the x-axis corresponding to configuration y (0^0) at room temperature (300 K) (Fig. 7) show almost no preference for any angle.

The most prominent energy minima of the above-mentioned interactions are further refined and the values thus obtained with all contributing terms to enable comparison have been listed in Table 1. The results indicate that due to the planarity of the molecule, the refinement corresponding to the stacking energy is maximum and the ultimate magnitude of the stacking energy is much higher than in-plane and terminal interaction energies.

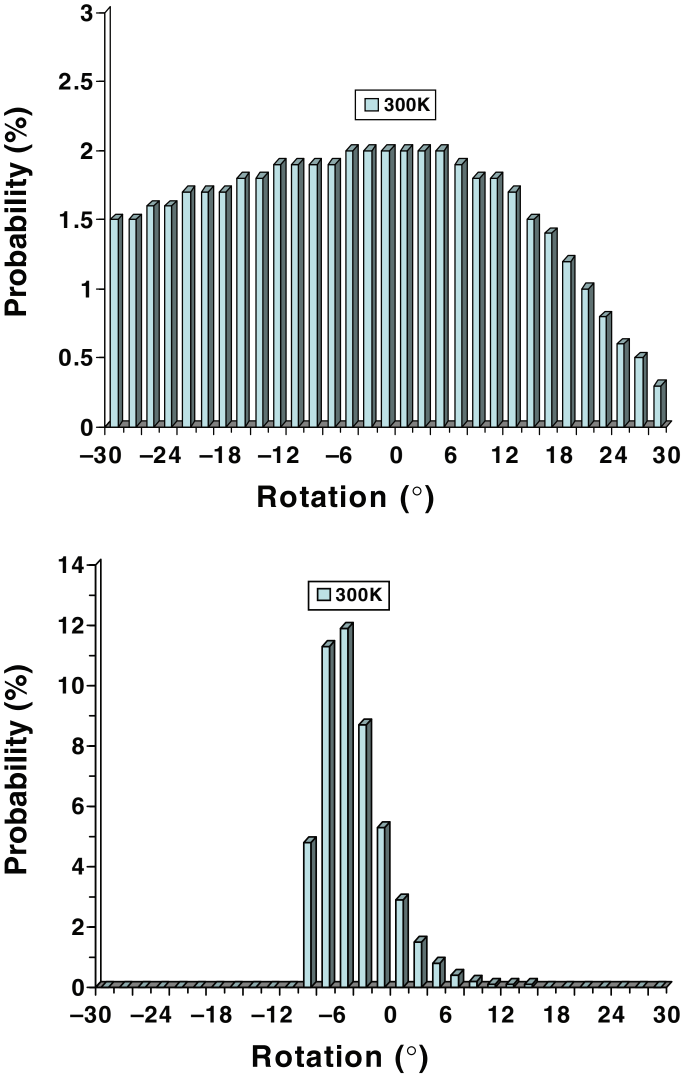


Figure 7. Variation of probability with respect to rotation about the x-axis during terminal interactions corresponding to configuration y (0^0) at room temperature (300 K) (Color figure available online).

Table 1. The minimum energy obtained after refinement during stacking, in-plane, and terminal interactions between a molecular pair of HCPP. Energy is expressed in kcal/mole

Energy terms	Stacking energy	In-plane energy	Terminal energy
U_{el}	0.07	−0.01	−0.14
U_{pol}	−0.09	−0.03	−0.34
U_{disp}	−13.47	−6.04	−1.33
U_{rep}	5.84	2.02	0.58
U_{total}	−9.65	−4.61	−1.23

U_{el} = electrostatic; U_{pol} = polarization; U_{disp} = dispersion; U_{rep} = repulsion; and U_{total} = total.

Table 2. Relative probabilities of different minimum energy configurations obtained for HCPP during stacking, in-plane, and terminal interactions in vacuum and in non-mesogenic, non-interacting solvent (benzene) in crystal phase (300 K). Average dielectric constant of benzene is taken as 2.25

Configuration	Energy in vacuum (kcal/mole)	Energy in dielectric medium (kcal/mole)	Probability (%)	
			A	B
$y\ (0^0)\ z\ (0^0)$[a]	−9.39	−4.17	67.56	60.24
$y\ (0^0)\ z\ (180^0)$[a]	−8.96	−3.98	32.43	35.54
$y\ (0^0)$[b]	−5.23	−2.32	0.00	2.40
$y\ (180^0)$[b]	−4.75	−2.11	0.00	1.80
$y\ (0^0)$[c]	−2.40	−1.06	0.00	0.00

[a] Stacking interactions.
[b] In-plane interactions.
[c] Terminal interactions.
A = Probability in vacuum.
B = Probability in dielectric medium.

Effect of Non-Mesogenic Solvent

In order to examine the effect of non-mesogenic and non-interacting solvent, i.e., benzene on a nematogen, various possible geometrical arrangements between molecular pairs have been considered that provide information about molecular arrangements inside bulk materials. Table 2 shows the relative probabilities of different minimum energy configurations, calculated for vacuum and dielectric medium during the different modes of interactions. Evidently, the energy/probabilities are redistributed in dielectric medium, and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. This provides theoretical support to the experimental observations [23]. Furthermore, the most favorable stacked configuration $y\ (0^0)\ z\ (0^0)$ of pairing (i.e., 60.24% probability) has been obtained with the energy of −4.17 kcal/mole in benzene at room temperature (300 K).

Molecular Conformations

It may be concluded from the above discussion that an isolated consideration for any particular degree of freedom manifests, in general, a preference for an aligned structure with some allowance of deviation from its minimum energy (maximum probability) configuration. Thus, in a molecular assembly a number of local minimum energy configurations exist. Each of these has its own importance, as in the case of close molecular packing. 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 cooling down from a very high temperature, where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the other minima have sequential preference depending on their individual relative probabilities.

Conclusions

- It may be concluded that a probabilistic approach on molecular conformations and interactions is helpful for a quantitative evaluation of mutual influence of intermolecular forces on equilibrium packing of molecules. Furthermore, the study on conformational behavior of the molecule provides valuable information on configurational freedom of the molecule that may be useful in understanding the mesophases, and phase behavior/transitions.
- The energies are redistributed in non-mesogenic solvent (benzene), and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. This provides information on relative order of configurations and the preference of a particular configuration over the other.

Acknowledgments

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