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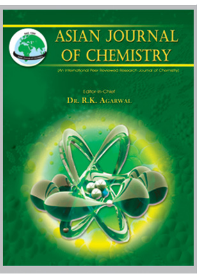

Influence of Dielectric Medium on a Cyano Containing Mesogenic Compound-A Statistical Study Based on Quantum Mechanics and Intermolecular Forces

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A statistical study based on quantum mechanics and intermolecular forces has been carried out for a cyano containing mesogenic compound 5-(*trans*-4-heptylcyclohexyl)-2-(4-cyanophenyl)pyrimidine with respect to translatory and orientational motions. The evaluation of net atomic charges and dipole moment at each atomic centre has been carried out through the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh-Schrodinger perturbation method along with multicentered-multipole expansion method has been employed to evaluate long-range intermolecular interactions, while a '6-exp' potential function has been assumed for short-range interactions. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration in a dielectric medium (*i.e.*, non-interacting and non-mesogenic solvent, benzene) at room temperature (300 K) using the Maxwell-Boltzmann formula. An attempt has been made to study the influence of dielectric medium on a mesogenic compound in the light of configurational probabilities of dimer complexes. On the basis of different modes of interaction energy calculations, all probable geometrical arrangements of pairs have been considered. The most favorable configuration of pairing has been obtained.

Key Words: Mesogen, Configurational probability, Dielectric medium.

INTRODUCTION

Research involving the search for new self-organizing molecular materials such as liquid crystals is an ongoing quest. It has become one of the most intriguing areas of modern science due to pioneer research on rich phase behaviour and applications across a wide spectrum of activities, in the field of soft condensed systems and nano-structured materials[1,2]. Studies on phase behaviour are of importance in an ample range of scientific fields through which considerable theoretical and experimental efforts were stimulated over the decades. Self organization in these molecular liquids was much explored by 'computer experiments'[3,4] that track organization and mode of motion of molecules. Their results contribute to improve our understanding regarding the physics of complex materials and, at the same time, the comparison with experimental data can be done for the quality of the theoretical accomplishments.

The liquid crystalline properties stem from the inherent ordered bulk structure driven by long-range forces[5]. The molecular design of liquid crystalline materials is not only attention-grabbing but also tricky owing to their complex structure and interactions[6]. A promising approach for the modeling of these classic organic structures involves the replacement of the explicit condensed phase environment of a molecule by an effective model potential[7]. Predicting or reproducing the physical properties and phase transitions of liquid crystals at a molecular level remains a major challenge in this approach. However, the macroscopic manifestations of molecular phenomena are monitored during a simulation, through which one can make prophecy of properties by constructing a model that authentically mimics reality[8]. Even though, the technique is computationally intensive and is typically limited corresponding to short simulation times and length scales, one can minimize computational requirements by using parallel computing techniques or by invoking approximations.

The induction and the formation of mesophases are mainly controlled and/or determined by attractive interactions between neighboring molecules. These weak interactions are of various types, such as dipole-dipole, dispersion, hydrogen bonding *etc*.[9]. An understanding of the interactions present in a given crystal structure can provide valuable information on the hydrogen-bonding and aggregation modes not just in the solid (crystal) state but also in the liquid-crystalline state[10,11]. The role of molecular interactions in mesomorphic compounds has engrossed the attention of several workers[12-14] based on the Rayleigh-Schrodinger perturbation method. Thus, the main emphasis was laid on finding out the minimum energy with observed crystal structure. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over the other depending on their energy values. These values, however, do not replicate the actual relative preference, which can only obtain through their probabilities corresponding to each configuration. Hence, in order to obtain a quantitative measure for the relative preference, authors have evaluated the relative probability of occurrence of each configuration. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on interaction energy results will provide information in this respect.

In the present article, we report the characteristic features of 5-(*trans*-4-heptylcyclohexyl)-2-(4-cyanophenyl)pyrimidine (7CHCPP) in terms of their configurational probabilities between a mole-cular pair of 5-(*trans*-4-heptylcyclohexyl)-2-(4-cyanophenyl)pyrimidine in dielectric medium (*i.e.*, the non-interacting and non-mesogenic solvent benzene, the average dielectric constant of which has been taken to be 2.25 for the entire temperature range) fully for a molecular pair 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. The choice of distance was made to eliminate the possibility of van der Waals contacts and to keep the molecule within the short and medium-range interactions. Furthermore, the most favorable stacked configuration has been reported. Through these computations one can obtain information on the influence of dielectric medium on dimer complexes; the relative freedom of a molecule during different modes of interactions.

COMPUTATIONAL METHOD

The molecular geometry of 7CHCPP has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles[15]. The simplified formula for interaction energy calculations requires the evaluation of atomic net charges and dipole moment components at each atomic centre 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 centre of the molecule.

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 as modified by Caillet and Claverie[18] for intermediate range interactions, the total pair interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy:

$$U_{pair} = U_{el} + U_{pol} + U_{disp} + U_{rep}$$

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

$$U_{el} = U_{QQ} + U_{QMI} + U_{MIMI} + \ldots$$

where U_{QQ}, U_{QMI} and U_{MIMI} *etc.*, 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[19]. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term.

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

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

$$U(\lambda, \nu) = K_\lambda K_\nu \left(-\frac{A}{Z^6} + Be^{-\gamma Z} \right)$$

where $Z = R_{\lambda\nu}/R^0_{\lambda\nu}$; $R^0_{\lambda\nu} = [(2R^w_\lambda)\ (2R^w_\nu)]^{1/2}$, where R^w_λ and R^w_ν are the van der Waals radii of atom λ and ν, respectively. The parameters A, B and γ do not depend on the 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[20].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom has been chosen at almost midpoint of the molecule. The x-axis along a bond parallel to the long molecular axis while the y-axis lies in the plane of the molecule and z-axis perpendicular to the molecular plane. The total interaction energy values obtained through these computations were used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula[20] in order to obtain a better insight:

$$P_i = \frac{\exp(-\beta\varepsilon_i)}{\sum_i \exp(-\beta\varepsilon_i)}$$

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

RESULTS AND DISCUSSION

The molecular geometry of 7CHCPP is shown in Fig. 1. The results of probability distribution corresponding to the different modes of interactions are discussed below:

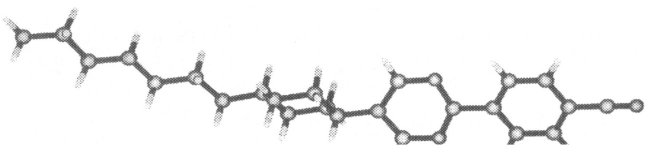

Fig. 1. Molecular Geometry of 7CHCPP

Stacking interactions in dielectric medium: In a molecular pair, one of the interacting molecules is fixed in x-y plane, while the second has been kept at a separation of 6 Å along the z-axis with respect to the fixed one. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1º in rotation of one molecule with respect to the other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computation. The global search for minimum energy configuration or the study of variation of interaction energy under pre-selected condition will have completely different path and, therefore, one has to be careful in choosing the specific route.

The nematic character of liquid crystals is manifested in their translational freedom along the long molecular axis. Therefore, variation of probability with respect to translations has been considered corresponding to the configuration y(0º) z(180º) as shown in Fig. 2. It may be observed that the configuration shows a sharp preference towards the minimum energy point. The variation of probability is almost constant in the region of (-2.4 ± 0.2) Å, which shows that a sliding of one molecule over the other is energetically allowed for a small range that may be correlated with the fluidity of compound maintaining its alignment in the mesophase. Fig. 3 shows the variation of probability with respect to rotation about x-axis corresponding to the configuration y (0º) z (0º) at room temperature (300 K). The maximum probability corresponds to 7CHCPP at -4º rotations indicating a slight preference for aligned structure of this configuration. However, at room temperature, the observed value indicating a strong binding but with the increase of temperature the molecules obtain sufficient freedom to rotate about the long molecular axis.

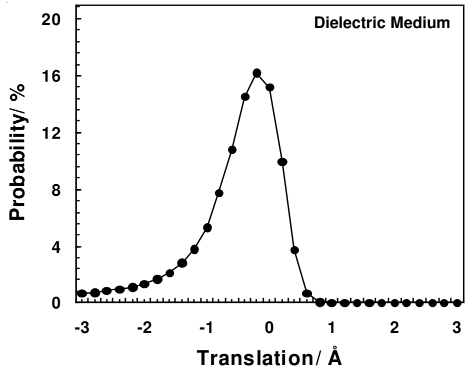

Fig. 2. Variation of probability with respect to translation along x-axis during stacking interactions at room temperature (300 K)

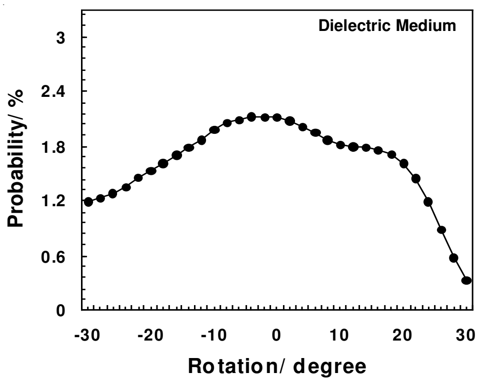

Fig. 3. Variation of probability with respect to rotation about x-axis during stacking interactions at room temperature (300 K)

In-plane interactions in dielectric medium: The interacting molecule has been kept at a separation of 8 Å along y-axis with respect to the fixed one. The similar calculations have been performed for in-plane interactions. Again rotations about the y- and z-axes have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes. The variation of probability with respect to translation along x-axis corresponding to configuration y (0º) at room temperature (300 K) is shown in Fig. 4. It may be observed that though there is no drastic preference for aligned structure, the smooth rise near -0.2 Å and an equilibrium position indicates the existence of an aligned structure at low temperature. Furthermore, the maximum probability occurs at an equilibrium position. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. The variation of probability with respect to rotation about x-axis corresponding to configuration y (180º) has been carried out as shown in Fig. 5. It has been observed that no pronounced peak exists at an equilibrium point and all the remaining regions have negligible probability as compared to this configuration. Thus, generally, the molecules may be assumed to be capable of free rotations except at lower temperature where the molecules prefer being in the same plane.

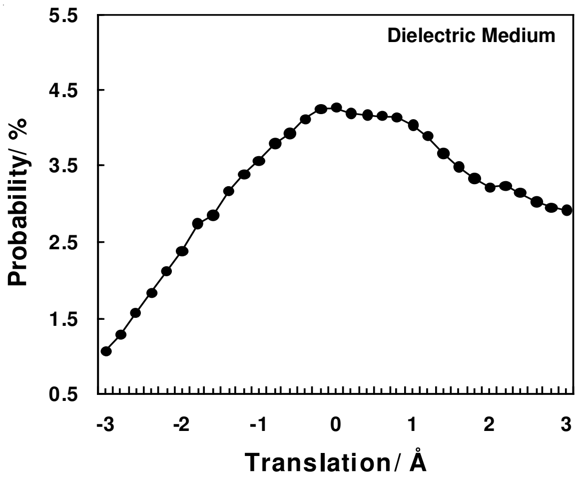

Fig. 4. Variation of probability with respect to translation along x-axis during in-plane interactions at room temperature (300 K)

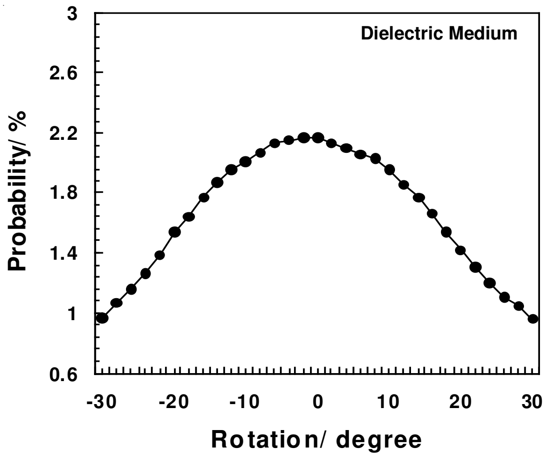

Fig. 5. Variation of probability with respect to rotation about x-axis during in-plane interactions at room temperature (300 K)

Terminal interactions in dielectric medium: The end-to-end interactions are weakest but become important when the molecule possesses a polar group at either or both of the ends or if there is a possibility of hydrogen bonding. To investigate the terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the x-axis by 22 Å with respect to the fixed one. The interactions are further refined with an accuracy of 0.1 Å in translation and 1° in rotation. It has been observed that, due to the planarity of the molecule, the refinement corresponding to stacking energy is much larger than the in-plane and terminal interactions. Rotation about the x-axis (Fig. 6) corresponding to configuration y(0°) shows no more preference for any angle *i.e.*, the molecules are completely free to rotate about their long molecular axis.

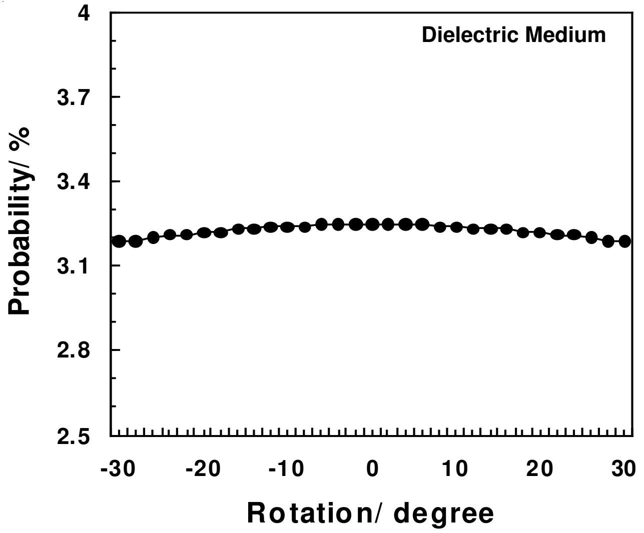

Fig. 6. Variation of probability with respect to rotation about x-axis during terminal interactions at room temperature (300 K)

Influence of dielectric medium: In order to examine the influence of dielectric medium more closely, the various possible geometrical arrangements between a molecular pair (during the different modes of interactions) have been considered. Table-1 shows the relative probabilities of different minimum energy configurations calculated for vacuum and dielectric medium during the different modes of interactions. Evidently, the most favorable stacked configuration y(0°) z (180°) of pairing in dielectric medium has been obtained with the energy -6.17 kcal/mol with 66 % probability at room temperature (300 K) due to redistribution of energies (Fig. 7).

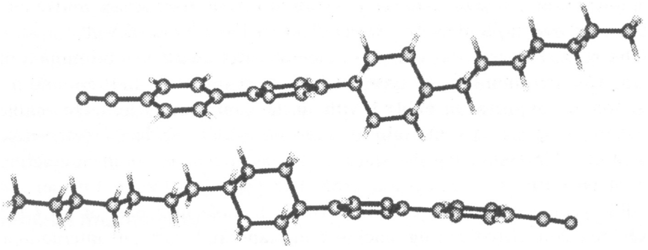

Fig. 7. Most favorable configuration obtained for stacked pair interactions with an energy -6.17 kcal/mol in dielectric medium

It may be accomplished 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 (or maximum probability) configuration. Thus, in a molecular assembly a number of local minimum energy configurations exist. Each of them has their own importance, as in case of closed 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 important because while descending a very high temperature where the molecules have a completely disordered distribution; the global minimum has the maximum probability of occupancy and the other have a sequential preference depending on their individual relative probabilities.

Conclusion

The present statistical study can afford a new and attention-grabbing model of a mesogen in non-interacting and non-mesogenic solvent, benzene. This provides valuable information regarding the influence of dielectric medium on a mesogenic compound in the light of configurational probabilities of dimer complexes, the relative freedom of a molecule in terms of variations in inclination, separation or sliding of one molecule over the other.

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TABLE-1
RELATIVE PROBABILITIES OF DIFFERENT MINIMUM ENERGY CONFIGURATION OBTAINED FOR STACKING, IN-PLANE AND TERMINAL INTERACTIONS IN VACUUM AND IN DIELECTRIC MEDIUM (BENZENE) AT ROOM TEMPERATURE (300 K). AVERAGE DIELECTRIC CONSTANT OF BENZENE IS TAKEN AS 2.25

Configuration	Energy in vacuum (kcal/mol)	Energy in dielectric medium (Kcal/mol)	Probability (%)	
			A	B
y(0°) z(180°)*	-13.89	-6.17	0.82	0.66
y(0°) z(0°)*	-12.97	-5.76	0.17	0.33
y (0°)**	-6.91	-3.07	0.00	0.00
y (180°)**	-5.98	-2.65	0.00	0.00
y (0°)***	-2.61	-1.16	0.00	0.00

*Stacking interactions; **In-plane interactions and ***Terminal interactions; A = Probability in vacuum and B = probability in dielectric medium.

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