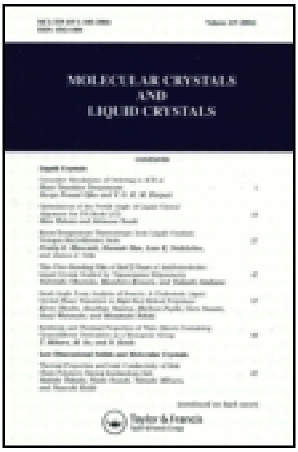

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Molecular Structure and Conformational Behavior of a Nematogen—A Statistical Approach

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Molecular structure and conformational behavior of a nematogen p-ethoxy salicylidene-n-butyl aniline (ESBA) has been studied 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 (CNDO/2) method. The modified Rayleigh-Schrodinger perturbation theory along with multicentered-multipole expansion method has been employed to evaluate the long-range intermolecular interactions, and 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. The effect of nonmesogenic and noninteracting solvent (benzene) has also been studied. Further, the analysis of conformational behavior provides valuable information on configurational freedom of a molecule that may be useful in understanding the structure of phases and their transitions.

Keywords CNDO/2 method; molecular structure; nematogen

Introduction

Liquid crystals (LCs) are promising molecular materials used in and proposed for a wide variety of applications, including light-emitting diodes, photovoltaic devices, and field effect transistors [1]. These systems usually present a number of mesophases, which differ by degree of randomness of the molecular motion. The determination of molecular structure is the simplest application of molecular modeling because the structural features influence the properties of materials at the molecular level [2]. The nematic phase is the simplest of liquid crystal states, in which atoms are distributed uniformly within the molecule. They tend to align along a preferred direction (the director) so that the phase is anisotropic and possesses a degree of orientational order [3]. The main objective of any theory of molecular structure is to provide some insight into the various physical laws governing the chemical constitution of molecules in terms of motions and interactions [4] of the constituent atomic nuclei and electrons. However, mathematical and computational complexities make this goal difficult to attain, and one must usually resort to approximate methods [5,6].

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The simulation methods are based on repeated energy calculations and the large number of coulomb pair contributions coupled to the long-range character of the molecule causes a major consumption of resources, even if computationally efficient methods are employed. For condensed fluid states, especially for LC systems, the chosen model has to be simulated at a number of state points (at various translations and rotations along/about x-, y-, and z-axes) during molecular motions to understand the configurational freedom of the molecule. Moreover, this is also helpful to achieve a good model of molecular interactions that provides valuable information about the structure of the phases formed and their transitions. In view of the practical difficulties and the increasing importance of predicting the properties of target molecular materials, it is of substantial significance to use statistical simulations for the calculation of physical properties [7–9]. It involves not only the precise method of obtaining the information on physical properties from a given electronic configuration but also resolving the probability of conformers (configurations) used as a statistical weighting for the molecules because most of the LC molecules are found to have a number of conformations at room temperature.

The role of molecular interactions in mesomorphic compounds has engaged the attention of several workers [10–14] based on the Rayleigh-Schrodinger perturbation method. These studies were aimed at establishing the anisotropic nature of the pair potential and subsequently finding out the minimum energy configuration of a pair of liquid-crystalline molecules. Thus, the main emphasis was on finding the minimum energy with the observed crystal structure, the basic motive for ordering of a molecule. 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 be obtained through their probabilities corresponding to each configuration. Hence, in order to obtain a quantitative measure for the relative preference, the present authors have evaluated the relative probability of occurrence of each configuration. The configurational probability calculations based on interaction energy results will provide valuable information regarding the most probable molecular aggregation.

The packing of the p-ethoxy salicylidene-n-butyl aniline (ESBA) molecule is of particular interest, because the liquid-crystal behavior of the compound is closely related to the crystal structure. A detailed knowledge of the structural features of LC substances in their crystal phase is of considerable value in understanding their structure and properties in the mesophase. Hence, in the present article, we report the molecular structure and conformational behavior of a nematogen ESBA at room temperature (300 K) only 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. Further, instead of finding the exact minimum energy configuration, a step has been put forward to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference.

Computational Methodology

The molecular geometry of ESBA has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [15]. The molecule has an intramolecular hydrogen bond O–H . . . N. The dihedral angle between the plane C-CH=N-C and the plane of the aniline ring is 20.6°; the angle between the same plane and the plane of the salicylidene fragment is 2° [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 because using only the Mulliken atomic net charges (given, for example, by an *ab initio* program) for the calculation of an electrostatic interaction would be incorrect for two reasons: (i) The atomic dipoles must be taken into account, and (ii) the homopolar dipoles must be taken into account, or else atomic net charges obtained according to Lowdin's procedure should be used. An *ab initio* program that gives only Mulliken net charges is therefore quite misleading as concerns a reasonable representation of the molecular charge distribution in terms of charges and dipoles. These are equivalent to Lowdin orthogonalized charges [17].

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [18] 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 [19], 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, the electrostatic term is expressed as

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

where U_{QQ}, U_{QMI}, U_{MIMI}, etc., are monopole–monopole, monopole–dipole, and dipole–dipole terms, respectively. In fact, the inclusion of higher order multipoles does not significantly affect the electrostatic interaction energy and the calculation only up to dipole–dipole term gives satisfactory result [10–14,20]. 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 semiempirical approaches, viz. the Lennard-Jones or Buckingham-type approaches, actually proceed in this way. Kitaygorodsky [21] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskaya [22] for hydrocarbon molecules and several other molecules and finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R^0{}_{\lambda\nu}$; $R^0{}_{\lambda\nu} = [(2\,R^w{}_\lambda)\ (2\,R^w{}_\nu)]^{1/2}$, where $R^w{}_\lambda$ 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 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 [23].

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 [20] in order to obtain a better insight:

$$P_i = \exp(-\beta\varepsilon_i) / \sum\nolimits_i \exp(-\beta\varepsilon_i)$$

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. An orthogonal coordinate system has been considered to facilitate the above calculation. The origin has been chosen at almost midpoint of the molecule. The x-axis has been chosen along a bond parallel to the long molecular axis, the y-axis lies in the plane of the molecule and, the z-axis is perpendicular to the x-y plane. Terms used like *stacking, in-plane*, and *terminal* interactions have been discussed below.

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 one. Translations along the long molecular axis (x-axis) have been given at an interval of 1 Å and the probability at each point has been calculated.

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. Translations along the x-axis have been given and the corresponding probability values have been reported.

Terminal Interactions. 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 and rotations have been allowed along the x-axis. The probability at each point has been reported. Many liquid-crystal phase transitions involve broken continuous symmetries in real space and their interactions are short range at the molecular level. Hence, in the three modes of interactions the choice of distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short- and medium-range interactions.

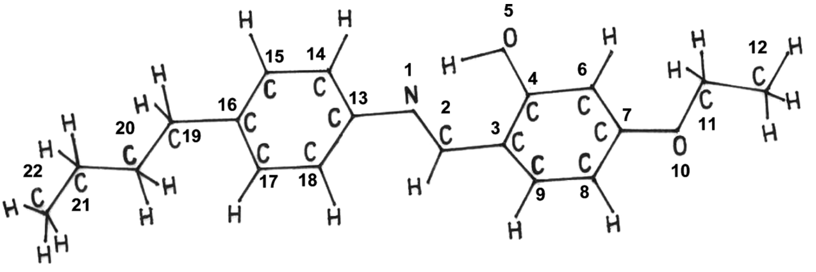

Figure 1. Molecular geometry of ESBA along with various atoms.

Results and Discussion

The molecular geometry of ESBA is shown in Figure 1. The atom-based partial charges on heavy atoms of ESBA are shown in Figure 2 to understand the molecular charge distribution that enables studying the different modes of intermolecular interactions and probability distribution.

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. An appropriate modeling of this fundamental molecular feature relies on the possibility of assigning a partial charge or a set of distributed multipoles to all atomic centers. Analysis of molecular charge distribution can deliver good information about local electrostatic interactions, which is not possible from an experimental point of view. To parameterize the inter- and intramolecular interactions for computer simulation studies, atom-positioned partial charges are helpful.

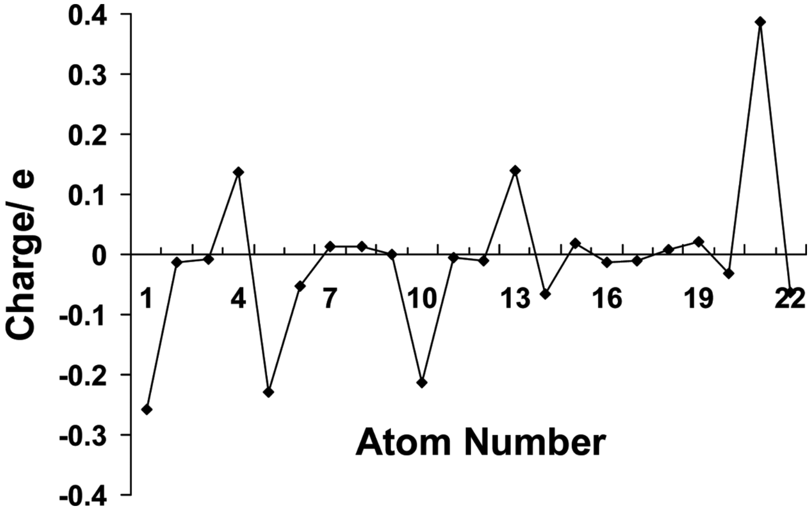

Figure 2. Partial charges on heavy atoms of ESBA.

Quantum chemical computations offer the possibility to take a detailed look at the electronic structure of the molecules. This can be done by determining atom-based partial charges, which are not quantum mechanical observables.

It has been observed from Figure 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 the carbon charges by the adjacent hydrogens, the correct electrostatic potential might be reproduced by different partial distributions. Further, strong alternation of the charges corresponding to atoms 21 and 22 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, because it can provide detailed insight into the molecular arrangement in mesophases. Further, 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 on configurational probability distribution during the different molecular motions is discussed in the following.

Role of Stacking Interactions

The variation of probability with respect to translation along the long molecular axis (x-axis) during stacking interactions corresponding to configuration y (0°) z (0°) in the crystal phase (300 K) is shown in Figure 3. The configuration shows a sharp preference toward the minimum energy point and the maximum probability has been obtained at -8 Å. The variation of probability is almost constant in the region of -18 ± 2 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 (0°) z (180°) is shown in Figure 4. The maximum probability has been achieved at $-2°$ 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°) y (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. An accuracy of 0.1 Å in translation and 1° 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 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.

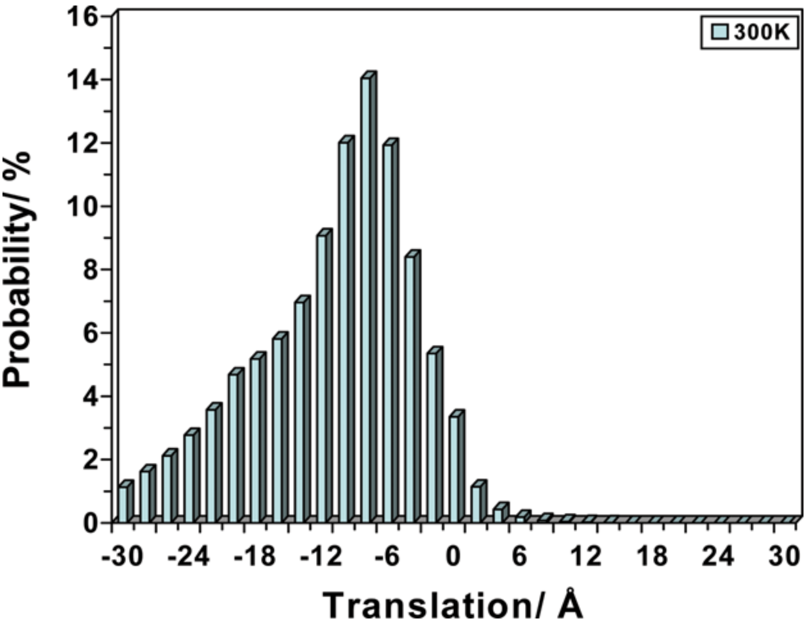

Figure 3. Variation of probability with respect to translation along the x-axis during stacking interactions corresponding to configuration y (0°) z (0°) at room temperature (300 K).

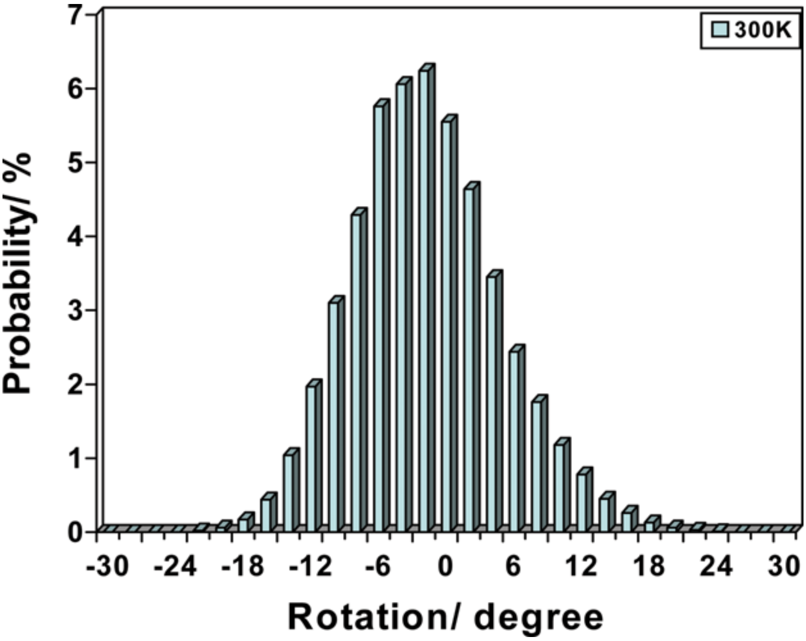

Figure 4. Variation of probability with respect to rotation about the x-axis during stacking interactions corresponding to configuration y (0°) z (180°) at room temperature (300 K).

Role of In-Plane Interactions

The electrostatic energy during in-plane interactions is more effective than that in stacking, because the anti-parallel orientation of molecular rings provides a more effective dipole–dipole attraction. Additionally, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped-anti-parallel molecular ring orientation. This ultimately causes the 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 during in-plane interactions corresponding to the configuration y (0°) at room temperature (300 K) has been plotted in Figure 5. Because in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at 2 Å. The interacting configurations have been refined with respect to translation along the x-axis at the equilibrium condition, 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 (180°) has also been carried out as shown in Figure 6. Evidently, a pronounced peak exists at 6° rotation point, and there is no drastic preference for the aligned structure. Further, it is observed that the rotational freedom is much more pronounced compared to the stacking interactions. The variation of the probability with respect to rotation about the y-axis corresponding to the configuration x (0°) has also been carried out, and it has been observed that the rotation about the y-axis does not alter the configurational probability drastically.

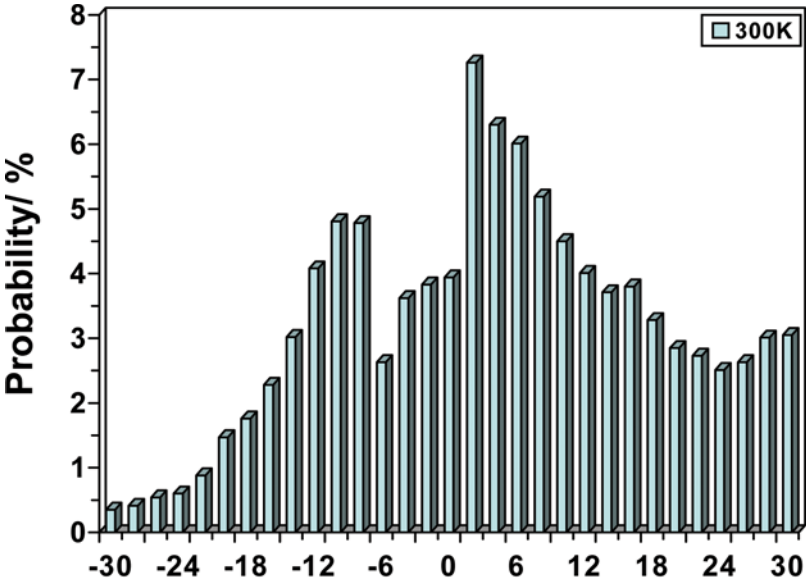

Figure 5. Variation of probability with respect to translation along the x-axis during in-plane interactions corresponding to configuration y (0°) at room temperature (300 K).

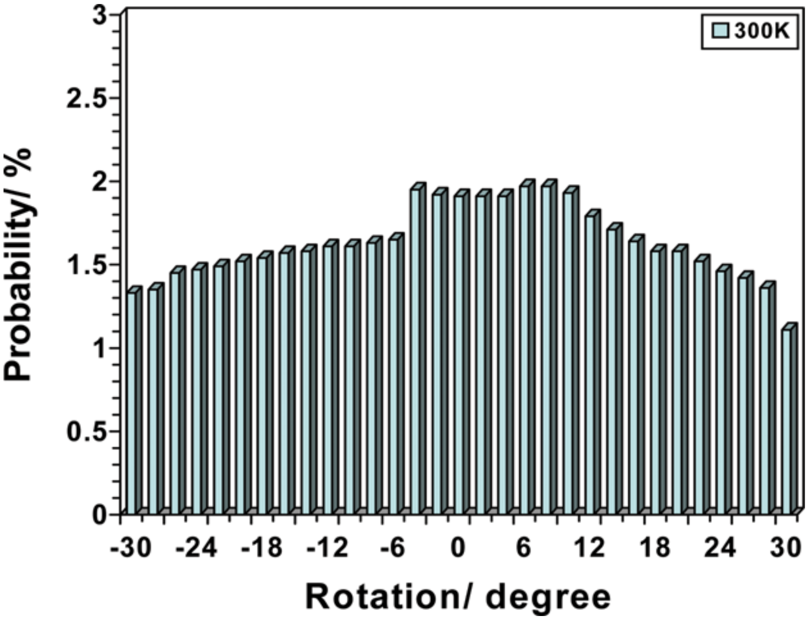

Figure 6. Variation of probability with respect to rotation about the x-axis during in-plane interactions corresponding to configuration y (180°) at room temperature (300 K).

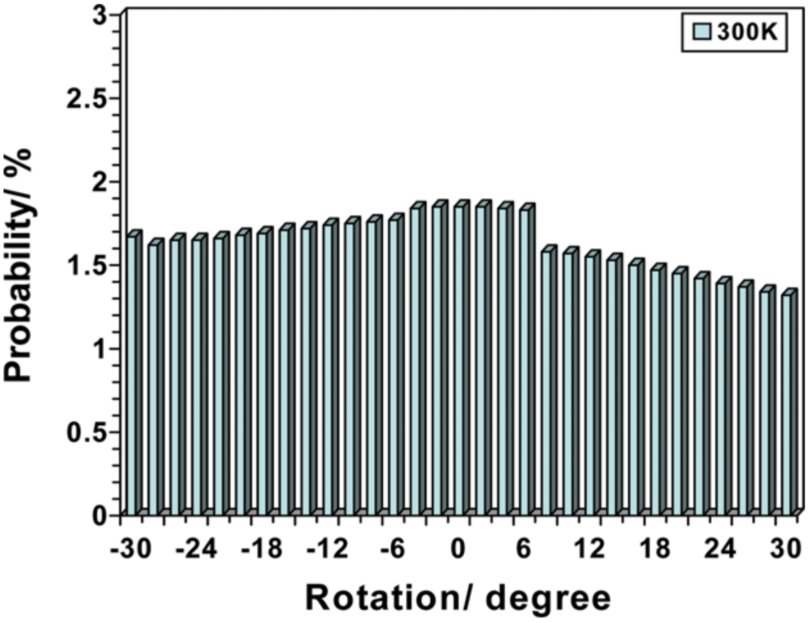

Figure 7. Variation of probability with respect to rotation about the x-axis during terminal interactions corresponding to configuration y (0°) at room temperature (300 K).

Table 1. Minimum energy obtained after refinement during stacking, in-plane, and terminal interactions between a molecular pair of ESBA

Energy terms	Stacking energy	In-plane energy	Terminal energy
U_{QQ}	0.18	−0.02	0.01
U_{QMI}	−0.02	−0.21	−0.08
U_{MIMI}	−1.09	−0.09	−0.01
U_{el}	−0.92	−0.32	−0.07
U_{pol}	−0.31	−0.13	−0.01
U_{disp}	−17.39	−4.99	−1.34
U_{rep}	4.23	1.07	0.47
U_{total}	−14.39	−4.37	−0.96

Energy is expressed in kcal/mole.

U_{QQ} = monopole–monopole; U_{QMI} = monopole–dipole; U_{MIMI} = dipole–dipole; U_{el} = electrostatic; U_{pol} = polarization; U_{disp} = dispersion; U_{rep} = repulsion; and U_{total} = total.

Role of Terminal Interactions

The end-to-end interactions are weakest but become more important when the molecules possess a polar group at either or both ends or if it there is a possibility of hydrogen bonding. The terminal interactions are much weaker compared to stacking or in-plane interactions. The rotations about the x-axis corresponding to configuration y (0°) at room temperature (300 K; Figure 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 have been listed in Table 1 with all contributing terms to enable comparison. The results indicate that due to the planarity of the molecule, the refinement corresponding to stacking energy is maximum and the ultimate magnitude of stacking energy is much higher than in-plane and terminal interaction energies.

Table 2. Relative probabilities of different minimum energy configurations obtained for ESBA during stacking, in-plane, and terminal interactions in vacuum and in nonmesogenic, noninteracting solvent (benzene) in crystal phase (300 K)

Configuration	Energy in vacuum (kcal/mole)	Energy in dielectric medium (kcal/mole)	Probability (%)	
			A	B
y (0°) z (0°)[a]	−12.72	−5.65	79.36	63.69
y (0°) z (180°)[a]	−11.93	−5.30	20.63	35.03
y (0°)[b]	−7.81	−3.47	0.00	1.27
y (180°)[b]	−6.44	−2.86	0.00	0.00
y (0°)[c]	−2.10	−0.93	0.00	0.00

Average dielectric constant of benzene is taken as 2.25.

[a] Stacking interactions.

[b] In-plane interactions.

[c] Terminal interactions.

A = Probability in vacuum; B = Probability in dielectric medium.

Role of Nonmesogenic and Noninteracting Solvent

In order to examine the effect of nonmesogenic and noninteracting solvent, that is, benzene on a nematogen, the various possible geometrical arrangements between molecular pairs have been considered that provide information about the molecular arrangements inside the bulk materials. Table 2 shows the relative probabilities of different minimum energy configurations, calculated for vacuum and dielectric media 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 same. This provides theoretical support to the experimental observations [24]. Furthermore, the most favorable stacked configuration y (0°) z (0°) of pairing (*i.e.*, 63.69% probability) has been obtained with the energy of -5.65 kcal/mol in benzene at room temperature (300 K).

Conformational Behavior

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 them has their 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 interaction energy/probability studies based on semiempirical quantum mechanical methods are helpful for a quantitative evaluation of mutual influence of intermolecular forces on equilibrium packing of molecules. Further, the study on conformational behavior of the molecule provides valuable information on configurational freedom of a molecule that may be useful in understanding the structure of phases and their transitions.
- The energies are redistributed in nonmesogenic and noninteracting 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 the relative order of configurations and the preference of a particular configuration over the other.

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