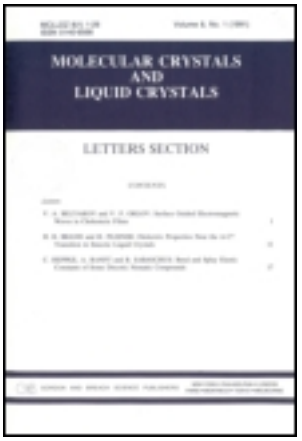

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The Influence of Organic Solvents and Conformational Behavior of Mesogenic Compounds: A Computational Approach

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The role of organic solvents and conformational behavior of liquid crystalline disubstituted biphenylcyclohexanes (BCHs) of the general formula R-C_6H_{10}-C_6H_4-C_6H_4-X with R: C_3H_7; X: H (BCH30) and R: C_5H_{11}; X: CN (BCH5CN) have been reported with respect to the 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 with the multicentered–multipole expansion method has been employed to evaluate the long-range interactions, and a "6-exp." potential function has been assumed for the short-range interactions. The minimum energy configurations obtained during the different modes of interactions have been taken as input to calculate the configurational probability using the Maxwell-Boltzmann formula in non-polar organic solvents, i.e., carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$), at room temperature 300 K. It has been observed that the molecules show the remarkable behavior in the solvents. A comparison of stacked dimers between both the molecules suggests that the extension of the chain length, a recognizable segregation of dimers into a highly tilted layer structured, has been obtained for BCH5CN molecule.

Keywords Liquid crystals; non-polar solvents; quantum chemistry

Introduction

In the science and technology of liquid crystals the study of the molecular orientation is one of the most significant and inevitable issues, as the degree of order influences the anisotropy of physical properties of these substances. Mesogens with terminal cyano group are of great interest [1]; short-range dipole–dipole interactions between these molecules form dimmers [2]. The stability of liquid crystal phase can often be enhanced by increasing the length and polarizability of the molecule or by adding a terminal cyano group promoting polar interactions in the molecular pair. Hence, it is evident that intermolecular forces are of immense importance in determining the positional and orientational order of mesomorphic compounds [3, 4].

The thermotropic liquid crystals have been paid considerable attention due to their extensive applications, such as liquid crystal displays, adaptive optic devices, and optical switchable windows [5]. It has been observed that the dissolving of a thermotropic

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liquid crystal compound in a non-polar organic solvent produces ferroelectric liquid crystals with remarkable properties [6]. The electro-optic properties of the solutions are, to some extent, better than those of "pure" liquid crystals. Study of the effect of solvents on the molecules forms an important subject for research, and it can play a significant role in photophysics. The solvent environment determines important changes in the electro-optical properties of the spectrally active molecules [6]. The roles of molecular interactions in mesomorphic compounds have been reported by several authors [7–11] based on the Rayleigh-Schrodinger perturbation method. These studies have indeed to establish the anisotropic nature of the pair potential, and subsequently find out the minimum energy configuration of a pair of mesogens.

Liquid crystals represent a class of complex fluids that has opened many doors for us to learn a great deal about molecular interactions, phase behavior, transitions, and the art of soft condensed matter [12]. The present article deals with the interaction energy/configurational probability of smectogen (BCH30) and nematogen (BCH5CN) in non-polar solvents, i.e., CCl_4 and $CHCl_3$ at room temperature 300 K, but the detailed results have been reported only for BCH5CN molecule. However, the salient features of others have also been reported. Interaction energies/configurational probabilities of a molecular pair have been computed at an intermediate distance 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for the terminal interactions.

Computational Methods

The determination of molecular structure is the simplest application of molecular modeling because the structural features influence the properties of materials at molecular level [13]. The molecular geometry of BCH30 and BCH5CN has been constructed on the basis of published crystallographic data [14] with the standard values of bond lengths and bond angles. In both the compounds, the molecules form layer in the crystalline state. The dihedral angles between the phenyl rings in the biphenyl unit are 2.4° (BCH5CN) and 23.8° (BCH30), respectively. The computations have been carried out in three steps:

First-Step Computation

It is expected that the specific charge distribution and electrostatic interactions in LC molecules play an influential role in the formation of various mesophases. The complete neglect differential overlap (CNDO/2) method [15] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule because 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. The program language is FORTRAN IV. The program is capable of computing CNDO wave functions for open- and closed-shell molecules containing the elements hydrogen to chlorine.

Second-Step Computation

The computational scheme based on simplified formula provided by Claverie [16] for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. The computer program INTER, originally developed by Claverie, has been used for this purpose with the further modification.

The total pair interaction energy of molecules (U_{pair}), according to the second-order perturbation theory for intermediate range interactions [17], is represented as sum of various terms contributing to the total energy:

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

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

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

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 affect significantly the electrostatic interaction energy and the calculation only up to dipole–dipole term gives satisfactory result. The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term.

The dispersion and short-range repulsion terms are considered together because the several semi-empirical approach, viz. the Lennard-Jones or Buckingham type approach, actually proceed in this way. Kitaygorodsky introduced [18] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [19] for hydrocarbon molecules, including several other molecules, who finally gave the expression:

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

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

where $Z = R_{\lambda\nu}/R^0{}_{\lambda\nu}$; $R^0{}_{\lambda\nu} = [(2R^w{}_\lambda)\,(2R^w{}_\nu)]^{1/2}$, where $R^w{}_\lambda$ and $R^w{}_\nu$ 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 $K_\lambda\ K_\nu$ allow the energy minimum to have different values according to the atomic species involved.

Third-Step Computation

In order to obtain a better insight, the total interaction energy values obtained through the different modes of interactions have been used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula [20]:

$$P_i = \exp(-\beta\varepsilon_i) / \Sigma_i \exp(-\beta\varepsilon_i),$$

where P_i stands for probability and $\beta = 1/kT$, where 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.

In this case, 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 while the y-axis lies in the plane of the molecule, and z-axis is perpendicular to the x–y plane. The terms like stacking, in-plane, and terminal interactions will be used to maintain the continuity with the previous work [20].

Computation of Stacking Interactions. The interacting molecule has been placed at a separation of 6 Å along the z-axis with respect to the fixed molecule. 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.

Computation of In-Plane Interactions. The interacting molecule has been kept at a separation of 8 Å along *y*-axis with respect to the fixed one. The distance chosen for these calculations are such that the possible van der Waals contacts are avoided.

Computation of Terminal Interactions. To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the *x*-axis by 22 Å with respect to the fixed one.

Results and Discussion

The molecular geometry of BCH30 and BCH5CN has been shown in Fig. 1. The results of configurational probability distribution during the different modes of intermolecular interactions in non-polar organic solvents, i.e., CCl_4 and $CHCl_3$, are discussed next.

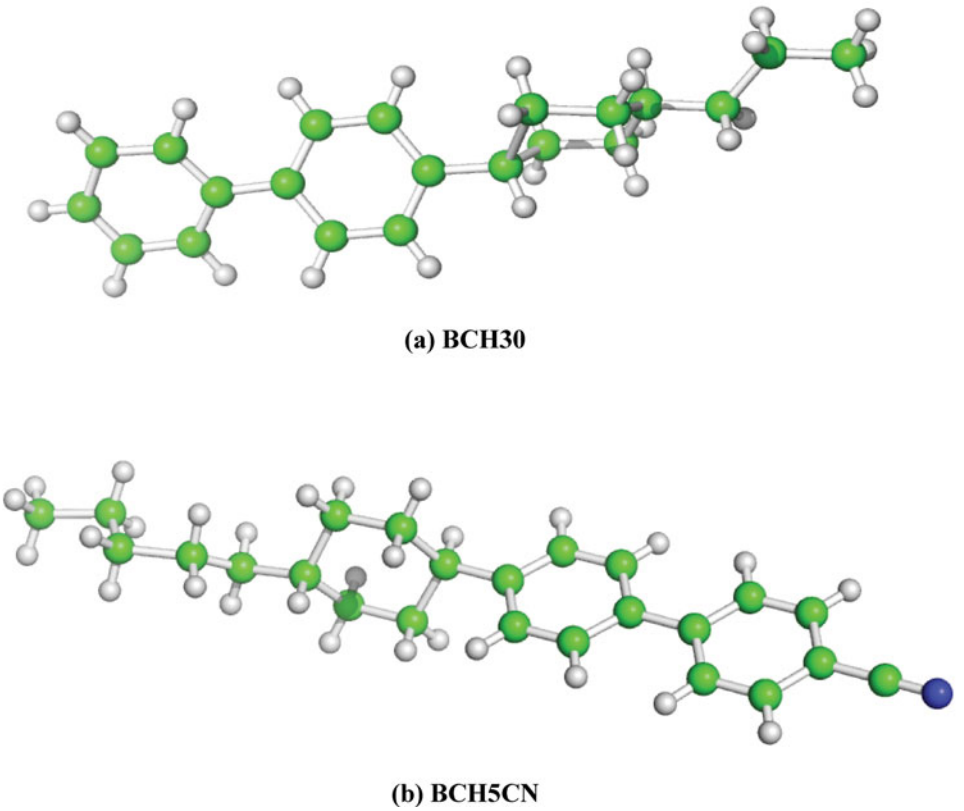

Figure 1. Molecular geometries of (a) BCH30 and (b) BCH5CN molecules.

Influence of Stacking Interactions on Organic Solvents

The variation of the probability with respect to translation along the long molecular axis (*x*-axis) corresponding to configuration *y* (0°) *z* (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K has been shown in Fig. 2. Evidently, the configuration shows a sharp preference toward the minimum energy point. The variation of probability is almost constant in the region of $2 \pm \underline{2}$ Å. It shows that the sliding of one molecule over another is allowed energetically in a small range that may be correlated with the 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 *x*-axis corresponding to configuration *y* (0°) *z* (180°) in CCl_4 and $CHCl_3$ at room temperature has been carried out that indicates a slight preference for the aligned structure of this configuration. The variation of probability with respect to rotation about *z*-axis corresponding to configuration *x* (0°) *y* (0°) has also been carried out in the organic solvents at room temperature 300 K. 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 pre-selected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route.

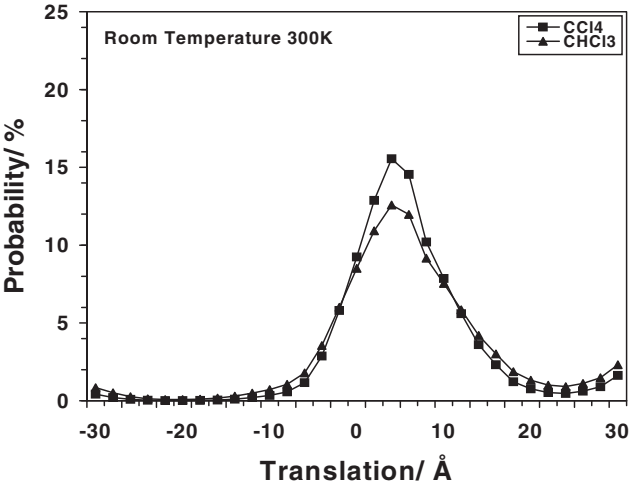

Figure 2. Variation of probability with respect to translation along *x*-axis during stacking interactions corresponding to configuration *y* (0°) *z* (0°) for BCH5CN molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

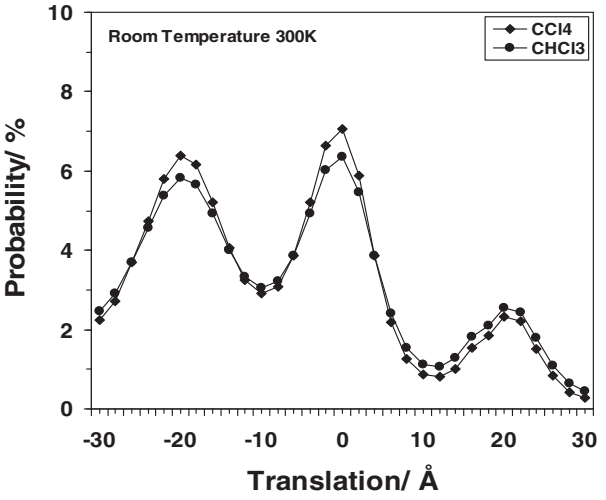

Figure 3. Variation of probability with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y* (0°) for BCH5CN molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

Influence of In-Plane Interactions on Organic Solvents

The variation of probability with respect to translation along *x*-axis corresponding to the configuration *y* (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K is shown in Fig. 3. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at an equilibrium position. 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 *x*-axis.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration *y* (180°) in CCl_4 and $CHCl_3$ at room temperature 300 K has been carried out. It has been observed that a pronounced peak exists at the one particular rotation point, and all the remaining regions have negligible probability as compared to this configuration. Furthermore, it is observed that the rotational freedom is much more pronounced as compared to the stacking interactions. The variation of the probability with respect to rotation about the *y*-axis corresponding to the configuration *x* (0°) in organic solvents at room temperature 300 K has also been carried out, and it is observed that the rotation about the *y*-axis does not alter the configurational probability drastically.

Influence of Terminal Interactions on Organic Solvents

The end-to-end interactions are weakest but become more important when the molecules possess polar group at either or both ends, or if there is a possibility of hydrogen bonding. Figure 4 shows the variation of probability with respect to rotation about *x*-axis corresponding to configuration *y* (0°) in CCl_4 and $CHCl_3$ at room temperature 300 K. The terminal interactions are much weaker as compared to stacking and in-plane interactions.

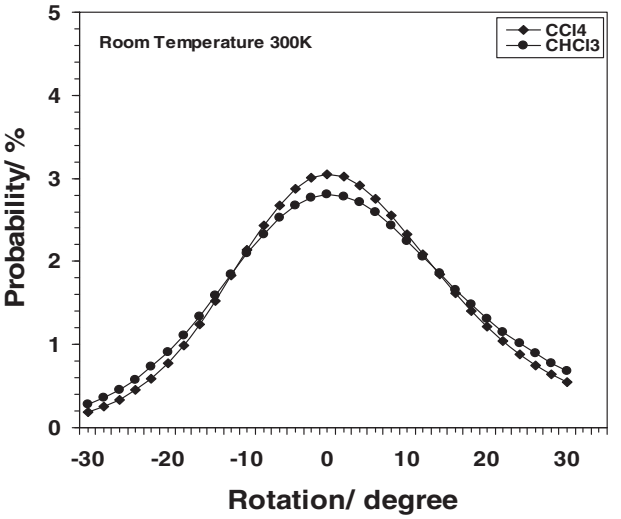

Figure 4. Variation of probability with respect to rotation about x-axis during terminal interactions corresponding to configuration y (0°) z (0°) for BCH5CN molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

Influence of Organic Solvents on Mesogens

In order to understand the influence of organic solvents on BCH30 (smectogen) and BCH5CN (nematogen), the various possible geometrical arrangements between a molecular pair during the different modes of interactions have been considered that provide information about the molecular arrangements inside the bulk materials. Table 1 shows the relative probabilities of different minimum energy configurations, calculated at room temperature (300 K) in CCl_4 and $CHCl_3$ with respect to translational and orientational motions. Further, it is clear from the above discussion that 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 local minimum energy configurations. The global minimum is, however, of paramount importance because while descending 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.

Conformational Behavior of BCH30 and BCH5CN Molecules

The conformational behavior of liquid crystals displays a large variation in intermolecular effects that depend on the nature and magnitude of interactions. Each conformation may show the distinct energy, and lower energy conformations will be populated in preference to those of higher energy. The most stable configurations of BCH30 and BCH5CN molecules observed in CCl_4 have been shown in Figs. 5 and 6, respectively. A comparison of stacked dimers between both the molecules suggests that the extension of the chain length, a recognizable segregation of the dimers into a highly tilted layer structure, has been obtained for BCH5CN molecule (Fig. 6). The mutual interaction between the dimers of BCH5CN in the structure is, however, quite weak, in particular to chain atoms. Hence, the end chains

Table 1. Relative probabilities of the different minimum energy configurations obtained for BCH30 and BCH5CN molecules during the stacking, in-plane, and terminal interactions in non-polar organic solvents, i.e., CCl_4 and $CHCl_3$, at room temperature 300 K

Configuration	Energy in vacuum (kcal/mole)	Probability (%) at 300 K	
		CCl_4	$CHCl_3$
BCH30 molecule			
x (0°) *y* (0°)[a]	–14.80	56.26	50.33
y (0°) *z* (0°)[a]	–13.55	43.72	44.72
y (0°)[b]	–4.69	0.00	2.04
x (180°)[b]	–4.27	0.00	1.76
y (0°)[c]	–2.99	0.00	1.12
BCH5CN molecule			
x (0°) y (0°)[a]	–14.70	59.07	51.30
y (0°) z (0°)[a]	–13.21	40.82	43.18
y (0°)[b]	–5.22	0.10	2.65
x (180°)[b]	–4.30	0.00	1.92
y (0°)[c]	–2.21	0.00	0.90

[a]Stacking interactions.
[b]In-plane interactions.
[c]Terminal interactions.

provide enough disorder to the crystal to pass on to nematic rather than smectic phase. This is due to the fact that the probability of thermal fluctuations as well as the occurrence of different conformations increase as alkyl chain becomes longer. The comparison of interaction energy values for both the molecules indicates that the BCH5CN dimers are more stable and, hence, cause high phase stability.

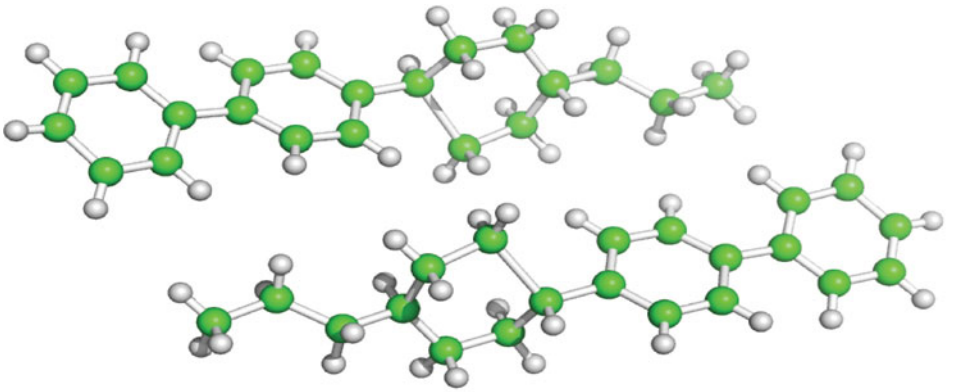

Figure 5. Energetically favorable structure of BCH30 molecule in CCl_4 during the stacking interactions at room temperature 300 K.

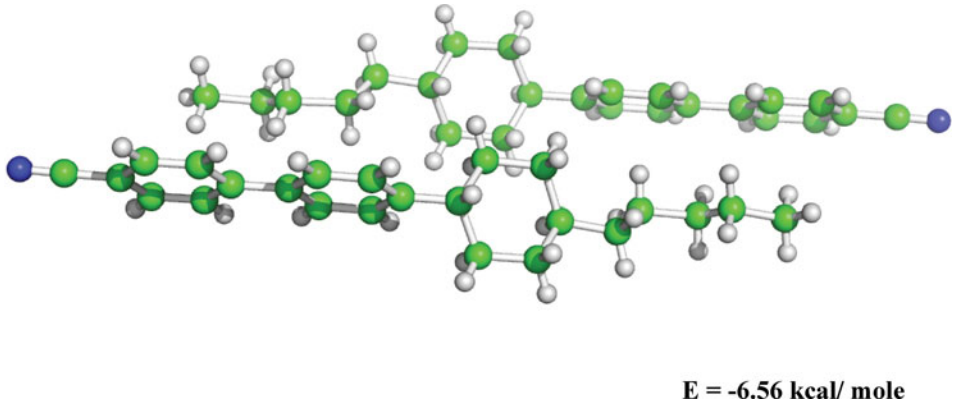

Figure 6. Energetically favorable structure of BCH5CN molecule in CCl_4 during the stacking interactions at room temperature 300 K.

Conclusions

The salient features of the present work are:

1. A comparative study on the stacked dimers between BCH30 and BCH5CN molecules suggests that the extension of the chain length, a recognizable segregation of dimers into a highly tilted layer structured, has been obtained for BCH5CM molecule. Further, the BCH5CN dimers are more stable and, hence, cause high phase stability.
2. The electrostatic energy during the in-plane interactions is more effective than during stacking since the anti-parallel orientation of molecular rings provides a more effective dipole–dipole attraction, which aids in the energetic stabilization of the mesophase.
3. The consideration of relative probabilities among the minimum energy configurations obtained during the stacking, in-plane, and terminal interactions provides information about the molecular arrangements inside a bulk of materials. Further, the considerable rise in the molecular interactions has been observed due to the redistribution of energy in CCl_4 and $CHCl_3$, i.e., the molecules produce the remarkable properties in solvents.

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