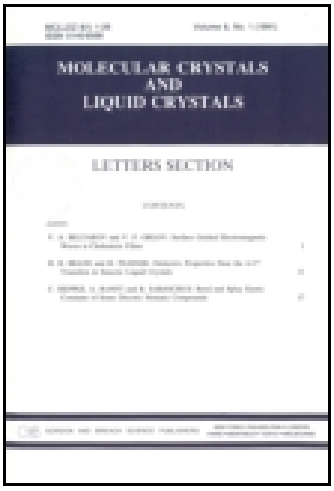

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Order–Disorder Phenomenon of Nematogens at Molecular Level—A Computational Approach

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The phase behavior of nematogenic p-n-Alkoxy cinamic acids (nOCAC) with alkyl chain carbon atoms (n = 2,4) has 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 nonpolar organic solvents, i.e., carbon tetrachloride (CCl_4), and chloroform ($CHCl_3$) at room temperature 300 K. Further, entropy of each configuration has been computed. It has been observed that the molecules show the remarkable behavior in the solvents. An attempt has been made to develop new and interesting computational model for nematogens in the solvents and order–disorder phenomenon at molecular level.

Keywords Configurational probability; entropy; nematogens; solvents

Introduction

The liquid-crystal technology has had a major effect in many areas of science and engineering, as well as device technology. Applications for this kind of materials are still being discovered and continue to provide effective solutions to many different problems. Material and phase stabilities are primary concern for all devices desiring to have a long operational lifetime [1, 2]. The most common nematic LC structure for displays consists of an alkyl chain, one or two cyclohexane rings, a phenyl rings, and a polar group. The aromatic ring system not only imparts structural anisotropy, but also plays a central role in determining the electrical, magnetic, and optical properties of the bulk materials [3].

The thermotropic liquid crystals have paid considerable attention due to their extensive applications, such as liquid crystal displays, adaptive optic devices, and optical switchable windows [4]. It has been observed that the dissolving of a thermotropic liquid-crystal compound in a nonpolar organic solvent produces ferroelectric liquid crystals with the remarkable properties [5]. 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 the photo

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physics. The solvent environment determines important changes in the electro-optical properties of the spectrally active molecules [5]. The molecular interactions in mesomorphic compounds based on the Rayleigh–Schrodinger perturbation method have been reported by the several authors [6–10]. 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.

The behavior of nematogens is believed to derive form anisotropy in their intermolecular interactions. This anisotropy is based in physical properties common to all nematogen molecules. The stability of the nematic phase arises from the existence of the strong interactions between pairs of molecules, which promote the positional and orientational order of the mesomorphic compounds. At molecular level, the phases of matter are basically determined by the interplay between molecular structure, intermolecular interactions, and the molecular motion. The present article is an attempt to establish an interesting computational model for nematogens (2OCAC and 4OCAC) in organic solvents, i.e., CCl_4 and $CHCl_3$ at room temperature 300 K but the detailed results have been reported only for 2OCAC molecule. However, the salient features of other have also been reported. Computations of configurationally probabilities/ entropy between a pair of molecules have been carried out at an intermediate distance 6Å for stacking and 8Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for the terminal interactions. The configurationally probability and entropy distribution picture based on the interaction energy results will provide valuable information in this respect. The molecules 2OCAC and 4OCAC show nematic to isotropic transition at 471 K, and 460.5 K, respectively [11].

Computational Details

The quantum chemical computations can yield more detailed information, but they are still restricted by the contemporary computer power due to the rather large size of mesogenic molecules. Therefore, the semi-empirical approaches are often used for calculations of molecular properties. It is well known that subtle alternations in molecular structure can have profound effects on the stability and properties of mesophases. The molecular geometries of *n*OCAC ($n = 2,4$) have been constructed on the basis of published crystallographic data [11] with the standard values of bond lengths and bond angles. The structures of the systems have the all-*trans* extended conformation, and the molecules exist in the crystals as planar hydrogen-bonded dimers. The advancing the structure and energetic effects are helpful in employing the molecular models. The computations have been carried out in three steps:

First Step Computation

The complete neglect differential overlap (CNDO/2) method [12] has been employed to compute the net atomic charge and dipole moment at each atomic centre 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 centre through an all-valance electron method. 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 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 [13] 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 [14], 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:

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

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. 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 [15] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [16] for hydrocarbon molecules and the several other molecules and finally gave the expression:

$$U_{\text{disp}} + U_{\text{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda, \nu)$$
$$U(\lambda, \nu) = K_{\lambda} K_{\nu} (-A/Z^6 + Be^{-\gamma Z})$$

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

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 [17]:

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

Further, the configurational entropy parameter [18] has been calculated to explain the order–disorder phenomenon at molecular level:

$$S = k \ln \Sigma_i \exp(-\beta\varepsilon_i) + (U/T)$$
$$U = \Sigma_i \varepsilon_i \exp(-\beta\varepsilon_i) / \Sigma_i \exp(-\beta\varepsilon_i)$$

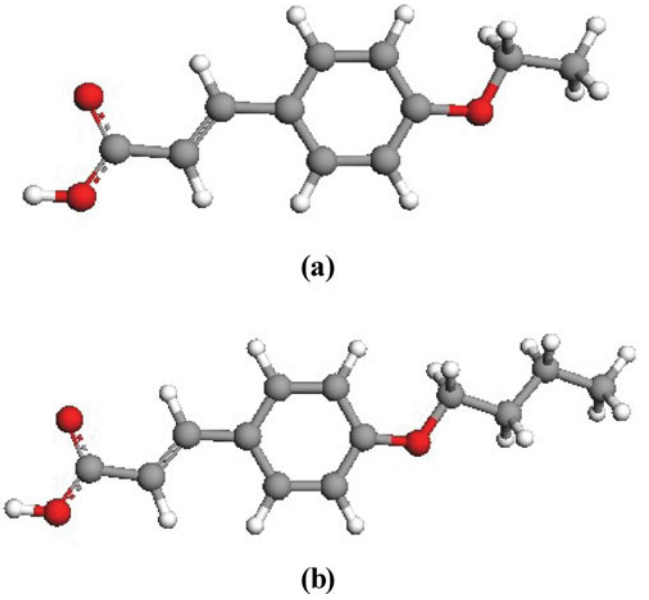

Figure 1. Molecular geometries of (a) 2OCAC and (b) 4OCAC molecules.

where P_i stands for probability, and S stands for entropy and U stands for internal energy. $\beta = 1/kT$, 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 and thermodynamic properties have been computed.

In this case, the origin has been chosen at almost midpoint of the molecule. The x-axis 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.

Results and Discussion

The molecular geometries of nOCAC (n = 2,4) have been shown in Fig. 1. The results of configurational probability distribution during the different modes of intermolecular interactions in nonpolar solvents, i.e., CCl_4, and $CHCl_3$ are discussed below.

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.

A graphical representation of the configurational probability distribution with respect to translation along the long molecular axis (x-axis) corresponding to configuration y (0^0) z (0^0) 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 16 ± 4 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.

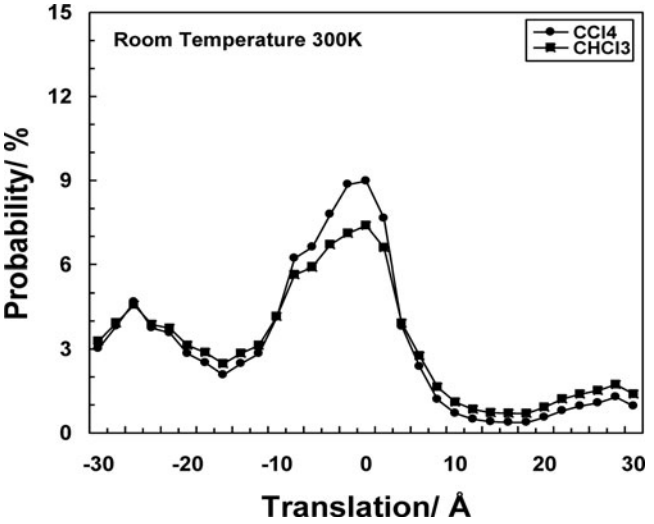

Figure 2. A graphical representation of configurational probability distribution with respect to translation along *x*-axis during stacking interactions corresponding to configuration *y* (0^0) *z* (0^0) for 2OCAC molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

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 *z*-axis corresponding to configuration *x* (0^0) *y* (0^0) has also been carried out in the 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 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. 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 have been achieved. It is important to note here that the path of minimization strictly depends on the objective of computations.

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.

A plot of configurational probability distribution with respect to translation along *x*-axis corresponding to the configuration *y* (0^0) 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.

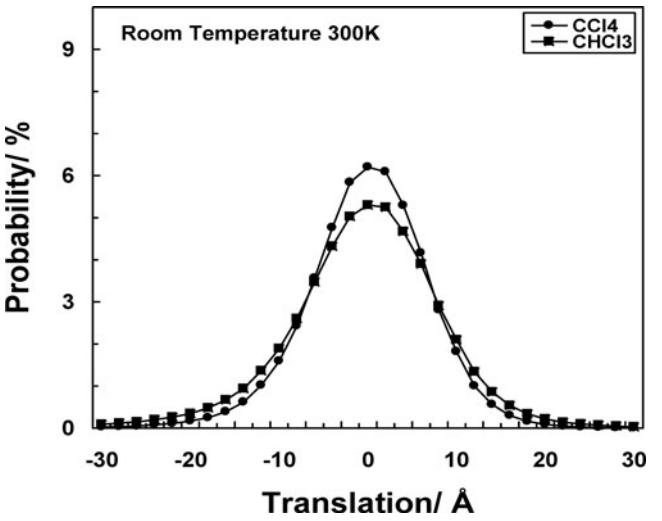

Figure 3. A plot of configurational probability distribution with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y* (0^0) for 2OCAC molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration *y* (180^0) 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* (0^0) in 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.

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.

The end-to-end interactions are weakest but become more important when the molecules possesses 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* (0^0) in CCl_4 and $CHCl_3$ at room temperature 300 K. The terminal interactions are much weaker as compared to stacking or in-plane interactions.

Influential Role of Organic Solvents on Nematogens

In order to understand the influential roles of solvents on nematogens (2OCAC and 4OCAC), 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 $CHCl_3$

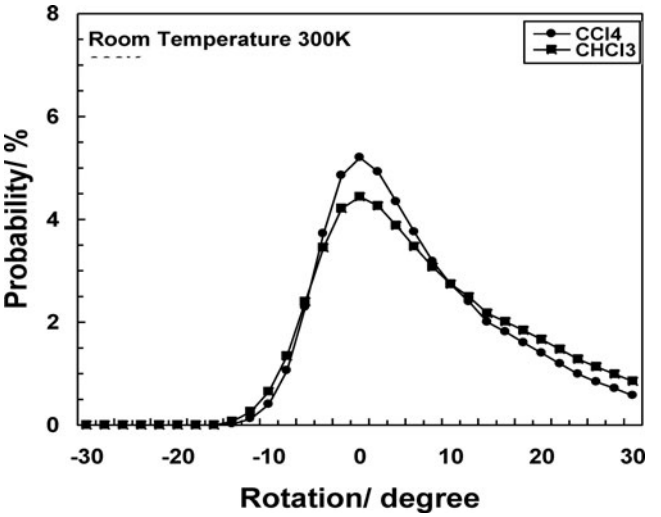

Figure 4. Variation of configurational probability with respect to rotation about *x*-axis during terminal interactions corresponding to configuration *y* (0^0) *z* (0^0) for 2OCAC molecule in CCl_4 and $CHCl_3$ at room temperature 300 K.

during the different modes of interactions 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.

Configurational Entropy and Role of Alkyl Chains

The nematic liquid crystals are generally manifested by its translational freedom along the long molecular axis. It has been observed that the most stable configuration of paring has been obtained in CCl_4 (Table 1) at room temperature 300 K. In view of this, the configurational entropy has been calculated along the long molecular axis for 2OCAC molecule during the stacking, and in-plane interactions in CCl_4 at room temperature (300 K), nematic-isotropic (471 K), and above transition temperature (550 K).

The terminal flexible chains reduce the stability of the solid crystal phase, and allow the appearance of liquid crystal phases. From the view point of entropy, alkyl chains play dominant role as they are very labile, and can easily make multi-conformational changes. Hence, alkyl chains can be regarded as source of entropy to realize a given condensed state or to tune the delicate balance between two energetically close phases. The entropy as a thermodynamic function is a measure of the disorder of molecules because the entropy is related to the number of microscopic states by Boltzmann's principle. The configurational entropy has been estimated with respect to translational and rotational motions during the stacking and in-plane interactions. Figure 5 shows the translational entropy as a function

Table 1. Relative probabilities of the different minimum energy configurations obtained for 2OCAC and 4OCAC molecules during the stacking, in-plane, and terminal interactions in nonpolar organic solvents, i.e., CCl_4, and $CHCl_3$ at room temperature 300 K

		Probability (%) at 300 K	
Configuration	Energy in vacuum (Kcal/mole)	CCl_4	$CHCl_3$
2OCAC molecule			
$x\,(0^0)\,y\,(0^0)$[a]	−13.87	56.26	50.33
$y\,(0^0)\,z\,(0^0)$[a]	−13.54	43.72	44.72
$y\,(0^0)$[b]	−4.69	0.00	2.04
$x\,(180^0)$[b]	−4.27	0.00	1.76
$y\,(0^0)$[c]	−2.99	0.00	1.12
4OCAC molecule			
$x\,(0^0)\,y\,(0^0)$[a]	−13.70	59.07	51.30
$y\,(0^0)\,z\,(0^0)$[a]	−13.21	40.82	43.18
$y\,(0^0)$[b]	−5.22	0.10	2.65
$x\,(180^0)$[b]	−4.30	0.00	1.92
$y\,(0^0)$[c]	−2.21	0.00	0.90

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

of temperature during stacking and in-plane interactions along the long molecular axis. It is noticed that translational entropy is 2.63 kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (346.9 K). However, at room temperature (300 K) the value is 2.45 kcal mole^{-1} K^{-1} indicating a strong binding at low temperature and less disorder. But with increase of temperature, the molecules obtain sufficient freedom to slide along the long molecular axis, which causes the increment of disorder. Such translational freedom is much more pronounced in planar interactions. Evidently, even at room temperature this value is 4.13 kcal mole^{-1} K^{-1}, which increased to 4.35 kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (346.9 K). It may be noted that though the freedom is considerable for smaller translation, longer translations are not generally permitted. Thus, in the mesomorphic range, small movements of molecule are only possible.

Most of the liquid crystalline molecules found to have a number of conformations which are thermally accessible. In the process of a phase transition from a low- to a high-temperature, the molecular motions of the alkyl chains would be excited and thereby the number of thermally accessible conformations would be increased. The translational entropy in the isotropic liquid state is increased from its room temperature (Fig. 5). It implies that the different modes of molecular motions (translational, rotational, etc.) are excited to an equal extent, particularly in the isotropic state. Translational entropy favors parallel alignment of the molecules because this arrangement gives less excluded volume (the volume into which the center of mass of one molecule can not move due to the impenetrability of the other molecule) and, therefore, more free space for the molecules to jostle around. However, the comparable values in both the cases (i.e., stacking, and in-plane interactions) show that the molecule 2OCAC do not show extraordinary preference in forming the stacked layers, hence justifies the nematic character.

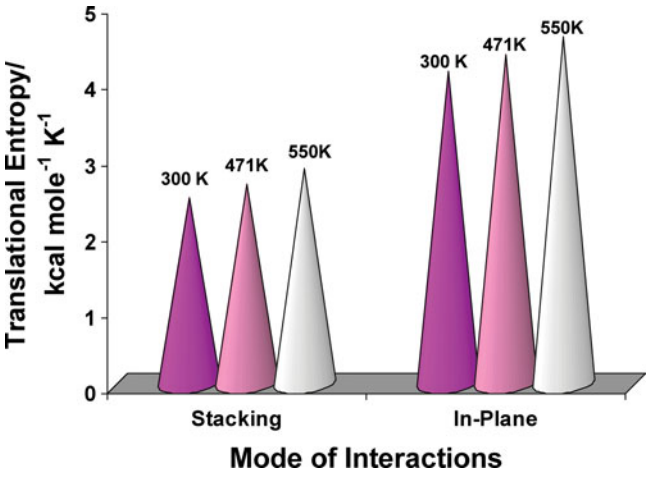

Figure 5. The translational entropy as a function of temperature along the long molecular axis during the stacking and in-plane interactions in CCl_4 for 2OCAC molecule at room temperature (300 K), nematic-isotropic (471 K), and above transition temperature (550 K).

Conclusions

The present computational analysis leads to the following conclusions:

1. The electrostatic energy during the in-plane interactions is more effective than stacking since the antiparallel orientation of molecular rings provide a more effective dipole-dipole attraction, which aids in the energetic stabilization of the mesophase.
2. The consideration of relative probabilities among the minimum energy configurations obtained during the stacking, in-plane and terminal interactions provide 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 property in solvents.
3. Translational entropy values indicate the flexibility of a particular configuration in each phase that has a direct relation with the phase transition property. The comparable values in both modes of molecular interactions are helpful to understand the relative flexibility/stability of each configuration over the other.

Acknowledgments

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