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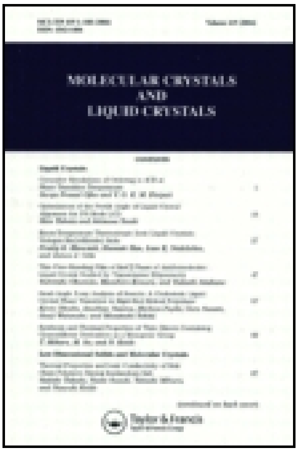

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Role of Molecular Interactions on Phase Stability and Phase Behavior of a Model Nematogen—A Thermodynamic Approach

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In this paper, we address the calculation of configurational interaction energy, entropy, and free energy of a liquid crystal molecule higher in the homologous series of p-n-alkyl benzoic acids (nBAC) with a heptyl group (7BAC). The atomic net charge and dipole moment at each atomic center has 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 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 have been used as input to calculate the thermodynamic parameters such as entropy and Helmholtz free energy of each configuration at room temperature, nematic-isotropic transition, and above transition temperature. An attempt has been made for theoretical interpretation of the role of molecular interactions on phase stability/behavior based on thermodynamic framework introduced in this paper.

Keywords CNDO/2 method; configurational entropy; Helmholtz free energy; phase stability

Introduction

Liquid Crystals (LCs) are molecular materials that are self-assembled and form ordered soft states. The order in these systems gives rise to important application properties, as anisotropic optical, electrical, and magnetic properties [1]. The anisometric rigid units and extension of end chain length in LCs is to adopt a long-range orientational order by maximizing the interaction energy, and minimizing the excluded volume, which is a phase organization principle of matter. This problem is particularly severe in the computational methods that can contribute to our understanding of LCs by relating detailed molecular interactions, and phase stability [2–4].

Intermolecular forces constitute a basis for deriving microscopic models, and the theory of the nematic liquid crystal (NLC). The attractive forces are made responsible solely for the high density of NLC and their anisotropy is regarded to be a factor of secondary significance [5]. Such a state-of-art justifies undertaking theoretical calculations of the energy of interaction between two nematogenic molecules. These studies can provide

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*Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada 520008, Andhra Pradesh, India. E-mail: durga_ojha@hotmail.com valuable information about the relative role of the different types of interactions, and estimate the order of magnitude and anisotropy of contributions to the energy due to these interactions. The interaction potential curves obtained in this way would permit an improved and more quantitative approach to the construction of the nematic phase models [6,7]. However, the energy values do not reflect the role of molecular interactions on phase stability of the different mesophases.

At molecular level, the phase stability is basically determined by the interplay between molecular structure, intermolecular interactions, and molecular motions. The stability of a given phase is principally governed by the Helmholtz free energy (A). Molecular motions have a direct effect on the entropy of a substance, and thereby the free energy is modulated. The demands with respect to the chemical properties and phase behavior being largely satisfied with numerous studies [8,9], attention has been shifted to methods of influencing the physical properties. However, there is a two-fold purpose in this regard; the properties of the molecules themselves, and the "interactions through which a molecular property" influences the phase stability/behavior.

The mesomorphic behavior of LC compounds has attracted the attention of several workers [10,11] based on the Rayleigh–Schrodinger perturbation method. 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 relative energies corresponding to each configuration. Further, in terms of multipole interactions, significant differences among the energies of various configurations are noticed, which must have marked affect on thermodynamic properties of the molecules. Hence, the relative energies have been used as an input to calculate the thermodynamic parameters.

The present articles deals with the thermodynamic parameters such as Helmholtz free energy, and configurational entropy for 7BAC molecule at room temperature (300 K), nematic-isotropic transition temperature (393 K), and above transition temperature (450 K) based on the relative energies between a molecular pair of 7BAC computed at an intermediate distance of 6 Å for stacking, 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. The choice of distance has been made to eliminate the possibility of Van der Waals contacts completely and to keep the molecules within the short- and medium-range interactions. The thermodynamic data of 7BAC molecule shows nematic to isotropic transition temperature at 393 K [12].

Computational Method

In view of the practical difficulties and the increasing enforcement to predict the properties of unsynthesized molecular materials, it is evidently of considerable importance to develop computational methods for the calculation of physical properties. It is well known that subtle alternations in molecular structure can have profound effects on the stability and properties of mesophases. The molecular geometry of 7BAC has been constructed on the basis of published crystallographic data [12] with the standard values of bond lengths and bond angles. 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 [13] 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 [14] 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 [15], 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

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

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. 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 [16] 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:

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

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

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

Third Step Computation

The total interaction energy values obtained through these computations have been used as input to calculate the following thermodynamic parameters [17] to explain order–disorder phenomenon at molecular level:

$$A = -kT \ \ln \sum\nolimits_i \exp(-\beta\varepsilon_i)$$
$$S = k \ \ln \sum\nolimits_i \exp(-\beta\varepsilon_i) + (U/T),$$
$$U = \sum\nolimits_i \varepsilon_i \ \exp\,(-\beta\varepsilon_i)/\sum\nolimits_i \exp(-\beta\varepsilon_i),$$

where A stands for Helmholtz free energy, and S for entropy. $\beta = 1/\mathrm{kT}$, k is the Boltzmann constant, T is the absolute temperature. U is the internal energy of the system and ε_i represents the energy of the configuration i to the minimum energy value.

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. The terms like stacking, in-plane, and terminal interactions will be used to maintain the continuity with the previous work [15].

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 contacting 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

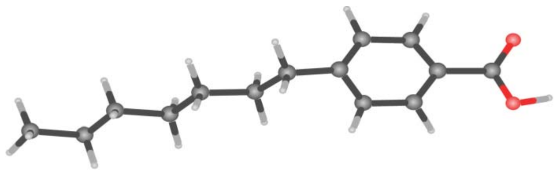
To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the x-axis by 22 Å with respect to the fixed one.

Results and Discussion

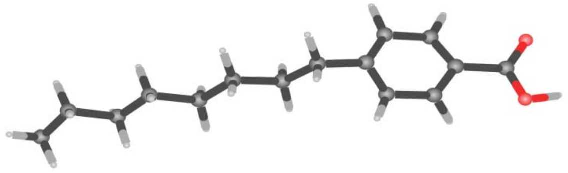
The molecular geometries of 7BAC, 8BAC, and 9BAC are shown in Fig. 1. A comparative picture of molecular parameters, such as total energy, binding energy, and total dipole moment of 7BAC with 8BAC and 9BAC is given in Fig. 2. Evidently, the increase of alkyl chain length causes a minimization in the total energy, binding energy, and increases the dipole moment of the molecules. The results of interaction energy calculations during the different modes of interactions are discussed below.

Role of Stacking Interactions

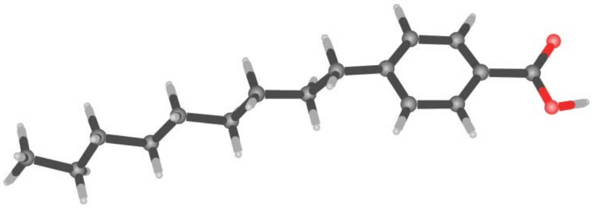
The variation of interaction energy components with respect to rotation about z-axis corresponding to the configuration x (0°) y (0°) has been carried out. It has been observed



(a) 7BAC



(b) 8BAC



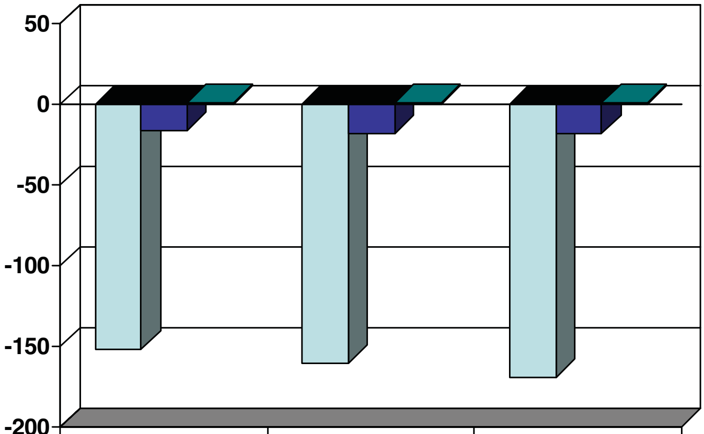
(C) 9BAC

Figure 1. Molecular geometry of 7BAC, 8BAC, and 9BAC.

that the dispersion energy is mainly responsible for the attraction between a pair of 7BAC molecules, although the exact minimum is estimated always from Kitaigorodsky energy curve, which is generally similar to the total energy curve.

Figure 3 shows the variation of interaction energy components along x-axis corresponding to configuration y (0°) z (180°) in the range of ±30 Å. It may be observed that all components increase in magnitude with increased overlapping although the extent of increase is relatively lesser for electrostatic and polarization terms. The variation of energy is almost constant in the region of -8 ± 4 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 the compound maintaining its alignment in mesophase.

The variation of interaction energy components with respect to rotation about the z-axis corresponding to configuration x (0°) y (0°) is shown in Fig. 4. An observation of figure reveals that the dominant component of total energy is the dispersion energy. The contribution of polarization energy is negligible and is almost constant through out the entire range, while the dispersion energy is mainly dependent on the extent of overlap during stacking. The magnitude of electrostatic term is much less as compared with the dispersion term but the symmetric fluctuation in the electrostatic term is reflected in the



	7BAC	8BAC	9BAC
▢ Total Energy(a.u)	-151.44	-160.12	-168.77
■ Binding Energy(a.u)	-16.19	-18.63	-18.69
■ Total Dipole Moment(Debye)	1.1	1.13	1.17

Figure 2. A comparative picture of molecular parameters of 7BAC with 8BAC and 9BAC.

nature of variation in the total energy. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to 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.

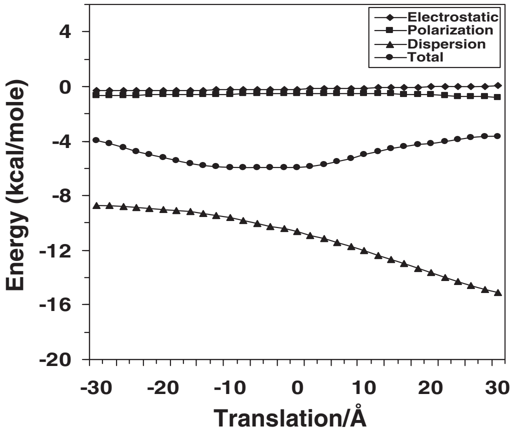


Figure 3. Variation of stacking interaction energy components with respect to translation along x-axis corresponding to the configuration y (0°) z (180°).

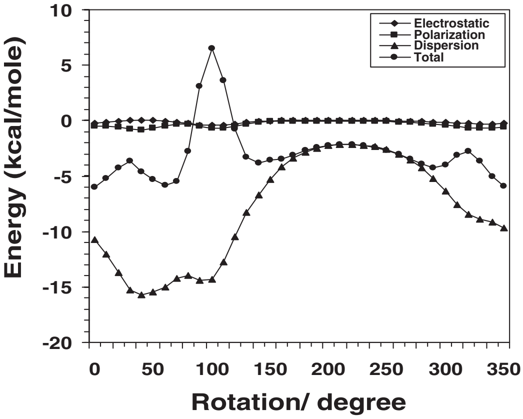


Figure 4. Variation of stacking interaction energy components with respect to rotation about x-axis corresponding to x (0°) y (0°).

Role of In-Plane Interactions

The similar calculations have been performed for in-plane interactions. Again, rotations about the y- and x-axis have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes.

The variation of interaction energy components with respect to rotation about the x-axis corresponding to configuration y (0°) has been carried out and it is observed that the main attractive part of the energy comes through dispersion term. Further, the observed in-plane interactions are more pronounced than the stacking interactions. The nematic character of liquid crystals is generally manifested by its translational freedom along the long molecular axis. Therefore, translations have been allowed along x-axis corresponding to configuration y (0°) as shown in Fig. 5. The total interaction energy is nearly constant in the range of

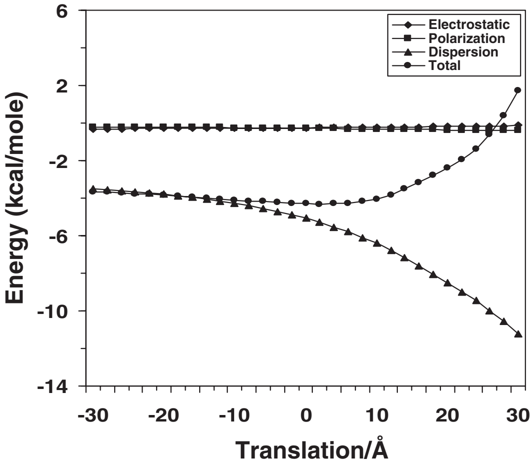


Figure 5. Variation of in-plane interaction energy components with respect to translation along x-axis corresponding to configuration y (0°).

−4 ± 4 Å, without any significant change in the energy and, hence, is capable of retaining the molecular order up to 30 Å.

Role of Terminal Interactions

It has been observed that the terminal interactions are much weaker than the stacking or in-plane interactions (after due consideration of short contact). The variation of interaction energy components with respect to rotation about x-axis corresponding to configuration y (0°) is shown in Fig. 6. It is clear that rotations about the x-axis show absolutely no preference for any angle, i.e., the molecules are free to rotate about their long molecular axis. However, for rotations about y-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

Role of Planarity of the Molecule

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

Role of Molecular Interactions on Phase Stability and Phase Behavior

In order to understand the ordering and phase stability of 7BAC molecule, the configurational entropy and Helmholtz free energy have been estimated with respect to translation along the long molecular axis during stacking, and in-plane interactions. These results may provide valuable information to analyze the role of molecular interactions on phase organization/stability of the compound.

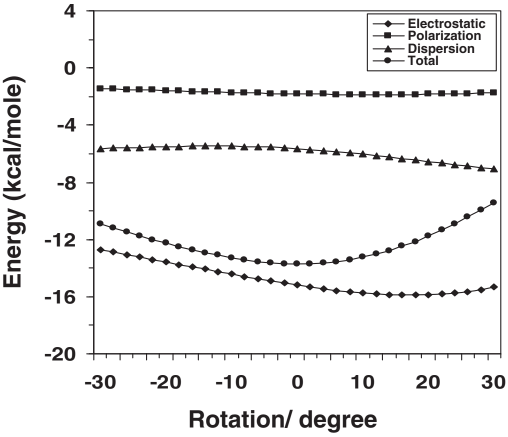


Figure 6. Variation of terminal interaction energy components with respect to rotation about x-axis corresponding to configuration y (0°).

Table 1. The minimum energy corresponding to stacking, in-plane, and terminal interactions between a pair of 7BAC molecules after refinement. Energy is expressed in kcal/mole

Energy terms	Stacking energy	In-plane energy	Terminal energy
E_{QQ}[a]	0.002	−0.372	−0.981
E_{QMI}[b]	−0.061	−0.022	−4.029
E_{MIMI}[c]	0.069	0.108	−1.985
E_{el}[d]	0.009	−0.286	−6.996
E_{pol}[e]	−0.426	−0.649	−0.816
E_{disp}[f]	−11.813	−6.118	−5.778
E_{rep}[g]	5.381	2.037	9.732
E_{total}[h]	−6.848	−5.017	−3.859

[a]monopole-monopole; [b]monopole-dipole; [c]dipole-dipole; [d]electrostatic; [e]polarization; [f]dispersion; [g]repulsion; and [h]total.

Phase Stability

A comparative picture of Helmholtz free energy with respect to translation along the long molecular axis during stacking and in-plane interactions for 7BAC molecule at room temperature (300 K), nematic-isotropic transition temperature (393 K), and above phase transition temperature (450 K) is given in Table 2. Evidently, the free energy during the stacking interactions at room temperature is -1.51 kcal mole^{-1}, which decreased to -2.07 kcal mole^{-1} at nematic-isotropic transition temperature, and confirms the stability (order) of molecule in nematic phase. Further, it is much high up during in-plane interactions. The free energy of molecular pair was found to have a minimum free energy value when the molecule has been shifted along y-axis (in-plane) rather that z-axis (stacking). Hence, the observed difference between free energy values of 7BAC molecule from phase transition temperature to room temperature during the in-plane interactions suggests the thermodynamic stability of nematic phase (Table 2).

Phase Behavior

The terminal flexible chains reduce the stability of solid crystal phase, and allow the appearance of liquid crystal phases. From the viewpoint of entropy, alkyl chains play a dominant role as they are very labile, and can easily make multi conformational changes.

Table 2. A comparative picture of Helmholtz free energy (*A*) along the long molecular axis during the stacking and in-plane interactions for 7BAC molecule at room temperature (300 K), nematic-isotropic transition temperature (393 K), and above phase transition temperature (450 K)

Mode of interactions	Configuration	Helmholtz free energy/kcal mole^{-1} 300 K	393 K	450 K
Stacking	y (0°) z (0°)	−1.51	−2.07	−2.43
In-Plane	y (0°)	−1.61	−2.19	−2.55

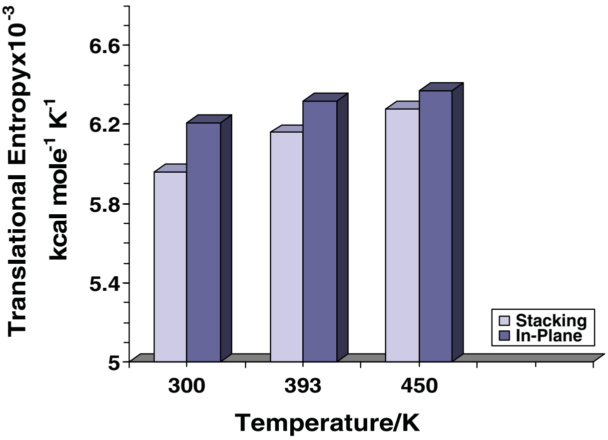


Figure 7. Variation of translational entropy of 7BAC during stacking and in-plane interactions at room temperature (300 K), nematic-isotropic transition temperature (393 K), and above transition temperature (450 K).

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 translational entropy as a function of temperature during the stacking and in-plane interactions along the x-axis for 7BAC molecule is shown in Fig. 7. It is noticed that translational entropy during stacking interactions is 6.16×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (393 K). However, at room temperature (300 K), the value 5.96×10^{-3} kcal mole^{-1} K^{-1} shows a strong binding at low temperature with less disorder, but with increase in 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, the value is 6.21×10^{-3} kcal mole^{-1} K^{-1}, which increased to 6.32×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (393 K).

It may be noted from the above discussion that though the freedom is considerable for smaller translation, longer translations are not generally permitted. Most of the liquid crystalline molecules are found to have a number of conformations that are thermally accessible. In the process of a phase transition from a low to a high temperature, the molecular motion 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 for molecule. 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 [18] and, therefore, more free space for the molecules to jostle around. Moreover, the parallel arrangement represents a state of low orientational entropy. However, the comparable values in both cases (i.e., stacking and in-plane interactions) show that 7BAC molecule does not show extraordinary preference in forming the stacked layers and, hence, justify the nematic character.

Conclusions

The salient features of the present work are as follows:

1. The increase of alkyl chain length causes a minimization in the total energy and binding energy, and increases the total dipole moment of the molecules. Further, the 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 flexible end chain of molecule provides enough configurational entropy to prevent the total crystallization of the core and expand the stability of mesophase range.
2. The observed translational entropy values during the stacking and in-plane interactions suggest that the molecule has a preferred orientation along the long molecular axis that justifies the nematic character.
3. The present computations are helpful in analyzing the role of molecular interactions on phase stability/behavior of nematogen at molecular level.

Acknowledgments

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