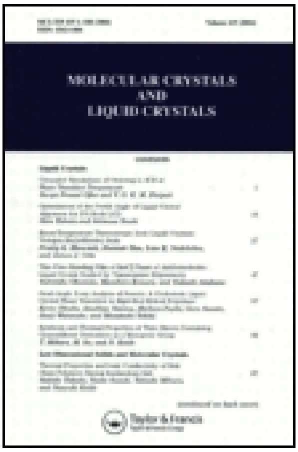

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 07 Oct 2011

To cite this article: P. L. Praveen & D. P. Ojha (2011): Thermodynamic Stability of the Nematic Phase and Configurational Entropy of Mesogens: A Molecular Simulation Approach, Molecular Crystals and Liquid Crystals, 548:1, 61-72

To link to this article: http://dx.doi.org/10.1080/15421406.2011.590360

Mol. Cryst. Liq. Cryst., Vol. 548: pp. 61–72, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.590360

Thermodynamic Stability of the Nematic Phase and Configurational Entropy of Mesogens: A Molecular Simulation Approach

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The thermodynamic stability of the nematic phase and the configurational entropy of mesogens–p-n-pentylbenzoic acid (5BAC) and p-n-hexylbenzoic acid (6BAC)–have been studied. 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, while a "6-exp" potential function has been assumed for short-range interactions. The interaction energy values obtained with respect to translational and orientational motions during the different modes of molecular interactions have been taken as input to estimate the configurational entropy and Helmholtz free energy at room temperature, nematic–isotropic transition temperature, and above transition temperature. The observed difference in free energy of the molecules between the mesophase and the crystal phase during in-plane interactions suggests the thermodynamic stability of the nematic phase. Further, the comparable values of translational entropy during stacking and in-plane interactions are helpful to understand the relative flexibility/stability of one configuration over the other.

Keywords Molecular interactions; perturbation theory; phase stability; translational entropy

Introduction

In tracing back the history, the liquid crystal (LC) phase has been a constant challenge to theoretical scientists to explicate and for exact prediction of the phase behavior/stability. LC phases are characterized by a long-range orientational order and a partial or complete positional disorder responsible for the flow properties. The vast interest in these molecular materials can be partly ascribed to the scores of technical applications, as well as to obtain a fundamental understanding of physicochemical aspects of the model systems that exhibit/cause liquid crystallinity [1,2]. The phase transitions occur in LC materials based on their intrinsic properties, which are characterized by the arrangement of the molecules, the conformation of the molecules, and intermolecular interactions [3–5].

Molecules forming LC phases typically comprise a rigid core with flexible substituents attached in such a way as to produce an extended rod-like shape. The end chains reduce the

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*Address correspondence to D. P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada 520 008, Andhra Pradesh, India. E-mail: durga_ojha@hotmail.com melting point of the compound. The rigid cores provide the anisotropic interactions necessary for the occurrence of the LC phase and, to a large extent, dictate the properties of the bulk material. An understanding of the behavior of flexible end chains in condensed phases is particularly important in the field of LCs. These appear to be an important component of the orienting mechanism for the mesogens. Knowledge about the conformational and orientational behavior contributes valuable information toward understanding the ordering of LCs. The simulation of LC phase behavior/stability represents a foremost challenge despite the extensive increase in computation power [6]. However, it is essential to study the simple model [7] in depth in order to understand the forces responsible for mesophase formation. The possibility also exists to extend these simple models by building in realistic features, such as molecular flexibility, complicated structural anisotropy, and electrostatic forces.

The importance of intermolecular interactions in physics, chemistry, and biology does not need to be stressed, which constitutes one of the major forces determining numerous specific properties and self-organization of condensed matter. The role of molecular interactions in mesogens has engrossed the attention of several researchers [8–12] based on the Rayleigh–Schrodinger perturbation method. These studies have been 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. 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 relative energies corresponding to each configuration. Further, the significant differences among the energies of various configurations are noted in terms of multipole interactions, which must have a marked effect on thermodynamic properties of the system [13]. In view of this, we have assessed thermodynamic properties such as Helmholtz free energy and entropy of p-n-pentylbenzoic acid (5BAC) and p-n-hexylbenzoic acid (6BAC) molecules based on interaction energy results to understand the microscopic properties and phase behavior/stability of the two compounds.

The present article deals with the computation of pair interaction energies, configurational entropy, and Helmholtz free energy between a molecular pair of the chosen compounds at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. The choice of distance 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. An examination of thermodynamic data has revealed that 5BAC exhibits nematic–isotropic transition temperature at 399.5 K [14] and 6BAC exhibits it at 387.5 K [14].

Computational Formalism

The molecular geometry of 5BAC and 6BAC molecules has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles [14]. A number of the following methodologies have been employed in this work.

Computation of Atomic Net Charge and Dipole Moments

In order to calculate the interaction energy between a molecular pair, it is necessary to compute atomic net charges and dipole moments through an all-valence electron method.

Hence, in the present work, the complete neglect differential overlap (CNDO/2) method [15] has been used to compute the net atomic charges and dipole moments at each atomic center of the molecule.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme, based on the simplified formula given by Claverie [17] for evaluating the interaction energy of a molecular pair, has been used to calculate the energy at fixed configurations. According to the second order of the perturbation theory is modified for intermediate-range interactions [16,18], the total pair interaction energy of the molecules (U_{pair}) is represented as a sum of several energy 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. In turn, the electrostatic energy term is expressed as:

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

where U_{QQ}, U_{QMI}, and U_{MIMI} are monopole–monopole, monopole–dipole, and dipole–dipole energy terms, respectively. In fact, the inclusion of higher-order multipoles does not affect the electrostatic interaction energy significantly and the calculation involving only the above energy terms gives satisfactory results [8–12,18]. The evaluation of the electrostatic energy term was, therefore, restricted by the dipole–dipole energy term.

In the present work, the dispersion and short-range repulsion energy terms are considered together because several semi-empirical approaches, viz. the Lennard–Jones or Buckingham approach, actually proceed in this way. Kitaygorodsky [19] introduced a Buckingham formula whose parameters have been later modified by Kitaigorodsky and Mirskay for hydrocarbon molecules and several other molecules, which finally gave the expression [20]:

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

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

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 radius of λ and ν atoms, respectively. A, B, and γ parameters are independent of particular species. But $R^{0}{}_{\lambda\nu}$ and K_{λ} K_{ν} factor, which determine the energy minimum, have different values according to the atomic species involved. The necessary formulae can be found elsewhere [21].

The origin has been chosen on an atom close to the center of mass of the molecule. The x-axis has been directed along a bond parallel to the long molecular axis, while the y-axis lies in the plane of the molecule, and the z-axis is normal to the molecular plane (x-y).

Computation of Thermodynamic Parameters

The total interaction energy values obtained through these computations have been used as input to calculate the following thermodynamic parameters [13] of a particular configuration

i in order to obtain a better insight into phase stability and configurational entropy of selected mesogens:

$$A = -kT \ln \sum\nolimits_i \exp(-\text{ß}\varepsilon_i)$$

$$S = k \ln \sum\nolimits_i \exp(-\text{ß}\varepsilon_i) + (U/T)$$

$$U = \sum\nolimits_i \varepsilon_i \exp(-\text{ß}\varepsilon_i) / \sum\nolimits_i \exp(-\text{ß}\varepsilon_i),$$

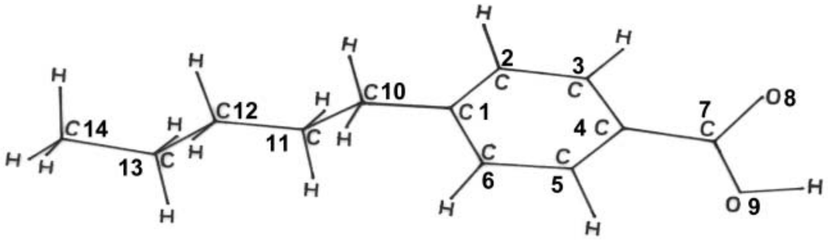
where A stands for Helmholtz free energy, S stands for entropy, $\beta = 1/kT$ (k is the Boltzmann constant, T is the absolute temperature), U is the internal energy of the system, and ε_i represents the energy of the each configuration i (i.e., i = 1, 2, 3, . . .) to the minimum energy value.

Results and Discussion

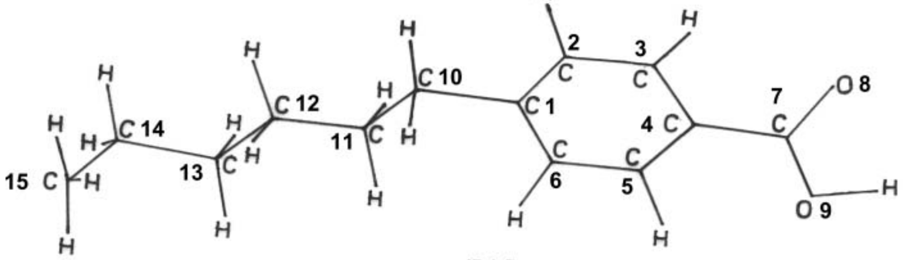
The molecular geometry of 5BAC and 6BAC is shown in Fig. 1. The atom-based partial charges on heavy atoms of the molecules have been reported in Fig. 2 to understand the molecular charge distribution that enables the study of the different modes of intermolecular interactions.

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



5BAC



6BAC

Figure 1. Molecular geometry of 5BAC and 6BAC.

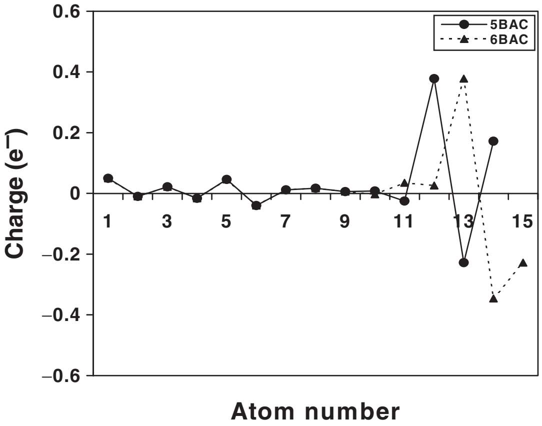


Figure 2. Partial charges on heavy atoms of 5BAC and 6BAC molecules.

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 intermolecular interactions for molecular simulation studies, atom-positioned partial charges are helpful, which are not quantum mechanical observables.

It has been observed from Fig. 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 in the charges results in a small variation in electrostatic potential around the molecule. In spite of these uncertainties, the full set of partial charges is very useful, as it can provide a detailed insight into the molecular arrangement in the mesophase.

Molecular Interactions

The results of interaction energy calculations during the different modes of interactions are discussed next.

Stacking Interactions. One of the interacting molecules has been fixed in the x-y plane such that the x-axis lies along a bond parallel to the long molecular axis, while the other is kept at a separation of 6 Å along the z-axis with respect to the fixed one. The variation in interaction energy components with respect to rotation about the x-axis corresponding to the configuration y (0°) z (0°) is shown in Figs 3 and 4 for 5BAC and 6BAC molecules, respectively. Evidently, the dispersion energy is mainly responsible for the attraction between molecular pairs of nBAC ($n = 5, 6$), since the face-to-face orientation of the molecular rings produces larger attractive dispersion energy. The exact minimum is always estimated from the Kitaigorodsky energy curve, which has gross similarity with the total energy curve.

The variation in interaction energy components with respect to translation along the x-axis corresponding to the configuration y (0°) z (180°) is shown in Figs 5 and 6 for 5BAC and 6BAC molecules, respectively. It may be observed that all components increase in magnitude with increased overlapping, although the extent of increase is relatively lesser

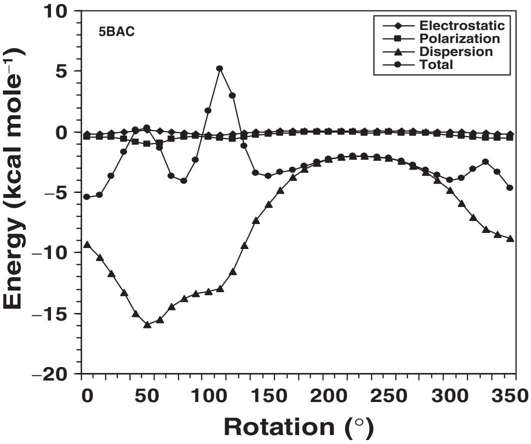


Figure 3. Variation in stacking interaction energy components with respect to rotation about the *x*-axis corresponding to the configuration *y* (0°) *z* (0°) for 5BAC molecules.

for electrostatic and polarization energy terms. Evidently, the stacked pair of *n*BAC ($n =$ 5, 6) molecules can slide one above the other in the range of −26 ± 4 Å, without any significant change in the energy, and is capable of retaining the molecular order up to 30 Å against increased thermal agitation. This may be correlated with the fluidity of the compound maintaining its ordering in the mesophase.

The variation in interaction energy components with respect to rotation about the *z*-axis corresponding to configuration *x* (0°) *y* (0°) has been carried out for 5BAC and 6BAC molecules. It has been observed 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 dispersion energy is mainly dependent on the extent of overlap during stacking. The magnitude of electrostatic energy term is much less as compared with the dispersion energy term, but the symmetric fluctuation in the electrostatic energy term is reflected in the nature of variation in the total energy. The energy has been

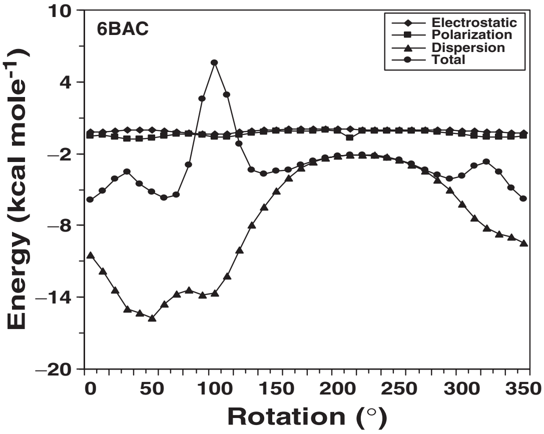


Figure 4. Variation in stacking interaction energy components with respect to rotation about the *x*-axis corresponding to the configuration *y* (0°) *z* (0°) for 6BAC molecules.

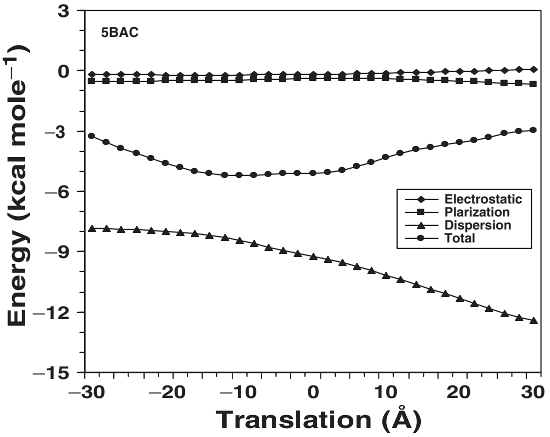


Figure 5. Variation in stacking interaction energy components with respect to translation along the *x*-axis corresponding to configuration *y* (0°) *z* (180°) for 5BAC molecules.

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 and the study of variation in interaction energy under preselected condition will have completely different paths, and therefore, one has to be careful in choosing the specific route.

In-Plane Interactions. An interacting molecule has been kept at a distance of 8 Å along the *y*-axis with respect to the fixed one in order to avoid the possibility of van der Waals contacts completely. Similar calculations have been performed for in-plane interactions. Again, rotations about the *y*- and *x*-axes have been carried out and the corresponding energy has been minimized with respect to translation and rotation about all axes.

The variation in interaction energy components with respect to rotation about the *x*-axis corresponding to configuration *y* (0°) has been carried out for both the molecules, and it is

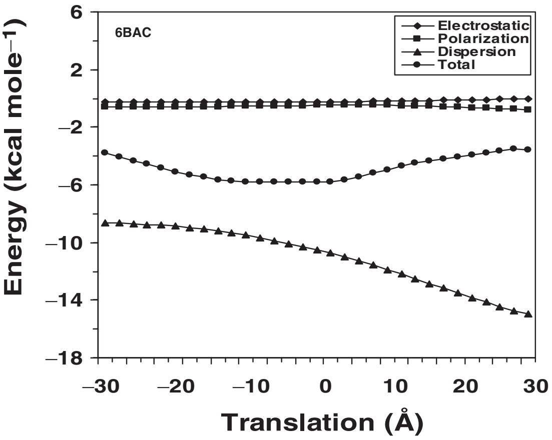


Figure 6. Variation in stacking interaction energy components with respect to translation along the *x*-axis corresponding to configuration *y* (0°) *z* (180°) for 6BAC molecules.

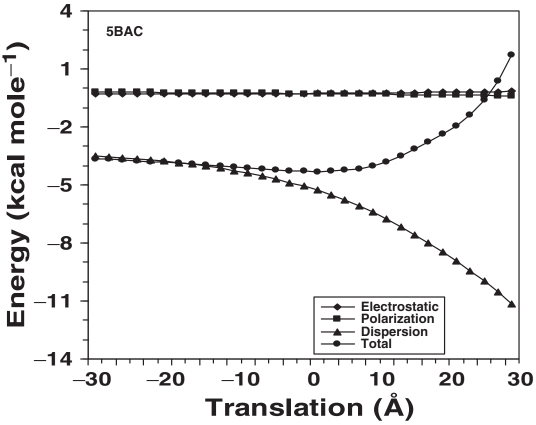


Figure 7. Variation in in-plane interaction energy components with respect to translation along the *x*-axis corresponding to configuration *y* (0°) for 5BAC molecules.

observed that the main attractive part of the energy comes through dispersion energy term. Electrostatic energy during in-plane interactions is more effective than during stacking, since the antiparallel 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 antiparallel molecular ring orientation. These factors ultimately cause the large variation in total interaction energy. Hence, the observed in-plane interactions are more pronounced than the stacking interactions. The nematic character of LCs is generally manifested by its translational freedom along the long molecular axis. Therefore, translations have been allowed along the *x*-axis corresponding to configuration *y* (0°). The variation in interaction energy components with respect to translation along the *x*-axis corresponding to configuration *y* (0°) is shown in Figs 7 and 8 for 5BAC and 6BAC molecules, respectively. The total interaction energy is nearly constant in the range of 2.2 ± 4 Å, without any significant change in the energy and, hence, is capable of retaining the molecular order up to 3 Å against increased thermal agitation.

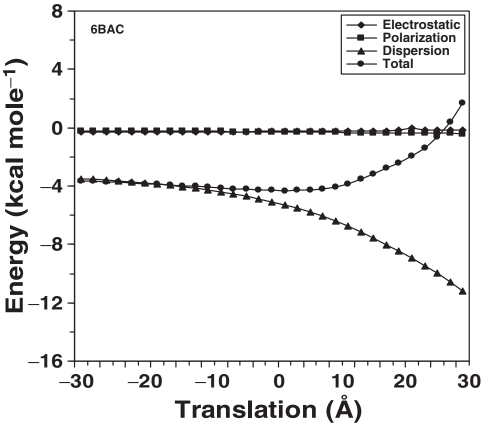


Figure 8. Variation in in-plane interaction energy components with respect to translation along the *x*-axis corresponding to configuration *y* (0°) for 6BAC molecules.

Terminal Interactions. To investigate terminal interactions, the interacting molecule has been shifted by 22 Å with respect to the fixed axis. 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 in interaction energy components with respect to rotation about the x-axis corresponding to configuration y (0°) has been carried out for 5BAC and 6BAC molecules. It has been observed 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 the y-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

Estimation of Thermodynamic Parameters

The nematic character of mesogens is generally manifested by their translational freedom along the long molecular axis. Hence, in order to examine the results more closely, the configurational entropy and Helmholtz free energy of 5BAC and 6BAC molcules have been estimated with respect to translational motion along the long molecular axis (during stacking and in-plane interactions) to understand the microscopic properties and phase behavior/stability of the compounds.

Thermodynamic Stability of the Nematic Phase. The present computations are helpful to correlate the nematic behavior of the compounds as well as to understand the role of molecular motions, interactions, and disordering of alkyl chains in a particular phase. Estimation of Helmholtz free energy of the system provides better understanding of ordering and phase stability at molecular level. A comparative picture of Helmholtz free energy with respect to translation along the x-axis during stacking and in-plane interactions of 5BAC and 6BAC molecules at room temperature, nematic–isotropic transition temperature, and above transition temperature is shown in Table 1. Evidently, the Helmholtz free energy of 5BAC molecules during stacking interactions is -1.50 kcal mole^{-1} at room temperature (300 K), which decreased to -2.10 kcal mole^{-1} at nematic–isotropic transition temperature (399.5 K). The same trend has been observed in 6BAC molecules. This increment in the negative free energy confirms the stability (order) of molecules in the nematic phase. A similar trend of more prominent nature may be observed for both molecules during in-plane interactions (Table 1).

Table 1. A comparative picture of Helmholtz free energy (A) corresponding to various configurations during stacking and in-plane interactions at room temperature (300 K), nematic–isotropic transition temperature (*), and above transition temperature (500 K) of 5BAC and 6BAC molecules with respect to translation along the x-axis

		Helmholtz free energy (kcal mole^{-1})		
Molecule	Configuration	300 K	399.5 K*	500 K
5BAC	y (0°) z (180°)[a]	−1.50	−2.10	−2.74
	y (0°)[b]	−1.60	−2.23	−2.87
6BAC	y (0°) z (180°)[a]	−1.50	−2.03	−2.73
	y (0°)[b]	−1.61	−2.16	−2.87

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

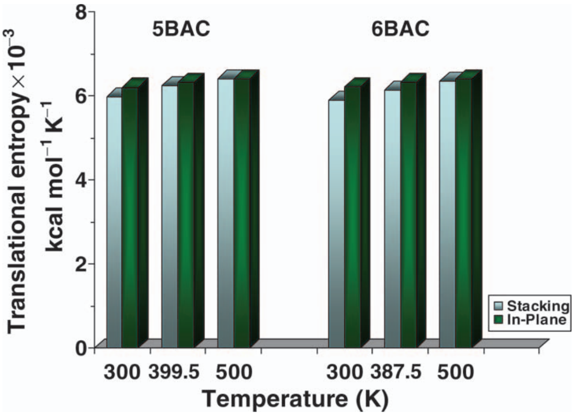


Figure 9. Variation in translational entropy during stacking and in-plane interactions at room temperature (300 K), nematic–isotropic transition temperature, and above transition temperature (500 K) for 5BAC and 6BAC molecules.

Estimation of Configurational Entropy. The terminal flexible chains reduce the stability of the solid crystal phase and allow the appearance of LC phases. From the viewpoint of entropy, alkyl chains play a dominant role as they are very labile and can easily make multi-conformational changes. Hence, alkyl chains can be regarded as a source of entropy to realize a given condensed state or to tune the delicate balance between two energetically close phases. Configurational entropy has been estimated with respect to translational motion during stacking and in-plane interactions for 5BAC and 6BAC molecules. Hence, configurational entropy can be regarded as translational entropy. The variation in translational entropy for 5BAC and 6BAC molecules at room temperature (300 K), nematic–isotropic transition temperature, and above transition temperature (500 K) during stacking and in-plane interactions along the long molecular axis is shown in Fig. 9. The observed value during stacking interactions is 6.24×10^{-3} kcal mole^{-1} K^{-1} for 5BAC molecules at nematic–isotropic transition temperature (399.5 K). However, at room temperature (300 K), the value is 5.98×10^{-3} kcal mole^{-1} K^{-1}, indicating a strong binding with less disorder at low temperature. But with increase in temperature, the molecules obtain sufficient freedom to slide along the long molecular axis, which causes increment in disorder. Such translational freedom is much more pronounced in planar interactions. Evidently, even at room temperature, this value is 6.20×10^{-3} kcal mole^{-1} K^{-1}, which increased to 6.33×10^{-3} kcal mole^{-1} K^{-1} at nematic–isotropic transition temperature. A similar trend may be observed for 6BAC molecules, as shown in Fig. 9.

It may be noted that though the freedom is considerable for smaller translations, longer translations are not generally permitted. Thus, in the mesomorphic range, only small movements of the molecule are possible. 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 phase, the molecular motions of the alkyl chains would be excited and thereby the number of thermally accessible conformations would be increased. Translational entropy in the isotropic liquid states is increased from its room temperature for each molecule (Fig. 9). 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 cannot move due to the impenetrability of the other molecule) 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 the cases (i.e., stacking and in-plane interactions) show that nBAC ($n = 5, 6$) molecules do not show extraordinary preference in forming stacked layers, hence justifying the nematic character.

Conclusions

In this study, the thermodynamic stability of the nematic phase and the configurational entropy of mesogens–p-n-pentylbenzoic acid (5BAC) and p-n-hexylbenzoic acid (6BAC)–were studied. A few conclusions that can be drawn from the study are:

- Flexible chains of the molecules provide enough configurational entropy to prevent total crystallization of the core and increase the stability of the mesophase range.
- The observed translational entropy during stacking and in-plane interactions suggests that the molecules have a preferred orientation along the long molecular axis (x-axis), which justifies the nematic character of the system.
- Translational entropy shows 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.

Acknowledgment

The financial support rendered by the Department of Science & Technology (DST) and the Council of Science & Technology (CSIR), New Delhi, India, is gratefully acknowledged.

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