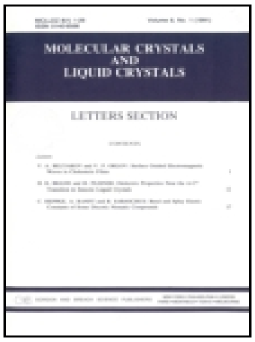

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Phase stability and ordering of nematogen at molecular level: A computer-aided modeling

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ABSTRACT

The present article deals with the phase stability and ordering of nematogen, viz., 6-octyloxy-2-naphthylyl-4-octoxybenzoate (ONOB) at molecular level. A comparative picture has been given between molecular charge distribution, and phase stability based on AM1, PM3, CNDO, and MNDO methods. The modified Rayleigh–Schrodinger perturbation method 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 the short-range interactions. The total interaction energy values obtained through these computations have been used to calculate the probability of each configuration at room temperature, nematic-isotropic transition temperature, and above transition temperature using the Maxwell–Boltzmann formula. Further, the entropy of each configuration has been computed during the different modes of interactions. An effort has been made to develop a computational model at molecular level based on configurational entropy, and translational rigidity parameters introduced in this article.

KEYWORDS

Configurational entropy; nematogen; quantum chemistry

Introduction

The nematic liquid crystal phase is technologically the most important mesophase. The underpinning prerequisite for liquid crystallinity is that the mesophase owes its stability to the anisotropic shape of the molecule [1]. Most of the known thermotropic LCs are calamitic structurally. The conventional structure of liquid crystals is rigid core attached to flexible chains. The core provides the source of anisotropy for the formation of liquid crystal phases, while the disorder associated with the terminal flexible chains reduces the stability of the solid crystal phase, and allows the appearance of liquid crystal mesophase. These calamitic molecules form both nematic and smectic mesophase depending upon the type of substituent and their combinations [2, 3].

The problem of predicting physical properties of liquid-crystalline compounds based upon molecular shape and intermolecular interactions requires the adoption of model potential [4]. The stability of 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. The potential energy is the key quantity, which embodies a link between the

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microscopic properties, phase behavior, and stability. The aspects of molecular structure and phase behavior of LC materials are of paramount importance in operation, and quality of any device format [5]. The various device formats require similar essential features (structure, substituents, etc.) of materials [6, 7].

The mesomorphic behavior of LC compounds has attracted the attention of several workers [8, 9]. 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. Further, in terms of multipole interactions, significant differences among the energies of various configurations are noticed, which must have marked effect on thermodynamic properties of the molecules. Hence, the relative energies have been used as an input to calculate the thermodynamic parameter.

The present articles deals with the phase stability and ordering for ONOB molecule at room temperature (300 K), nematic-isotropic transition temperature (406.1 K), and above transition temperature (500 K) based on the relative energies between a molecular pair of ONOB computed at an intermediate distance of 8 Å for stacking, 10 Å for in-plane interactions. Similarly, a distance of 24 Å has been kept for terminal interactions. The thermodynamic data of ONOB molecule shows nematic to isotropic transition temperature 406.1 K [10].

Computational details

An increasing enforces to predict the properties of unsynthesized molecular materials; it is 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 ordering, and phase behavior of mesophases. The molecular geometry of ONOB has been constructed on the basis of published crystallographic data [10] 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 as given below.

The AM1, MP3, and MNDO charges have been obtained by MOPAC calculations available via VEGA ZZ package [11]. The CNDO method [12] has been employed to compute the net atomic charge for interaction energy calculation.

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:

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

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

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_λ K_ν allows the energy minimum to have different values according to the atomic species involved.

The total interaction energy values obtained through these computations have been used as input to calculate the configurational entropy [4] to explain the ordering and phase behavior of ONOB molecule at molecular level:

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

$$U = \sum_i \varepsilon_i \exp(-\beta \varepsilon_i) / \sum_i \exp(-\beta \varepsilon_i)$$

where 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 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.

(a) Computation of stacked molecular pair interactions

The interacting molecule has been placed at a separation of 8 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.

(b) Computation of in-plane molecular pair interactions

The interacting molecule has been kept at a separation of 10 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.

(c) Computation of terminal molecular pair interactions

To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the x-axis by 24 Å with respect to the fixed one.

Table 1. AM1, MP3, MNDO, and CNDO group charges and nematic-isotropic transition temperature for ONOB molecule.

Group Charges	AM1	MP3	MNDO	CNDO	T/K [10]
Core	– 0.36	– 0.32	– 0.41	– 0.34	406.1 K
Side group	0.18	0.16	0.20	0.17	
End group	0.18	0.16	0.21	0.17	

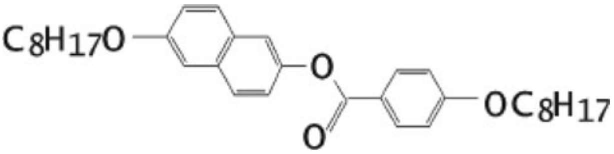
Results and discussion

Group charges and chemical stability

The group charges are needed to explain the phase stability and details of transition temperatures of mesogens. Computed AM1, MP3, MNDO, and CNDO group charges are reported in Table 1. These group charges have been computed to establish the correlation between molecular charge distribution and phase stability of molecule. The results show that the core structure plays a vital role on charge distribution, and phase stability.

Evidently, the large negative charge has been noticed for the core structure of ONOB, which will strongly attracted by the highly positive charged side as well as groups, causing the formation of tight binding between core, side group, and the end group. Due to the tight binding, more thermal energy has to be supplied in obtaining the mesophases of the ONOB molecule. Therefore, the phase stability is expected to be high for ONOB molecule. The nematic-isotropic transition temperature of the molecule reported by the crystallographers (Table 1) is in accordance with the findings.

The charge at each atomic center is assigned by the sum of its nuclear charge (atomic number) and the number of electrons occupying the orbital belonging to that atom. The aromatic rings along with the oxygen atoms have been considered as core. The left and right side of the core have been taken as side and end group. Evidently, the core in the ONOB molecule consists of a negative charge. Hence, it will be strongly attracted by both side and end groups to provide enough chemical stability. The chemical structure of ONOB has been given below.



The molecular structure of ONOB is shown in Fig. 1. The configurational probability based on molecular pair interaction energy results during the different modes of interactions are discussed below.

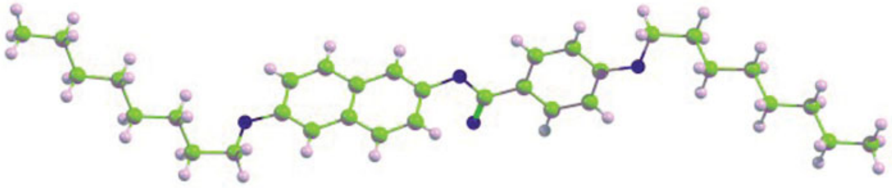


Figure 1. Molecular Geometry of ONOB ($C_{33}H_{44}O_4$) molecule.

Stacked molecular pair interactions

The study of the variation of configurational probability with respect to translation along the *x*-axis corresponding to configuration *y* (0^0) *z* (0^0) is shown in Fig. 2 at room temperature (300 K), nematic-isotropic transition temperature (406.1 K), and above the phase transition temperature (500 K). Evidently, the variation of probability is constant in the region of 22 ± 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 compound maintaining its alignment in the mesophase. Having refined the interacting configuration with respect to translation along *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 minimum energy thus obtained is taken as the starting point and the entire process is repeated for small intervals. The energy has been minimized with respect to translation and rotation about *x*-, *y*-, and *z*-axis. An accuracy of 0.1 Å in translation and 1^0 in rotation of one molecule with respect to other has been achieved. The global search for minimum energy configuration or the study of variation of interaction energy under preselected condition will have completely different path and, therefore, one has to be careful in choosing the route of computations.

In-plane molecular pair interactions

The similar calculations have been performed for in-plane interactions. Again, rotations about the *y*- and *x*-axes have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes. The variation of configurational probability with respect to translation along *x*-axis corresponding to configuration *y* (0^0) is shown in Fig. 3 at room temperature (300 K), nematic-isotropic transition temperature (406.1 K), and above phase transition temperature (500 K). The electrostatic energy during in-plane is more effective that the stacking interactions. Additionally, repulsive quadrapole–quadrapole interactions become less effective, which ultimately affects the configurational probability.

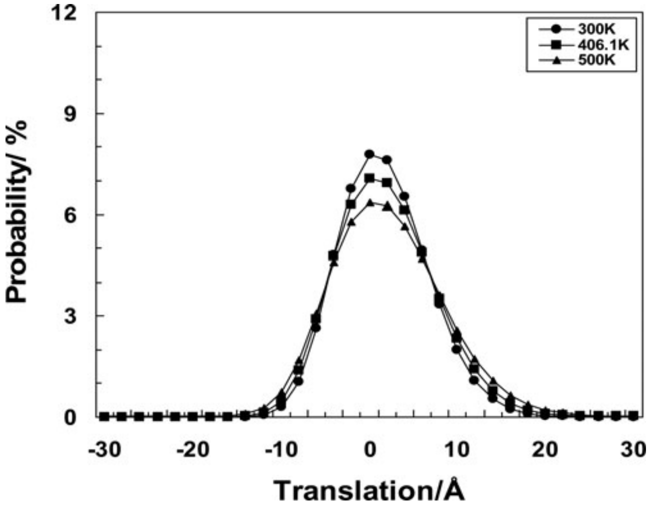


Figure 2. The variation of configurational probability with respect to translation along *x*-axis during stacking interactions corresponding to configuration *y* (0^0) *z* (0^0) at room temperature (300 K), nematic–isotropic transition temperature (406.1 K), and above transition temperature (500 K).

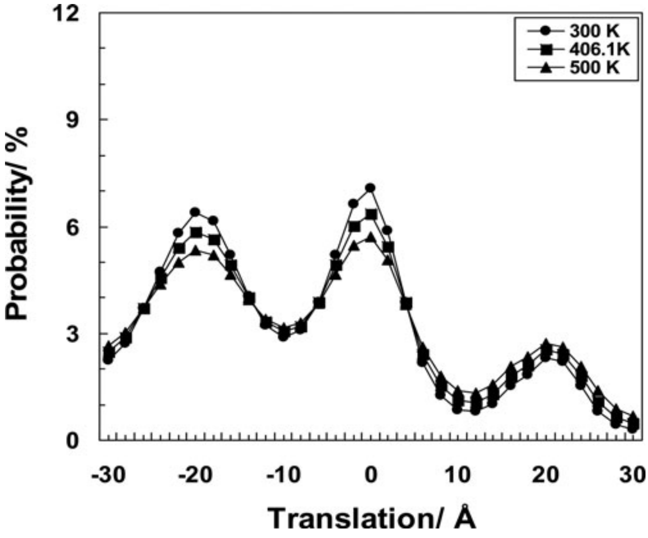


Figure 3. The variation of configurational probability with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y* (0^0) at room temperature (300 K), nematic–isotropic transition temperature (406.1 K), and above transition temperature (500 K).

Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. It is evident from the figure that the maximum probability occurs 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 configurational probability is further investigated with respect to rotation about x-axis.

Terminal molecular pair interactions

The terminal interactions are weakest but become important when the molecule possess a polar group at either or both of the ends or if there is a possibility of hydrogen bonding. The rotations about x-axis corresponding to configuration y (0^0) has been carried out and show no more preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis.

Configurational entropy and translational rigidity

The 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 source of entropy to realize a given condensed state. The configurational entropy has been estimated with respect to translation and orientation along/about the long molecular axis during the different modes of interactions

The translational entropy as a function of temperature during the stacking and in-plane interactions along the x-axis for ONOB molecule is shown in Fig. 4. It is noticed that translational entropy during stacking interactions is 3.84×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (406.1 K). However, at room temperature (300 K), the value 3.49×10^{-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

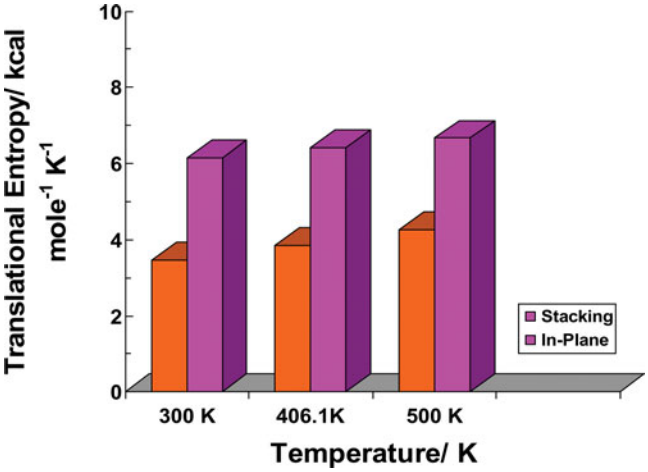


Figure 4. The variation of translational entropy as a function of temperature during stacking, and in-plane interactions at room temperature (300 K), nematic–isotropic transition temperature (406.1 K), and above transition temperature (500 K).

molecular axis, which causes the increment of disorder. A plot of translational rigidity (i.e., defined as the ratio of probability being at maximum probable point having ±2 Å displacement along the long molecular axis) as a function of temperature (Fig. 5) also supports the same. Such translational entropy is much more pronounced in planar interactions. Evidently, even at room temperature the value is 6.41×10^{-3} kcal mole^{-1} K^{-1}, which increased to 6.51×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (406.1 K).

In the process of phase transition from a low to 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

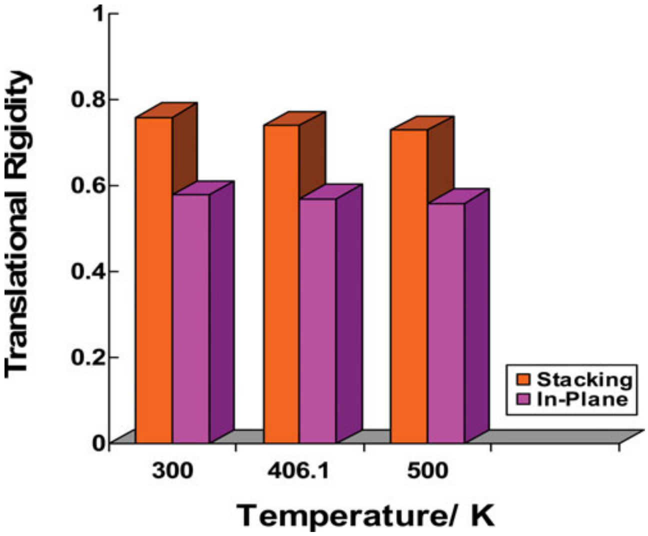


Figure 5. The variation of translational rigidity as a function of temperature during stacking, and in-plane interactions at room temperature (300 K), nematic– isotropic transition temperature (406.1 K), and above transition temperature (500 K).

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 and, therefore, more free space for the molecules to jostle around.

The variation of translational rigidity as a function of temperature during the different modes of interactions indicates that the parallel arrangement represents a state of low orientational entropy (Fig. 5). The observed difference between the translational rigidity from transition temperature to room temperature supports this finding. However, the comparable values in both the cases show that the molecule ONOB does not show extraordinary preference in forming the stacked layers, hence justifies the nematic phase behavior.

Conclusions

The salient features of the present work are as follows:

1. Evidently, the core in the ONOB molecule consists of a negative charge. Hence, it will be strongly attracted by both sides, and end groups to provide enough chemical stability.
2. The alkyl chains can be regarded as source of entropy to realize a given condensed state. Translational entropy favors parallel alignment of the molecules because this arrangement gives less excluded volume and, therefore, more free space for the molecules to justle around.
3. The present computations are helpful in analyzing the phase stability and ordering of nematogen at molecular level.

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