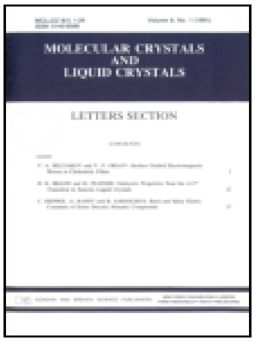

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Ordering and Nematic Phase Behavior of a Naphthyl Ester: A Computational Model Based on Semiempirical Approach

DURGA P. OJHA*

Liquid Crystal Research Laboratory, School of Physics, Sambalpur University, Sambalpur, Odisha, India

The present article deals with the ordering and nematic phase behavior of naphthyl-ester, viz., 4-octylphenyl-6-octyloxy-2-naphthoate based on semiempirical approach at a molecular level. The atomic net charge and dipole moment at each atomic centre has been evaluated using the complete neglect differential overlap method. 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 thermodynamic parameter introduced in this article.

Keywords Configurational entropy; naphthyl-ester nematogen; quantum chemistry

Introduction

Liquid crystals (LCs) are an enthralling set of soft condensed matter characterized by the insight amalgamation of long-range order, and fluidity. They are best known for their exceptionally booming application in flat panel displays, but they exhibit a plethora of unique and attractive properties that offer incredible prospective interest [1] for fundamental science [2] as well as innovative applications well beyond the realm of displays [3]. The unique subtle balance between order and fluidity is not only deeply fascinating from a scientific point of view, but it gives rise to broad range of spectacular spectral phenomena that are far from fully explored.

The physical properties of liquid crystalline materials are highly dependent on the molecular shape [4]. The rode-like molecules are well known to play an important role in nematic ordering. The Nematic LCs with different shapes [5–7] attracted much interest for their wide variety of new phases, and physical phenomena.

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*Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, School of Physics, Sambalpur University, Jyoti Vihar 768 019, Sambalpur, Odisha, India. E-mail: durga_ojha@hotmail.com

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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 interaction energy between two nematogenic molecules. These studies can provide valuable information about the relative role of the different types of interactions, estimate the order of magnitude, and anisotropy of contributions to the energy due to interactions. The interaction potential curves obtained would permit an improved and more quantitative approach in the construction of 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. 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]. 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 affect 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 ordering, and thermodynamic parameter such as configurational entropy for 4-octylphenyl-6-octyloxy-2-naphthoate (OPON) molecule at room temperature (300 K), nematic-isotropic transition temperature (380.2 K), and above transition temperature (430 K) based on the relative energies between a molecular pair of OPON 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 OPON molecule shows nematic to isotropic transition temperature at 380.2 K [12].

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 OPON 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 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. 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:

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

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:

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

where U_{QQ}, U_{QMI}, U_{MIMI}, etc. are monopole-monopole, monopole-dipole, and dipole-dipole terms, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy and the calculation only up to dipole-dipole term gives satisfactory result. The computation of electrostatic term has, therefore, been restricted only up to dipole-dipole energy term.

The dispersion, and short-range repulsion terms are considered together because the several semi-empirical approach, viz., the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky introduced [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:

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

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

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_{λ} K_{ν} 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 Configurational entropy [17] to explain the ordering and phase behavior of OPON molecule at molecular level:

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

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.

Computation of Stacking 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.

Computation of In-Plane 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.

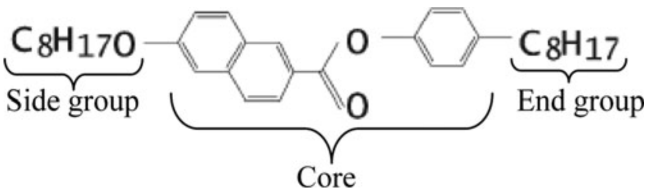
Computation of Terminal Interactions

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

Results and Discussion

Geometry and Chemical Stability

The charge at each atomic centre 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 OPON 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 OPON is given below.



Scheme 1.

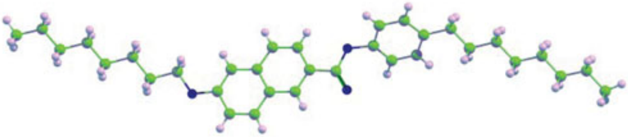


Figure 1. Molecular geometry of OPON molecule ($C_{33}H_{44}O_3$).

The molecular structure of OPON is shown in Fig. 1. The results of interaction energy calculations during the different modes of interactions are discussed below.

Ordering in Stacking 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 (380.2 K), and above the phase transition temperature (340 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-axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. The global search for minimum energy

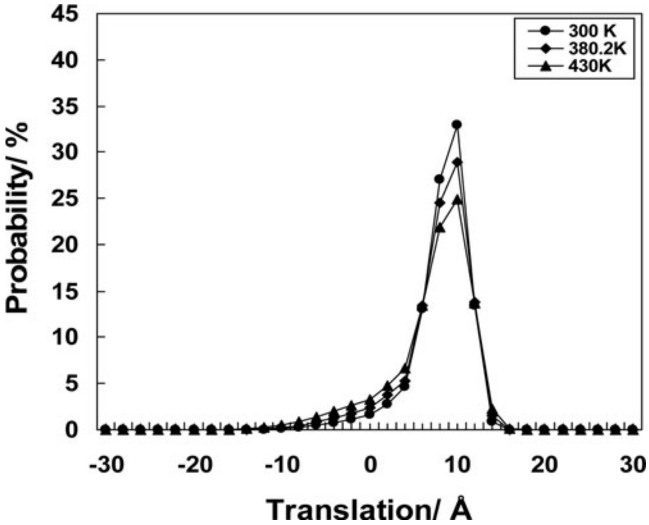


Figure 2. The variation of Configurational probability with respect to translation along x-axis during stacking interactions corresponding to configuration y (0°) z (0°) at room temperature (300 K), nematic-isotropic transition temperature, and above transition temperature (430 K).

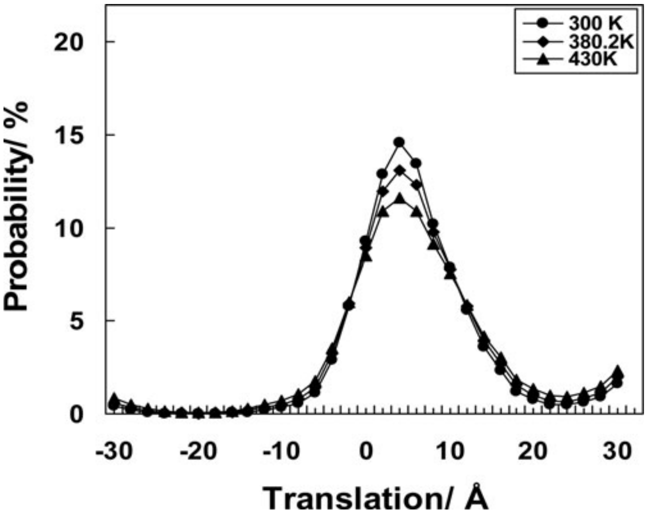


Figure 3. The variation of Configurational probability with respect to translation along *x*-axis during in-plane interactions corresponding to configuration *y* (0°) at room temperature (300 K), nematic-isotropic transition temperature, and above transition temperature (430 K).

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 route of computations.

Ordering in In-Plane 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°) is shown in Fig. 3 at room temperature (300 K), nematic-isotropic transition temperature (380.2 K), and above phase transition temperature (430 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. 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 5 Å. 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.

Ordering in Terminal Interactions

The terminal interactions are weakest but become important when the molecule posses a polar group at either or both of the ends or if there is a possibility of hydrogen bonding. The rotations about *x*-axis (Fig. 4) corresponding to configuration *y* (0°) show no more preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis.

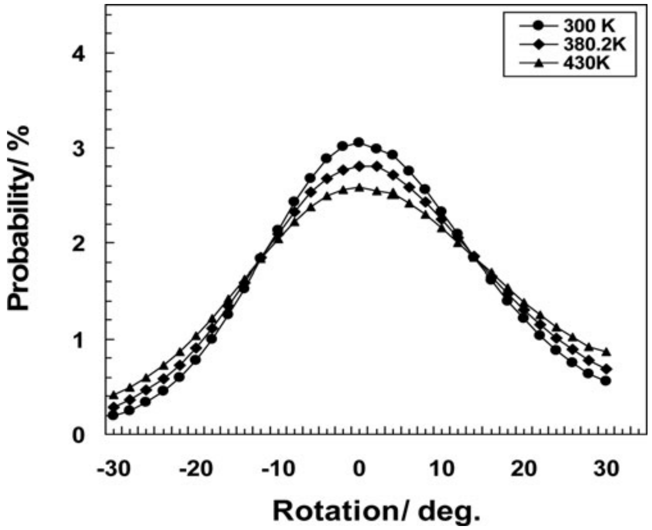


Figure 4. The variation of configurational probability with respect to rotation about *x*-axis during terminal interactions corresponding to configuration *y* (0°) at room temperature (300 K), nematic-isotropic transition temperature, and above transition temperature (430 K).

Phase Behavior of OPON

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.

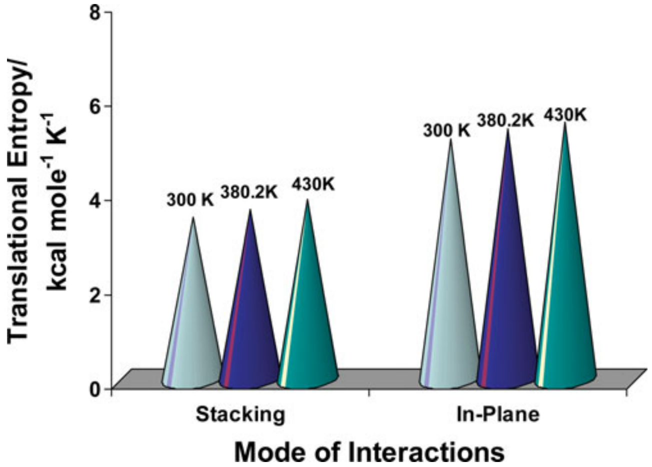


Figure 5. The variation of translational entropy as a function of temperature during stacking, and in-plane interactions at room temperature (300 K), nematic-isotropic transition temperature, and above transition temperature (430 K).

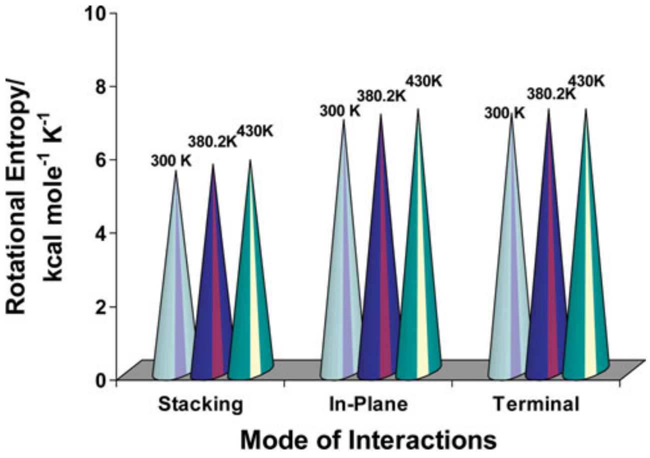


Figure 6. The variation of rotational entropy as a function of temperature during stacking, in-plane, and terminal interactions at room temperature (300 K), nematic-isotropic transition temperature, and above transition temperature (430 K).

The translational entropy as a function of temperature during the stacking and in-plane interactions along the *x*-axis for OPON molecule is shown in Fig. 5. It is noticed that translational entropy during stacking interactions is 3.60×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (380.2 K). However, at room temperature (300 K), the value 3.42×10^{-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 5.10×10^{-3} kcal mole^{-1} K^{-1}, which increased to 5.32×10^{-3} kcal mole^{-1} K^{-1} at nematic-isotropic transition temperature (380.2 K).

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

The variation of rotational entropy during the different modes of interactions indicates that the parallel arrangement represents a state of low orientational entropy (Fig. 6). The observed difference between the rotational entropy from transition temperature to room temperature supports this finding. However, the comparable values in both the cases show that the molecule OPON 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 OPON molecule consists of a negative charge. Hence, it will be strongly attracted by both sides, and end groups to provide enough chemical stability.
2. Translational entropy values indicate the flexibility of a particular configuration in each phase that has relation with the phase transition property.
3. The observed difference between rotational entropy from transition temperature to room temperature are low compared to translational entropy values during the stacking, and in-plane interactions. This reveals that the molecule has a preferred orientation along the long molecular axis (x-axis), which justifies the nematic phase behavior.
4. The present computations are helpful in analyzing the ordering, and phase behavior of naphtyl-ester nematogen at molecular level.

Acknowledgments

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