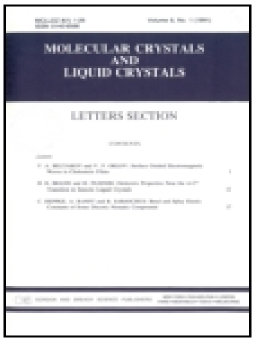

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Theoretical study of *closo*-decaborate novel nematogen: Thermodynamic behavior and phase stability

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ABSTRACT
The present article deals with the thermodynamic behavior and phase stability of closo-decaborate nematogen viz. dinitrogen-10-(4-pentyl-1-thiacyclohexyl)-closo-decaborate (DPTD) at a molecular level. The atomic net charge and dipole moment at each atomic center have been evaluated using the complete neglect differential overlap (CNDO) 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 (300 K), nematic–isotropic transition temperature (435 K), and above transition temperature (500 K) using the Maxwell–Boltazman formula. Further, the entropy of each configuration has been computed during the different modes of interactions. The adopted framework provides valuable information on thermodynamic behavior, and phase stability of novel nematogen based on parameters, i.e., molecular and thermodynamic, introduced in this article.

KEYWORDS
Configurational entropy; 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].

It is well known that liquid crystallinity can be affected by molecular shape [4], conformation [5], and intermolecular interaction [6]. The exact nature of the configurational freedom or degree of molecular motion of flexible end chains in condensed phases needs special consideration. The structure of the nematic phase near the transition can, therefore, be approximated as a calculable perturbation of the structure of coexisting isotropic liquid. The short-range angular correlation, which develops either due to hindered rotation or anisotropy in intermolecular interactions or both, is already present in the isotropic phase [7].

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Based on the Rayleigh–Schrodinger perturbation method, the role of molecular interactions in mesomorphic compounds has engrossed the attention of several researchers [8,9]. These studies have intended to established the anisotropic nature of pair potential, and subsequently find out the minimum energy configuration of a pair of liquid crystalline molecules. 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 molecule DPTD is of meticulous interest, since it provides opportunity to perform fundamental structure–property relationship studies that may provide additional insight on the liquid crystalline state. Hence, in this paper, the authors report the thermodynamic behavior and phase stability for DPTD molecule at room temperature (300 K), nematic–isotropic transition temperature (435 K), and above transition temperature (500 K) based on the relative energies between a molecular pair of DPDT computed at an intermediate distance of 8 Å for stacking, 10 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. The thermodynamic data of DPTD molecule show nematic to isotropic transition temperature at 435 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 the molecular structure can have profound effects on the thermodynamic behavior and phase stability of mesophases. The molecular geometry of DPTD 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 CNDO method [11] has been employed to compute the net atomic charge for interaction energy calculation.

The computational scheme based on simplified formula provided by Claverie [12] 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 [13], 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}, $U_{\text{pol},}$ U_{disp}, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively. Again, electrostatic term is expressed as

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

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 the dipole–dipole term gives satisfactory result. The computation of electrostatic term has, therefore, been restricted only up to the dipole–dipole energy term.

The dispersion and short-range repulsion terms are considered together because several semi-empirical approach, viz. the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky introduced [14] a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [15] for hydrocarbon molecules and 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 $R^{w}{}_{\lambda}$ 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 the ONOB molecule at a molecular level:

$$S = k\ln\Sigma_{\mathrm{i}}\exp(-\beta\varepsilon_{\mathrm{i}}) + (U/T)$$

$$U = \Sigma_{\mathrm{i}}\varepsilon_{\mathrm{i}}\exp(-\beta\varepsilon_{\mathrm{i}})/\Sigma_{\mathrm{i}}\exp(-\beta\varepsilon_{\mathrm{i}})$$

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 the 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 the 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 22 Å with respect to the fixed one.

Results and discussion

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

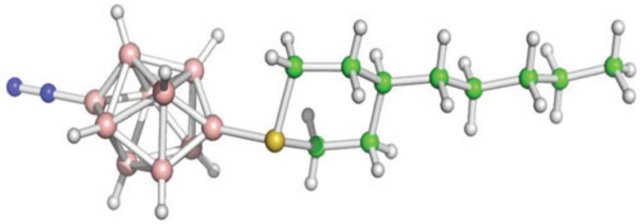

Figure 1. Molecular geometry of the DPTD molecule.

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 (435 K), and above the phase transition temperature (500 K). Evidently, the variation of probability is constant in the region of 24 ±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 the *x*-axis at the equilibrium condition, the energy is brought down and the configurational probability is further investigated with respect to rotation about the *x*-axis.

The 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.

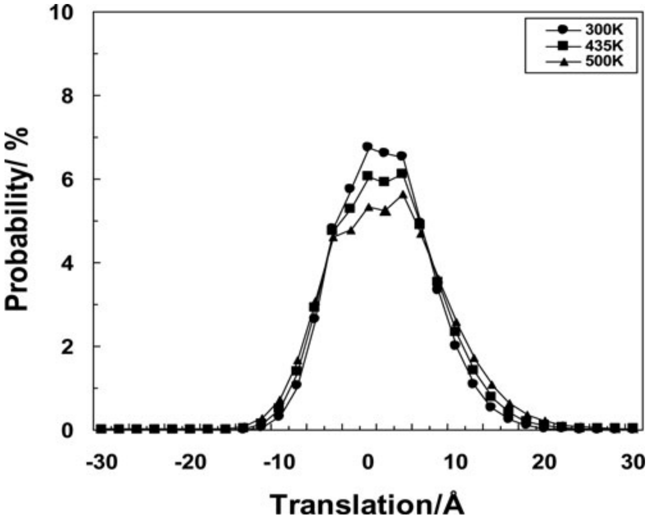

Figure 2. The variation of configurational probability with respect to translation along the *x*-axis during stacking interactions corresponding to configuration $y(0^0)z(0^0)$ at room temperature (300 K), nematic–isotropic transition temperature (435 K), and above transition temperature (500 K).

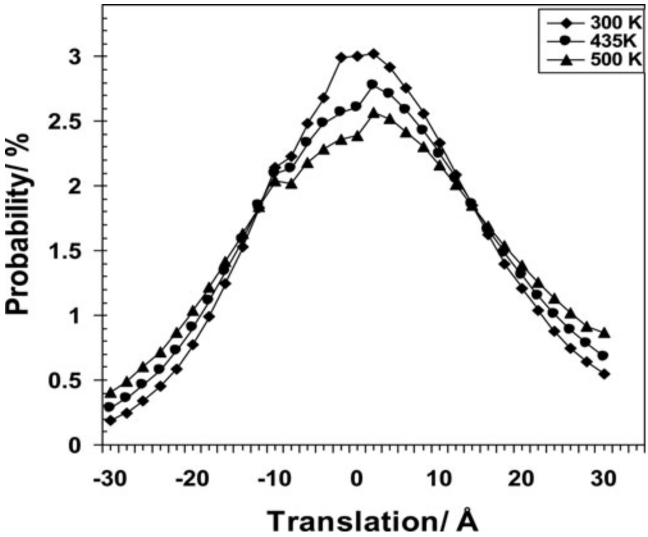

Figure 3. The variation of configurational probability with respect to translation along the *x*-axis during in-plane interactions corresponding to configuration $y(0^0)$ at room temperature (300 K), nematic–isotropic transition temperature (435 K), and above transition temperature (500 K).

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 the x-axis corresponding to configuration y (0^0) is shown in Fig. 3 at room temperature (300 K), nematic–isotropic transition temperature (435 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. 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-axix at the equilibrium condition, the energy is brought down, and the configurational probability is further investigated with respect to rotation about the x-axis.

Terminal molecular pair interactions

The rotations about the 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. The terminal interactions are weakest but become important when the molecule possesses a polar group at either or both of the ends or if there is a possibility of hydrogen bonding.

Effect of molecular motion

The present calculation may be reasonably correlated with the nematic character of the system based on various molecular motions namely; translational and orientational motions.

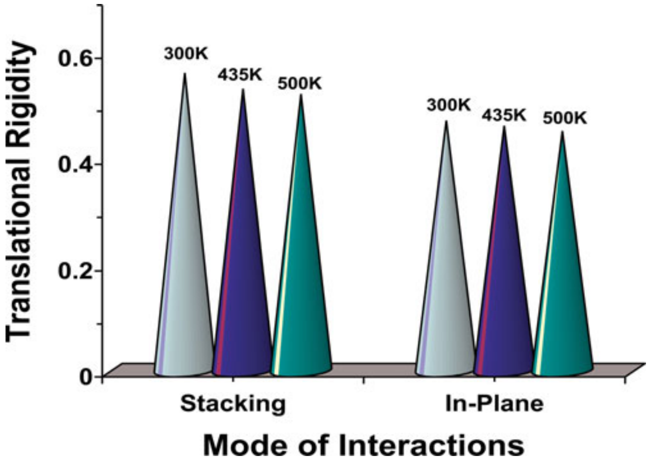

Figure 4. The variation of translational rigidity as a function of temperature during stacking, and in-plane interactions at room temperature (300 K), nematic– isotropic transition temperature (435 K), and above transition temperature (500 K).

The nematic character of liquid crystals is generally manifested by their translational freedom along the long molecular axis. In order to understand the phase behavior of DPTD, translational rigidity parameter (i.e., define as the ratio of probability being at maximum probable point having ± 2 Å displacement along the long molecular axis) has been estimated as a function of temperature during stacking and in-plane interactions (Fig. 4). Evidently, the translational rigidity along the long molecular axis (i.e., x-axis) is 0.53 at nematic–isotropic transition temperature (435 K). However at room temperature (300 K), the value is 0.56, indicating a strong binding at low temperature but with increase of temperature the molecules obtain sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature, the value is 0.47, which reduced to 0.46 at nematic–isotropic transition temperature (435 K). Similarly, rigidity parameter has also been estimated during stacking and in-plane interactions with respect to the x-axis. It has been observed that the values have a decrement compared to translational motion. It may be noted that, though the freedom is considerable for smaller translation, in general, longer translations are not permitted. Thus, in general, small movements of molecules are only possible. However, the comparable values in both cases (i.e., stacking and in-plane interactions) show that the molecule DPTD does not show extraordinary preference in forming the stacked layers, hence justifies the nematic character.

Estimation of configurational entropy

The terminal flexible chains reduce the stability of the solid crystal phase, and allow the appearance of liquid crystal phases. From the view point of entropy, chains play a dominant role as they are very labile and can easily make multi conformational changes. Hence, chains can be regarded as source of entropy to realize a given condensed state or to tune the delicate balance between to energetically close phases.

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 temperatures during the stacking and in-plane interactions along the x-axis for DPTD molecule is shown in Fig. 5. It is noticed that translational entropy

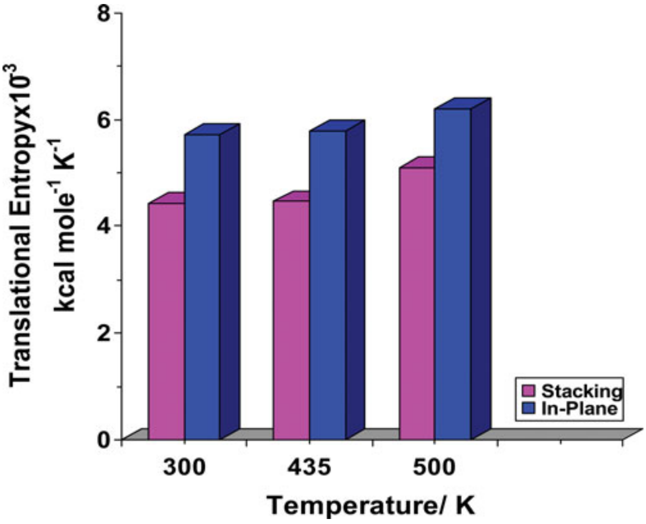

Figure 5. The variation of translational entropy as a function of temperature during stacking, and in-plane interactions at room temperature (300 K), nematic–isotropic transition temperature (435 K), and above transition temperature (500 K).

during stacking interactions is 4.46×10^{-3} kcal mole^{-1} K^{-1} at nematic–isotropic transition temperature (435 K). However, at room temperature (300 K), the value 4.42×10^{-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 entropy is much more pronounced in planar interactions. Evidently, even at room temperature the value is 5.71×10^{-3} kcal mole^{-1} K^{-1}, which increased to 5.78×10^{-3} kcal mole^{-1} K^{-1} at nematic–isotropic transition temperature (435K).

In the process of phase transition from a low to high temperature, the molecular motion of the 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. Moreover, the parallel arrangement represents a state of low orientational entropy. However, the comparable values in both the cases support the nematic behavior of molecule.

Conclusions

The salient features of the present work are as follows:

1. The present study is helpful in analyzing the thermodynamic properties and phase stability of *closo*-decarborate nematogen at a molecular level.
2. The flexible end chains of a molecule provide enough configurational entropy to prevent the total crystallization of core and expand the stability of mesophase range. Translational effect shows the flexibility of configuration at a particular temperature, which has an indirect relation with the phase transition property.

3. The observed translational entropy value during the stacking and in-plane interactions suggests that the molecule has a preferred orientation along the long molecular axis that justifies the nematic character of the molecule.
4. The observed translational entropy value during the stacking and in-plane interactions suggests that the molecule has a preferred orientation along the long molecular axis that supports the nematic character of the molecule.

Acknowledgment

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