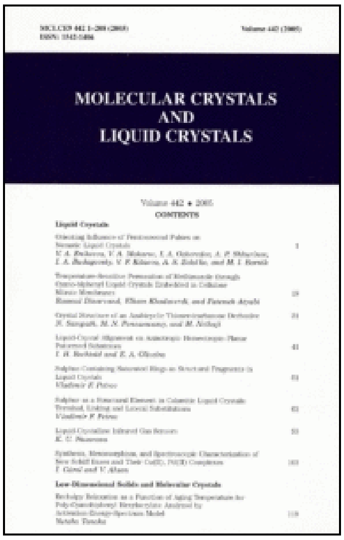

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Molecular Order-Disorder Phenomenon of a Nematogen: A Computational Analysis

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The system chosen for the present investigation, para-*azoxyanisole (4AA), exhibits a nematic-isotropic transition temperature at 408 K. A computational analysis based on quantum mechanics and statistical thermodynamics has been carried out with respect to translational and orientational motions. The evaluation of net atomic charges and dipole moment at each atomic center has been carried out through 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, and the* 6-exp *potential function has been assumed for short-range interaction. The total interaction energy values obtained through these computations have been used as input to calculate the probability of occurrence of a particular configuration using the Maxwell-Boltzmann formula. Further, thermodynamic parameters such as Helmholtz free energy, entropy at room temperature (300 K), nematic-isotropic transition temperature (408 K), and above transition temperature (500 K) have been computed. An attempt has been made to understand the order-disorder phenomenon exhibited by a nematogen and to develop a new and interesting model for structure-phase stability relationships at the molecular level.*

Keywords Nematogen; order-disorder phenomenon; phase stability

Introduction

The transition from the highly ordered crystalline state to the disordered isotropic liquid state often occurs in a multistep process through mesophases in many organic materials, which are designated as liquid-crystalline (LC) phases [1]. In these phases the order of the crystalline state is partly lost and a certain degree of mobility will be attained by the individual molecules. The quest of computational and experimental studies for elucidating the struture-phase stability relationship at the molecular level is the continuing theme of LC science [2,3]. At the molecular level, the phases of matter are basically determined by the interplay between molecular struture, intermolecular interaction [4], and molecular motions. The stability of a given phase is principally governed by the Helmholtz free energy (A). Molecular motions have a

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direct effect on the entropy of a substance and thereby the free energy is modulated. Because the intramolecular electronic energy is much higher than the intermolecular potential energy, a phase transition results in a very small change in the electronic energy of a molecule. In such cases, the molecular struture remains unchanged despite the phase transitions.

The phase struture arises from a delicate interplay between the internal molecular struture and the molecule–molecule interaction energy, which has a close relation with the anisotropy of physical properties [5,6]. This extraordinary sensitivity to the details of the molecular structure arises from a complex interplay between energetic effects (as the molecular orientations: electrostatic, dispersive forces) and entropic ones like positional and orientational distributions. Delicate interplay between energy and entropy controls many complex materials such as liquid crystals. A statistical perspective on thermodynamic parameters can bring a unique insight into this interplay and behavior of chemicals systems. It is also helpful in designing new materials with desired properties. Invaluable qualitative and quantitative information can be achieved from thermodynamic data at and in the vicinity of their phase transitions, which provides first evidence on molecular structure-phase stability relations [7]. The statistical perspective is not only capable of reproducing thermodynamics properties of matter but provides a critical insight into the microscopic details behind these properties [8].

The role of molecular interactions in mesomorpic compounds has captured the attention of several workers [9–12] based on the Rayleigh-Schrodinger perturbation method. These studies were 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. Thus, the main emphasis was on finding out the minimum energy with observed crystal structure, the basic motive for the ordering of a molecule. 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 reflect the actual relative preference, which can only be obtained through their probability corresponding to each configuration. Further, in terms of multipole interactions, significant differences among the energies of various configurations are noticed, which must have a marked effect on thermodynamic properties of the system. Hence, the relative energies are used as an input to calculate the thermodynamic parameters of 4AA.

In the present communication, an attempt has been made to explain the molecular interpretation of order-disorder phenomenon of a nematogen (4AA) in light of its thermodynamic properties. The relative energies between a molecular pair of 4AA have been computed at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 20 Å has been kept for terminal interactions. The selection of intermolecular separations has been made to allow the molecule to have full freedom corresponding to rotation and translation relative to each other. Furthermore, instead of finding the exact minimum energy configuration an attempt has been made to elucidate the general behavior of the molecules surrounding a fixed molecule in a particular frame of reference. An examination of thermodynamic data has revealed that 4AA exhibits nematic-isotropic transition temperature at 408 K [13].

Computational Methodology

The molecular geometry of 4AA has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [13]. The following computations have been carried out.

Computation of Atomic Net Charge and Dipole Moments

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. In the present computation, the complete neglect differential overlap (CNDO/2) method [4] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule because using only the Mulliken atomic net charges (given, for example, by an *ab inito* program) for the calculation of an electrostatic interaction would be incorrect for two reasons: (1) The atomic dipoles must be taken into account, and (2) the homopolar dipoles must be taken into account or atomic net charges obtained according to Lowdin's procedure should be used. An *ab initio* program that gives only Mulliken net charges is therefore quite misleading regarding a reasonable representation of the molecular charge distribution in terms of charges and dipoles. These are equivalent to Lowdin orthogonalized charges [15,16]. A revised version QCPE No. 142 of program, which is an extension of the original program QCPE No. 141 for the third row elements of periodic table, has been used. The program language is FORTRAN IV.

Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on a simplified formula provided by Claverie and Pullman [17] for the evalution of interaction energy between a molecular pair has been used to calculate the energy for a fixed configuration. The computer program INTER, originally developed by Claverie and later modified at Chemical Physics Group, Tata Institute of Fundamental Research, Bombay, India, by Govil and associates has been used for this purpose with further modification. According to the second-order perturbation theory for intermediate-range interactions [18], the total pair interaction energy of molecules (U_{pair}) is represented as the 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 repulasion energy terms, respectively.

Again, the electrostatic term is expressed as

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

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 significantly affect the electrostatic interaction energy and calculation only up to the dipole–dipole term gives a satisfactory result [9–12,19]. The computation of electrostatic terms has, therefore, been restricted only up to dipole–dipole energy term.

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

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

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

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 atoms λ and ν, respectively. The parameters A, B, and γ do not depend on the atomic species. But $R^0_{\lambda\nu}$ and factor $K_{\lambda}\ K_{\nu}$ allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [21].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin has been chosen at almost the midpoint of the molecule. The x-axis along a bond is parallel to the long molecular axis, whereas the y-axis lies in the plane of the molecule and the z-axis is perpendicular to the molecular plane.

Computation of Configurational Probabilities and Thermodynamic Parameters

The total interaction energy values obtained through these computations were used as input to calculate the probability of occurrence of a particular configuration i using the Maxwell-Boltzmann formula [19] in order to obtain better insight:

$$P_i = \exp(-\beta\varepsilon_i) \Big/ \sum_i \exp\ (-\beta\varepsilon_i)$$

Further, the following thermodynamic parameters [8] have been calculated to explain order-disorder phenomenon at the molecular level:

$$A = -kT\, ln \sum_i \exp(-\beta\varepsilon_i)$$

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

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

Where P_i stands for probability, A stands for Helmholtz free energy, U is the internal energy, and S stands for entropy. $\beta = 1/kT$, where k is the Boltzmann constant,

T is the absolute temperature, and ε_i represents the energy of the configuration i to the minimum energy value in a particular set for which the probability distribution is computed.

Results and Discussion

The molecular geometry of 4AA with various atoms is shown in Figure 1. The results of the probability distribution corresponding to the different modes of interactions are discussed below.

Stacking Interactions

One of the interacting molecules is fixed in the x-y plane, and the second has been kept at a separation of 6 Å along the z-axis with respect to the fixed one. The study of the variation of probability with respect to translation along, the x-axis corresponding to configuration y (0°) z (0°) is shown in Figure 2 at room temperature (300 K), the nematic-isotropic transition temperature (408 K), and above the phase trasition temperature (500 K). Evidently, the variation of probability is constant in the region of $-10\,\text{Å} \pm 2\,\text{Å}$, which shows that the sliding of one molecule over the other is energetically allowed for a small range, which may be correlated with the fluidity of the 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 repect to rotation about the x-axis.

The variation of probability with respect to rotation about the x-axis corresponding to configuration y (180°) z (0°) has been carried out. It has been observed that the maximum probability indicates a slight preference for the aligned structure of this configuration. The maximum energy thus obtained is taken as the starting point and the entire process is repeated for small intervals. The energy is minimized with respect to translations and rotations about the x, y, and z-axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for minimum energy configuration or the study of variation of interaction energy under preselected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route.

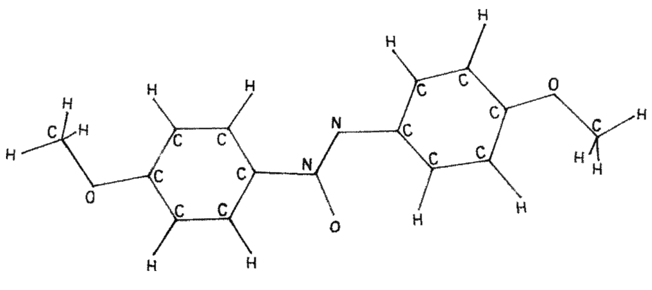

Figure 1. Molecular Geometry of 4AA along with various atoms.

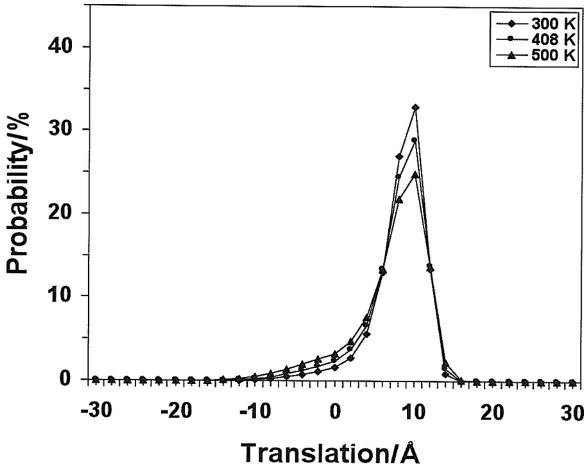

Figure 2. Variation of probability with respect to translation along the x-axis during stacking interactions at room temperature (300 K), the nematic-isotropic transition temperature (408 K), and above the phase transition temperature (500 K).

In-Plane Interactions

The interacting molecule has been kept at a separation of 8 Å along the y-axis with respect to the fixed one. The effect of translation along the x-axis corresponding to the configuration y (0°) is shown in Figure 3 at room temperature (300 K), the nematic-isotropic transition temperature (408 K), and above the phase transition temperature (500 K). Because in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with the maximum probability at 4 Å. The interacting configurations have been refined with

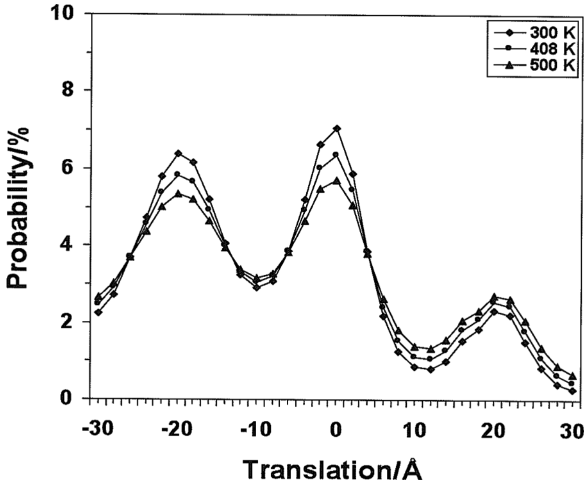

Figure 3. Variation of probability with respect to translation along the x-axis during in-plane interactions at room temperature (300 K), the nematic-isotropic transition temperature (408 K), and above the phase transition temperature (500 K).

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 the x-axis.

The variation of probability with respect to rotation about the x-axis corresponding to configuration y (180°) has been carried out. It has been observed that a pronounced peak exists at one particular rotation point, and all of the remaining regions have negligible probability compared to this configuration. Furthermore, it is observed that the rotational freedom is much more pronounced compared to the stacking interactions. The variation of the probability with respect to rotation about the y-axis corresponding to the configuration x (0°) has also been carried out, and it is observed that the rotation about the y-axis does not alter the configurational probability drastically.

Terminal Interactions

The end-to-end interaction are the 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. To investigate the terminal interactions apart from van der Waals forces, the interacting molecules have been shifted along the x-axis by 20 Å with respect to the fixed one, and rotations were allowed about the x-axis. The rotations about the x-axis corresponding to configuration y (0°) show (Fig. 4) no preference for any angle; that is the molecules are completely free to rotate about their long molecular axis.

Correlation of Results

The present calculations may be reasonably correlated with the order-disorder phenomenon as well as nematic character of the chosen system. The nematic

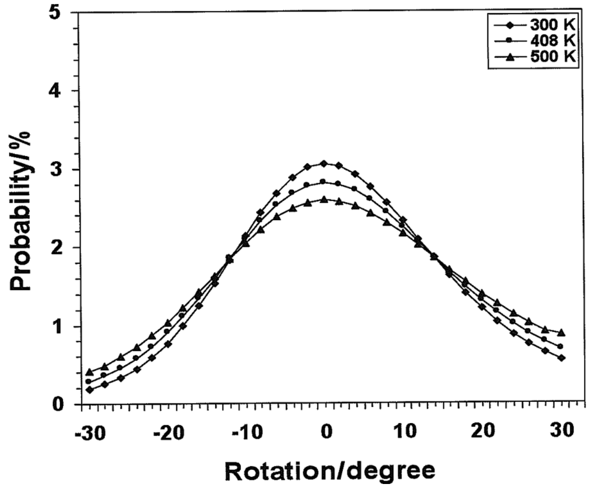

Figure 4. Variation of probability with respect to translation along the x-axis during terminal interactions at room temperature (300 K), the nematic-isotropic transition temperature (408 K), and above the phase transition temperature (500 K).

character of a liquid crystal is generally manifested by its translational freedom along the long molecular axis. To have a closer observation of the nematic character, the thermodynamic parameters such as Helmholtz free energy and entropy are computed with respect to translation along the *x*-axis during the different modes of interactions.

Molecular Order-Disorder Phenomenon of a Nematogen

It is interesting to estimate the Helmholtz free energy of the system to have a detailed picture of ordering and phase stability at a molecular level. A comparative picture of Helmholtz free energy with respect to translation and rotation during the different modes of interactions at room temperature (300 K), the nematic-isotropic transition temperature (408 k), and above the phase transition temperature (500 K) is provided in Table 1. As the negative free energy increases, the phase stability of the system also increases. It is evident from Table 1 that the Helmholtz free energy during the stacking interactions at room temperature is −85.37 kcal mol, whereas it is increased to −94.58 kcal mol at the nematic-isotropic transition temperature, which confirms the stability (order) of a molecule in the nematic phase. It is much more prominent during in-plane and terminal interactions as observed from Table 1.

The translational entropy as a function of temperature during stacking and in-plane interactions along the long molecular axis is shown in Figure 5. It is noticed that the translational entropy during stacking interactions is 3.84 kcal mol^{-1} K^{-1} at the nematic-isotropic transition temperature (408 K). However, at room temperature (300 k) the value is 3.49 kcal mol^{-1} K^{-1}, indicating a strong binding at low temperature with less disorder. But with increase of 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 6.41 kcal mol^{-1} K^{-1}, which increased to 6.51 kcal mol^{-1} K^{-1} at the nematic-isotropic transition temperature (408 K). It may be noted that though the freedom is considerable for smaller translation, longer translations are not generally permitted. Thus, in the mesomorphic range, small movements of molecules are only possible. In the process of a phase

Table 1. A Comparative Picture of Thermodynamic Parameter, Helmholtz Free Energy (*A*) Corresponding to Various Configurations during the Different Modes of Interactions at Room Temperature (300 K), the Nematic-isotropic Transition Temperature (408 K), and Above the Phase Transition Temperature (500 K)

Mode of interactions	Configuration	Helmholtz free energy/kcal mol^{-1}		
		300 K	408 K	500 K
Stacking[a]	*y* (0°) *z* (0°)	−85.37	−94.58	−106.45
Stacking[b]	*y* (180°) *z* (0°)	−51.13	−59.99	−71.21
On-plane[a]	*y* (0°)	−46.43	−55.55	−67.69
In-plane[b]	*y* (180°)	−41.58	−49.86	−60.75
Terminal[b]	*y* (0°)	−38.13	−45.84	−56.05

[a] Translation along the *x*-axis.

[b] Rotation about the *y*-axis.

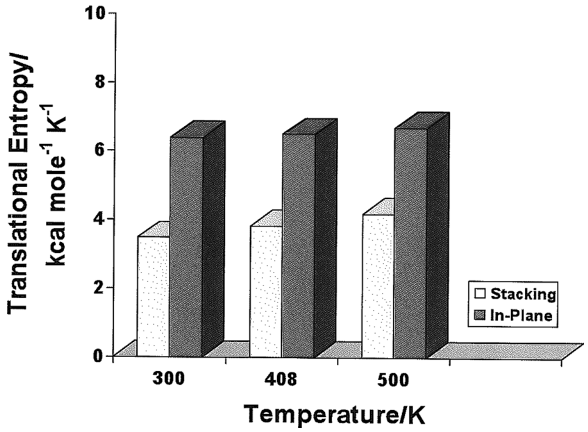

Figure 5. Translational entropy as a function of temperature during stacking and in-plane interactions at room temperature (300 K), The nematic-isotropic transition temperature (408 K), and above the phase transition temperature (500 K).

transition from a low to a high temperature, the molecular motions would be excited and thereby the number of thermally accessible conformations would be increased. The translational entropy in the isotropic liquid states is increased from its room temperature value (Figure 5). This implies that the different modes of molecular motions (transitional, rotational, etc) are excited to an equal extent, particularly in the isotropic state. However, the comparable values in both cases (i.e., stacking and in-plane interactions) show that the molecule 4AA does not show extraordinary preference in forming the stacked layers and hence justifies the nematic character.

Conclusion

The present computational analysis based on quantum mechanics and statistical thermodynamics encompasses both the development of a model and the molecular order-disorder phenomenon for a nematogen. Further, the translational entropy shows the flexibility of configuration at a particular temperature, which has a direct relation with the phase transition property. This provides a new and interesting way to understand the struture-phase stability relationship at a molecular level.

Acknowledgments

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