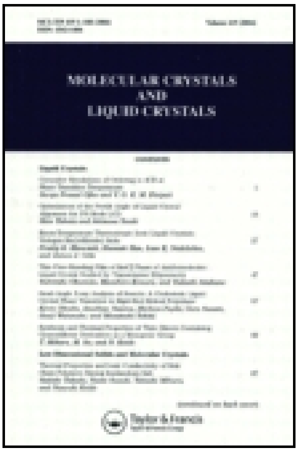

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Molecular Structure and Ordering in a Fluorinated Smectogenic Compound—A Statistical Thermodynamic Approach

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In the present paper, molecular structure and ordering in a fluorinated smectogenic compound 4-propyloxyphenyl 4-(4-trifluoromethyl-benzoyloxy) benzoate (FLUORO) with respect to translatory and orientational motions have been reported. The evaluation of net atomic charges and dipole moments at each atomic center has been carried out through the complete neglect differential overlap (CNDO/2) 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), smectic–isotropic transition temperature (488 K), and above transition temperature (550 K) using the Maxwell–Boltzmann formula. Further, thermodynamic parameters such as Helmholtz free energy and entropy have been computed during the different modes of interactions. An attempt has been made to understand the phase behavior and ordering of the compound based on the thermodynamic parameters introduced in the paper.

Keywords Entropy; helmholtz free energy; molecular structure; phase stability

Introduction

Liquid crystals (LCs) serve as a medium to link basic crystal physics, and chemistry to other scientific disciplines owing to their fascinating features such as multiphase, and multidisciplinary nature [1]. The simulation of phase behavior at molecular level in complex fluids, such as LCs, is a multifaceted and challenging task in spite of swift increase in computer power [2]. The scenario of phase transitions requires the breakdown of the molecular packing order under influence of rapid rotation about the long axis of the molecule to give a "smectic" LC phase [3], in which the long-range positional order is lost. When the local packing order is destroyed, but the orientational order still remains with the molecules reorganizing so that their long axes lie in the same direction producing the "nematic" LC phase [4].

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One of the classical challenges of the physical chemistry of LCs is to understand the relation between the molecular interactions, and the thermodynamic parameters. At molecular level, a thermodynamic parameter of high relevance is the phase equilibria since one often finds a much more affluent phase behavior than in simpler liquids. Particularly for this type of self-organizing molecules, the phase behavior is affluent, and it is indispensable in any study of such systems to establish the phase behavior. This has lead to an accumulation of a large amount of experimental data on phase behavior. It is only during the recent years that extensive attempts have been made to interpret these experimental findings in terms of molecular models [5]. There is a twofold purpose of establishing such relations between molecular interactions, and phase behavior. The observed thermodynamic equilibrium data provide information on the situation at molecular level that can be very difficult to obtain by other means. On the other hand, a good understanding of the molecular features that are controlling the equilibrium between different phases makes it possible to design systems with desirable phase properties [6]. The problem of predicting physical properties of LC compounds based upon molecular shape and intermolecular interactions requires the adoption of a model potential [7]. The stability of the phase arises from the existence of the strong interactions between pairs of molecules, which promote the positional and orientational order of the mesomorphic compounds [8].

The role of molecular interactions in mesomorphic compounds has engrossed 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, much prominence was laid on finding out the minimum energy with observed crystal structure, the basic motive for 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. In terms of multipole interactions, significant differences among the energies of various configurations are noticed, which must have a marked affect on thermodynamic properties of the system. Hence, these relative energies are used as an input to calculate the thermodynamic properties of 4-propyloxyphenyl 4-(4-trifluoromethyl-benzoyloxy) benzoate (FLUORO).

In the present paper, we report molecular structure and ordering in a smectogenic fluorinated compound in terms of relative energies, thermodynamic parameters between a molecular pair at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 30 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. Furthermore, the most favorable configuration among the different modes of interactions has been reported. An examination of thermodynamic data has revealed that FLUORO exhibits smectic–isotropic transition temperature at 488 K [13].

Method of Calculation and Thermodynamic Approach

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

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 [14] has been employed to compute the net atomic charge and dipole moment at each atomic center of the molecule. A revised version QCPE No. 142 of the 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 simplified formula provided by Claverie [15] 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 and later on 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 as modified by Caillet and Claverie for intermediate range interactions, the total pair interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy,

$$U_{\text{pair}} = U_{\text{el}} + U_{\text{pol}} + U_{\text{disp}} + U_{\text{rep}}, \tag{1}$$

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

$$U_{\text{el}} = U_{\text{QQ}} + U_{\text{QMI}} + U_{\text{MIMI}} + \dots \quad , \tag{2}$$

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 [16]. The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term.

The polarization energy of a molecule (s) is obtained as the sum of polarization energies of the various bonds,

$$U_{\text{pol}}^{(s)} = C(-1/2) \sum_{u}^{(s)} \xi_u^{(s)} A_u^{=(s)} \xi_u^{(s)}, \tag{3}$$

where $\overset{=}{A}_u$ is the polarizability tensor of the bond u and $\xi_u^{(s)}$ the electric field created at this bond by the surrounding molecules. If the molecular charge distributions are represented by the atomic charges, it is found that

$$\xi_u^{(s)} = \sum_{t \neq s} \sum_{\lambda}^{(t)} q\, \lambda^{(t)} R_{\lambda\mu} / R_{\lambda\mu}^3, \tag{4}$$

where $R_{\lambda\mu}$ is the vector joining the atom λ in molecule t to the "center of polarizable" charge on the bond u of the molecule (s).

In the present computation, the dispersion and short-range repulsion terms are considered together because several semiemperical approach, viz., the Lennard–Jones or Buckingham-type approach, actually proceed in this way. Kitaygorodsky [17] introduced a

Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [18] for hydrocarbon molecules and several other molecules and finally gave the expression

$$U_{\text{disp}} + U_{\text{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda, \nu), \tag{5}$$

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

where $Z = R_{\lambda\nu}/R^{0}{}_{\lambda\nu}$; $R^{0}{}_{\lambda\nu} = [(2R^{\text{w}}_{\lambda})\ (2R^{\text{w}}_{\nu})]^{1/2}$, 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 $K_{\lambda}\ K_{\nu}$ allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [19].

An orthogonal coordinate system is considered to facilitate the above calculation. The origin on an atom has been chosen at almost midpoint of the molecule. The *x*-axis along a bond parallel to the long molecular axis while the *y*-axis lies in the plane of the molecule and *z*-axis 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 [20] in order to obtain a better insight,

$$P_{i} = \exp\,(-\beta\varepsilon_{i}) / \sum_{i} \exp\,(-\beta\varepsilon_{i})\ . \tag{7}$$

Further, the following thermodynamic parameters [6] have been calculated to explain order–disorder phenomenon at molecular level,

$$A = -kT\ \ln \sum\nolimits_{i} \exp\,(-\beta\varepsilon_{i})\ , \tag{8}$$

$$S = k\ \ln \sum\nolimits_{i} \exp\,(-\beta\varepsilon_{i}) + (U/T)\ , \tag{9}$$

$$U = \sum\nolimits_{i} \varepsilon_{i}\ \exp(-\beta\varepsilon_{i}) / \sum\nolimits\ _{i} \exp\,(-\beta\varepsilon_{i})\ , \tag{10}$$

where P_{i} stands for probability, A stands for Helmholtz free energy, and S stands for entropy. $\beta = 1/kT$, 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 FLUORO is shown in Fig. 1. The results of configurational probability distribution during the different modes of interactions are discussed below.

Stacking Interactions

One of the interacting molecules is fixed in the *x*–*y* plane, while the second has been kept at a separation of 6 Å along the *z*-axis with respect to the fixed one. The variation

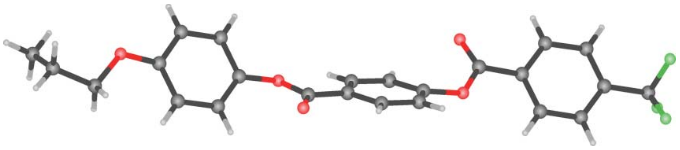

Figure 1. Molecular geometry of FLUORO.

of probability with respect to translation along *x*-axis corresponding to configuration* *y* (0°) *z* (0°) has been carried out at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above phase transition temperature (550 K). It has been observed that the variation of probability is constant in one particular translation region, which shows a sliding of one molecule over 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 respect to rotation about the *x*-axis.

The variation of probability with respect to rotation about *x*-axis corresponding to configuration *y* (180°) *z* (0°) has been studied and it is noticed that the maximum probability corresponds to FLUORO at a particular degree of rotation, indicating a slight preference for the aligned structure of this configuration. Similarly, the variation of probability with respect to rotation about *z*-axis corresponding to the configuration *x* (0°) *y* (0°) reveals that the flexibility of rotation about *z*-axis is rather small, which accounts for smectic character of the molecule. The minimum 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 *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 was 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.

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°) at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above phase transition temperature (550 K). Since in-plane interactions are much prominent than the stacking interactions, a greater freedom corresponding to translation is observed. It has been observed that maximum probability occurs at one particular value of separation. 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.

The variation of probability with respect to rotation about the *x*-axis corresponding to configuration *y* (180°) shows that a pronounced peak exists at an equilibrium point, and

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*Configuration *y* (θ_1°) *z* (θ_2°) means that the molecule has been rotated from its initial position by θ_1° about *y*-axis and by θ_2° about *z*-axis. Configurational probability has been calculated after displacing the molecule to a specified distance with molecule initial position.

all the remaining regions have negligible probability as compared to this configuration. Furthermore, the observed rotational freedom is much more pronounced as 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 has been observed that the rotation about the y-axis does not alter the configurational probability drastically.

Terminal Interactions

The end-to-end 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. To investigate the terminal interactions apart from van der Waals forces, the interacting molecule have been shifted along the x-axis by 22 Å with respect to the fixed one and rotations have been allowed about x-axis. The observed rotations about the x-axis corresponding to configuration y (0°) show no preference for any angle, that is, the molecules are completely free to rotate about their long molecular axis.

The most favorable stacked configuration of pairing for FLUORO has been obtained (Fig. 5) with entropy 6.75 kcal mol^{-1} K^{-1} and Helmholtz free energy of -44.16 kcal mol^{-1}. This configuration agrees with those obtained from crystallographic studies [12].

Correlation of Results with Smectic Character and Ordering

The present calculation may be reasonably correlated with smectic character as well as molecular structure-phase stability relationship. The smectic character of LC is generally manifested by its rotational flexibility about z-axis. To have a closer observation towards the smectic character, thermodynamic parameters such as Helmholtz free energy and entropy are computed during different modes of interactions.

Phase Stability and Ordering

It is interesting to estimate Helmholtz free energy of the system to have a detailed picture of phase stability (ordering) at molecular level. The variation of free energy with respect to translation and rotation during different modes of interactions at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above phase transition temperature (550 K) is reported in Table 1. It is evident from Table 1 that free energy with respect to rotation about z-axis during stacking interactions is minimum rather than rotation about y-axis during in-plane and rotation about x-axis during terminal interactions, which confirms the stability (order) of molecule in smectic phase. Evidently, the Helmholtz free energy of FLUORO during stacking interactions is -48.01 kcal mol^{-1} at room temperature (300 K) that decreased to -74.90 kcal mol^{-1} at smectic–isotropic transition temperature (366 K). The increment in negative free energy confirms stability of the mesophase at transition temperature.

The entropy as a thermodynamic function is a measure of the disorder of molecules because the entropy is related to the number of microscopic states by Boltzmann's principle. Figure 2 shows the translational entropy as a function of temperature during stacking and in-plane interactions along the long-molecular axis. It is noticed that translational entropy during stacking interactions is 6.48 kcal mol^{-1} K^{-1} at smectic–isotropic transition temperature (488 K). However, at room temperature (300 K) the value is 6.21 kcal mol^{-1} K^{-1} indicating a strong binding at low temperature with less disorder. Most of the liquid

Table 1. Helmholtz free energy (*A*) of various configurations during the different modes of interactions at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above transition temperature (550 K) for FLUORO molecule

		Helmholtz free energy/kcal mol^{-1}		
Mode of interaction	Configuration	300 K	488 K	550 K
Stacking[a]	*y* (0°) *z* (0°)	−48.01	−74.90	−83.75
Stacking[b]	*y* (180°) *z* (0°)	−47.86	−70.89	−78.16
Stacking[c]	*x* (0°) *y* (0°)	−44.16	−67.37	−74.86
In-Plane[a]	*y* (0°)	−48.54	−74.33	−83.05
In-Plane[b]	*y* (180°)	−40.33	−62.88	−70.28
Terminal[b]	*y* (0°)	−36.71	−59.73	−67.32

[a] Corresponds to translation along *x*-axis.
[b] Corresponds to rotation about *x*-axis.
[c] Corresponds to rotation about *z*-axis.

crystalline molecules found to have a number of conformations which are thermally accessible. In the process of a phase transition from a low- to a high-temperature, the molecular motions of the alkyl chains would be excited and thereby the number of thermally accessible conformations would be increased [21]. The translational entropy in the isotropic liquid state is increased from its room temperature (Fig. 2). It implies that the different modes of molecular motions (translational, rotational, etc.) are excited to an equal extent, particularly in the isotropic state. Figure 3 shows the variation of rotational entropy about

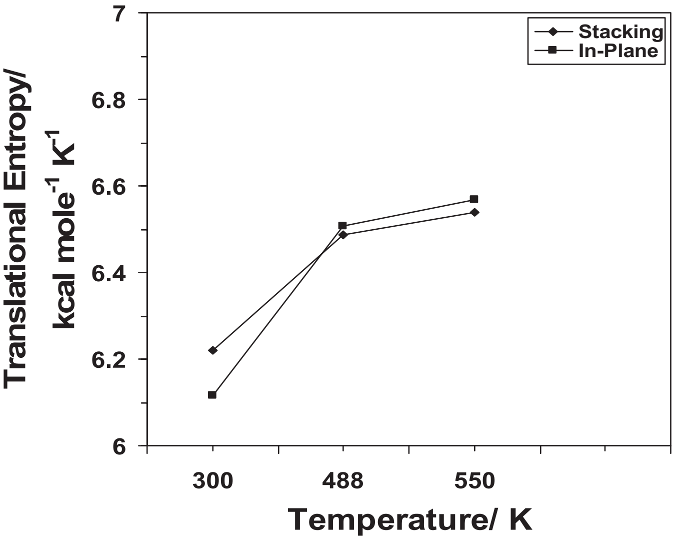

Figure 2. Variation of translational entropy along x-axis during stacking and in-plane interactions at room temperature (300 K), smectic-isotropic transition temperature (488 K), and above transition temperature (550 K).

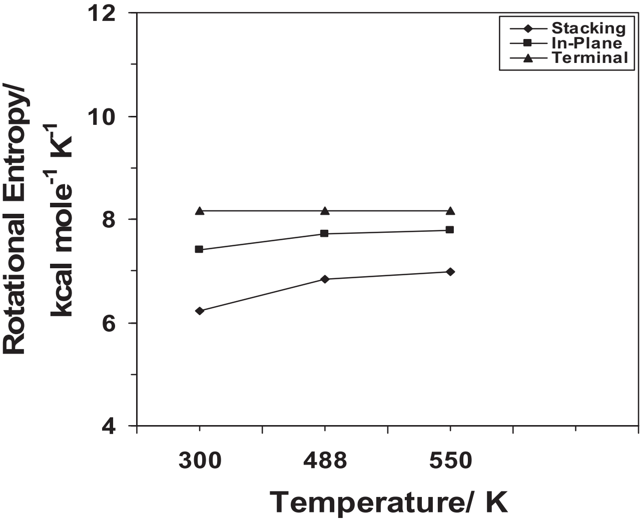

Figure 3. Variation of rotational entropy about *x*-axis during stacking, in-plane, and terminal interactions at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above transition temperature (550 K).

long molecular axis (*x*-axis) as a function of temperature during different modes of interactions along the long molecular axis. To correlate the smectic nature of the compound, the variation of entropy with respect to rotation about *z*-axis at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above transition temperature (550 K) has been carried out (Fig. 4), while the rotation is extended about the *y*-axis for in-plane and

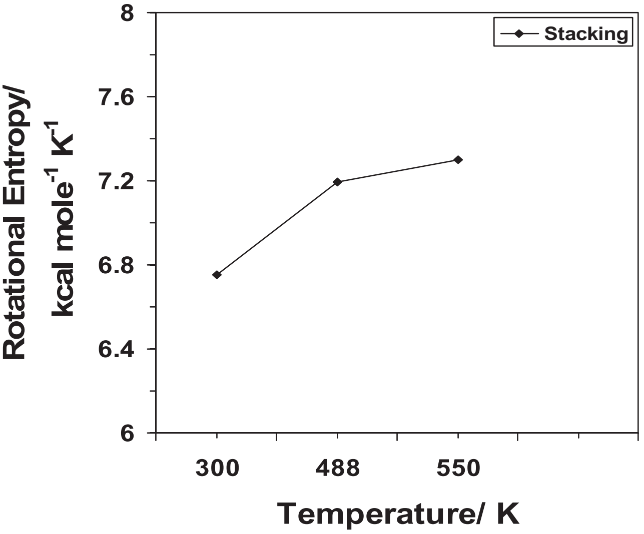

Figure 4. Variation of rotational entropy about *z*-axis during stacking interactions at room temperature (300 K), smectic–isotropic transition temperature (488 K), and above transition temperature (550 K).

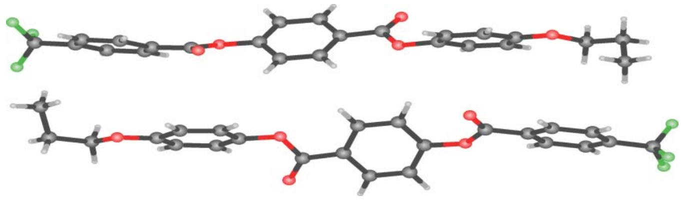

Figure 5. The most favorable stacked configuration of pairing obtained for FLUORO with entropy 6.75 kcal mole-1 K-1 and Helmholtz free energy −44.16 kcal/mole.

x-axis for terminal interactions (Fig. 3). Further, the comparable values of configurational entropy during the both modes of interactions (i.e., stacking and in-plane) suggest that the molecule has higher ordering along *z*-axis (stacking), which subsequently confirms the smectic behavior of the molecule. It may, therefore, be concluded that flexibility of rotation about the *z*-axis is small, which accounts for the smectic character of the molecule.

Conclusions

(1) The present computations provide information about the probability of dimer complexes, the relative freedom of a molecule in terms of their inclination, separation, or sliding of a molecule over the other.

(2) Configurational entropy shows the flexibility of a particular configuration in each phase that has a direct relation with the phase transition property. Further, the analysis of different molecular motions (translational, rotational) and interactions (stacking, in-plane, etc.) are helpful to analyze the phase behavior/stability of mesophases.

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