Estimation of Configurational Probability and Phase Behaviour of *N*-*n*-undecyl-D-gluconamide having V-Shaped Conformation – A Molecular Simulation Approach

P. Lakshmi Praveen and Durga P. Ojha

Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada-520 008, A.P., India

Reprint requests to D. P. O.; E-mail: durga_ojha@hotmail.com

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The present article deals with the configurational probabilities of a smectogen *N*-*n*-undecyl-D-gluconamide (GAM11). The complete neglect differential overlap (CNDO/2) method has been employed to compute the net atomic charge and atomic dipole moment components at each atomic center. The modified Rayleigh–Schrödinger perturbation theory along with the multicentered-multipole expansion method has been employed to evaluate the long-range intermolecular interactions, while a '6-exp' potential function has been assumed for short-range interactions. The total interaction energy values obtained during different modes of molecular interactions have been used as input to calculate the configurational probability at room temperature (300 K), and smectic-isotropic transition temperature (429.7 K) using the Maxwell–Boltzmann formula. The various possible geometrical arrangements of molecular pairs have been considered. Further, an attempt has been made to explain the smectic behaviour of GAM11 in terms of their relative order based on the molecular parameters introduced in this paper.

Key words: *N*-*n*-Undecyl-D-Gluconamide; Smectogen; Molecular Rigidity.

1. Introduction

The liquid state of many molecular substances is an impressive challenge in condensed matter [1]. In ordinary molecular liquids, there is a competition between short-range molecular packing (repulsive, excluded-volume interactions) and long-range intermolecular attraction (electrostatic interactions). The net result of these competitive interactions is a fluid phase with full rotational and translational symmetry, i.e., all the physical features of the fluid are invariant under arbitrary rotations and translations. However, attractive interactions and repulsive interactions conspire to enable varying degrees of translational and/or orientational molecular order within a limited temperature range. Smectic liquid crystals have higher molecular order which leads to potential applications in functional devices and the fabrication of new type of anisotropic materials.

The role of the anisotropic shape as inimitable feature necessary to observe liquid crystalline phases has been confirmed by many reports [2, 3]. It is known that the structure of a fluid is dominated by short-range repulsive interactions [4]. In fact, they were the starting point of later studies focusing on the effect on phase behaviour of adding attractive interactions [5], dipolar forces [6], flexible terminal chains [7], and, also, of the combined presence of both the latter [8]. Carbohydrate liquid crysals (LCs) have a sizeable attention, and numerous studies [9 – 11] have reported on amphiphillic compounds that are relevant for biological functions or for monophillic mesogens. The LC research only explicitly recognizes the structure–property relationships [11] of many compounds, which have never been tested for their mesomorphic properties, and the relation between the 'physical state' of matter for their biological functions. Even though advances in synthesis and characterization explore many achievements in explaining the phase behaviour, it is often desirable to have a sense of material/phase behaviour before it is synthesized. The present calculations are able to provide both the prediction of molecular properties and the approximate prediction of phase behaviour prior to synthesis. Therefore, they play a role in the molecular engineering of new materials and industrial applications.

The role of molecular interactions in mesomorphic compounds has engrossed the attention of several workers [12 – 15] based on the Rayleigh–Schrödinger 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. 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 replicate the actual relative preference, which can only obtain through their probabilities corresponding to each configuration. Hence, in order to obtain a quantitative measure for the relative preference, authors have evaluated the relative probability of occurrence of each configuration. Since mesogenic properties are related to molecular aggregation in a specific manner, the configurational probability distribution picture based on interaction energy results will provide valuable information in this respect.

An interesting feature associated with phase behaviour and thermotropic transitions of GAM11 is the melting point, which is relatively consistent irrespective of the alkyl chain length. This suggests that the transition from crystal to liquid crystal a core of stacked alkyl chains is retained rather than hydrogen-bonded carbohydrate moieties [16]. Moreover, gluconamides with alkyl chains longer than eight carbon atoms form monolayers, and those with shorter chains form micelles. In the present article, we report the ordering and phase behaviour of a smectogen GAM11 at room temperature (300 K) and smectic-isotropic transition temperature (429.7 K). Configurational probabilities of a molecular pair have been computed at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 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. An examination of thermodynamic data has revealed that GAM11 exhibits a smectic-isotropic transition at 429.7 K [16].

2. Computational Method

The molecular geometry of GAM11 has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [16]. The following computations have been carried out:

2.1. 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 centre through an all-valance electron method. In the present computation, the complete neglect differential overlap (CNDO/2) method [17] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. A revised version QCPE (Quantum Chemistry Program Exchange) No. 142, 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. The program is capable of computing CNDO wave functions for open- and closed-shell molecules containing the elements hydrogen to chlorine. The matrices in the program are large enough to allow molecules containing up to 35 atoms or 80 basis functions (whichever is smaller). One atomic orbital basis function is allowed for hydrogen ($1s$), four each to the elements sodium through chlorine.

2.2. Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on the simplified formula provided by Claverie and Pullman [18] 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 for intermediate range interactions [19, 20], the total pair interaction energy of molecules (U_{pair}) is represented as sum of various terms contributing to the total energy:

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

where U_{el}, U_{pol}, U_{disp}, and U_{rep} are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively. Further, the electrostatic term is expressed as

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

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 the dipole–dipole term gives a satisfactory result [12–15, 20]. The computation of the electrostatic term has, therefore, been restricted only up to the dipole–dipole energy term.

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

$$U^{(s)}_{\mathrm{pol}} = C(-1/2)\sum_{u}^{(s)} \xi_u^{(s)} \overset{=}{A}{}_u^{(s)}\, \xi_u^{(s)} \ ,$$

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

$$\xi_u^{(s)} = \sum_{t\neq s}\sum_{\lambda}^{(t)} q_\lambda^{(t)} R_{\lambda\mu}/R^3_{\lambda\mu},$$

where $R_{\lambda\mu}$ is the vector joining the atom λ in molecule (t) to the 'centre 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 semiempirical approaches, viz. the Lennard–Jones or Buckingham type approach, actually proceed in this way. Kitaygorodsky [21] introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskay [22] for hydrocarbon molecules and several other molecules and finally gave the expression

$$U_{\mathrm{disp}} + U_{\mathrm{rep}} = \sum_{\lambda}^{(1)}\sum_{\nu}^{(2)}{}' U(\lambda,\nu)$$
$$U(\lambda,\nu) = K_\lambda K_\nu\left(-A/Z^6 + B\,\mathrm{e}^{-\gamma Z}\right),$$

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 $K_\lambda K_\nu$ allows the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [22].

2.3. Computation of Configurational Probabilities

The total interaction energy values obtained through these computations have been used as an input to calculate the probability of occurrence of a particular configuration i using the Maxwell–Boltzmann formula [23] in order to obtain a better insight:

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

where P_i stands for probability. $\beta = 1/kT$, 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. An orthogonal coordinate system has been considered to facilitate the above calculation. The origin has been chosen at almost midpoint of the molecule. The x-axis has 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.

3. Results and Discussion

The molecular geometry of GAM11 is a V-shaped conformation as shown in Figure 1. The results of the probability distribution corresponding to the different modes of interactions are discussed below.

3.1. Role of Stacking Interactions

In a molecular pair, one of the interacting molecules has been kept at a separation of 6 Å along the z-axis with respect to the fixed molecule. The variation of

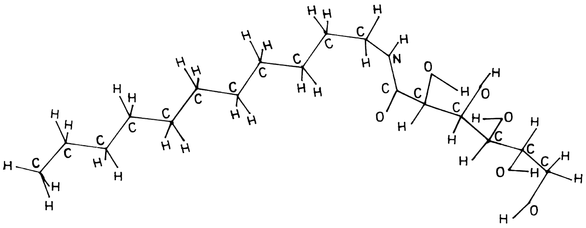

Fig. 1. Molecular geometry of GAM11 along with various atoms.

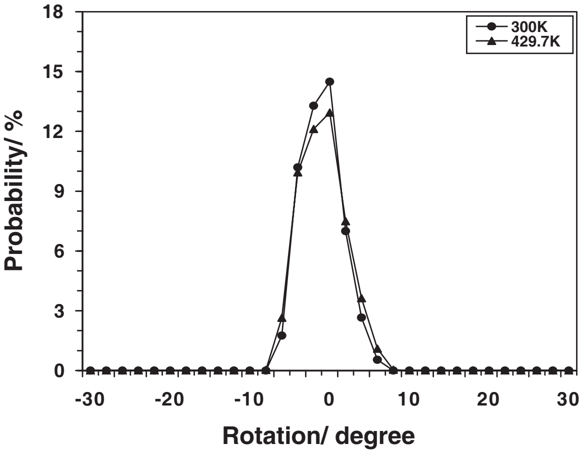

Fig. 2. Variation of probability with respect to rotation about z-axis during stacking interactions at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $x(0°)\ y(0°)$.

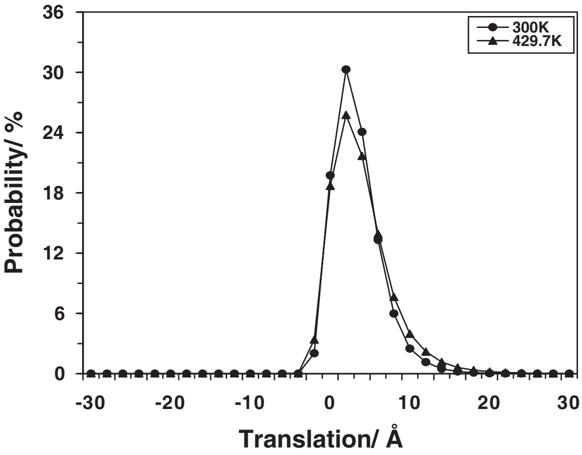

Fig. 3. Variation of probability with respect to translation along x-axis during stacking interactions at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $y(0°)\ z(0°)$.

probability with respect to rotation about the z-axis at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to the configuration[1] $x(0°)\ y(0°)$ is shown in Figure 2. It has been observed that the configuration shows a sharp preference towards the minimum-energy point with the maximum probability at the equilibrium position. The flexibility of rotation is sufficiently small, which accounts for the smectic character of the molecule. Further, it indicates that a finite probability for alignment at low temperature exists when the thermal vibration does not drastically disturb the molecular alignments.

The variation of the probability with respect to translation along the long molecular axis (x-axis) at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to the configuration $y(0°)\ z(0°)$ is shown in Figure 3. Evidently, the configuration shows a sharp preference toward the minimum energy point. The variation of probability is almost constant in the region of (20 ± 4) Å without any significant change in energy, and hence is capable of retaining the molecular order against increased thermal agitation. The maximum probability has been achieved at 2 Å. 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 the rotation about the x-axis.

The variation of probability with respect to a rotation about the x-axis at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to the configuration $y(0°)\ z(180°)$ has been carried out. It has been observed that the maximum probability achieved at 2° rotation indicating a slight preference for the aligned structure of this configuration. The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for small intervals. The energy minimization is an auto process. The energy has been 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 the minimum energy configuration or the study of variation of interaction energy under pre-selected conditions will have completely different paths and, therefore, one has to be careful in choosing the specific route. Further, the effectiveness/appropriateness of minimization methods also depend on the objective of computation.

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[1] Configuration $x\ (\theta_1^\circ)\ y\ (\theta_2^\circ)$ means that the molecule has been rotated from its initial position by θ_1° about the x-axis and by θ_2° about the y-axis. The configurational probability has been calculated after displacing the molecule to a specified distance with respect to the molecule initial position.

3.2. Role of 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 electrostatic energy during in-plane interactions is more effective than stacking, since the anti-parallel orientation of molecules provides a more effective dipole–dipole attraction. Additionally, repulsive quadrupole–quadrupole interactions become very much less effective due to the slipped-antiparallel molecular orientation. These factors ultimately causes the large variation in total interaction energy and, thereby, in the probability of the configuration. The variation of probability with respect to a translation along the *x*-axis at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to the configuration $y(0^\circ)$ is shown in Figure 4. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed with a maximum probability at 4 Å. The interacting configurations have been refined with respect to a translation along the *x*-axis at the equilibrium condition, the energy is brought down, and the probability is further investigated with respect to a rotation about the *x*-axis.

The variation of probability with respect to a rotation about the *x*-axis corresponding to the configuration $y(180^\circ)$ has been carried out as shown in Figure 5. It has been observed that a pronounced peak exists at the 2°-rotation point, and all the remaining regions have negligible probability as compared to this configuration. Furthermore, it is observed that the rotational freedom is much more pronounced as compared to the stacking interactions. The variation of the probability with respect to a rotation about the *y*-axis corresponding to the configuration $x(0^\circ)$ has also been carried out. It has been observed that the rotational freedom of the molecule is restricted along the *y*-axis and favours an overlapped layered structure in mesophase.

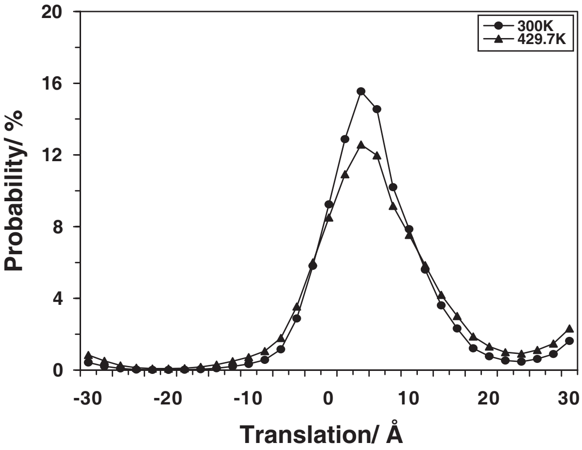

Fig. 4. Variation of probability with respect to translation along *x*-axis during in-plane interactions at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $y(0^\circ)$.

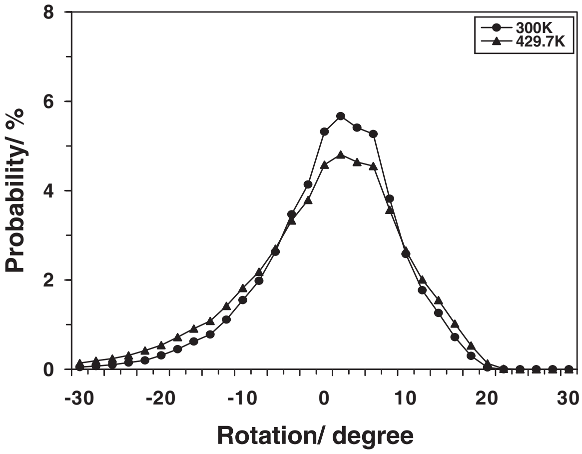

Fig. 5. Variation of probability with respect to rotation about *x*-axis during in-plane interactions at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $y(180^\circ)$.

3.3. Role of Terminal Interactions

The end-to-end interactions are weakest but become more important when the molecules possess a polar group at either or both ends, or if there is a possibility of hydrogen bonding. To investigate the terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the *x*-axis by 22 Å. Figure 6 shows the variation of the probability with respect to a rotation about the *x*-axis at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $y(0^\circ)$. The terminal interactions are much weaker as compared to stacking or in-plane interactions. However, a significant peak has been observed at the equilibrium position due to the possibility of hydrogen bonding. The various possible geometrical arrangements of the molecular pair during the different

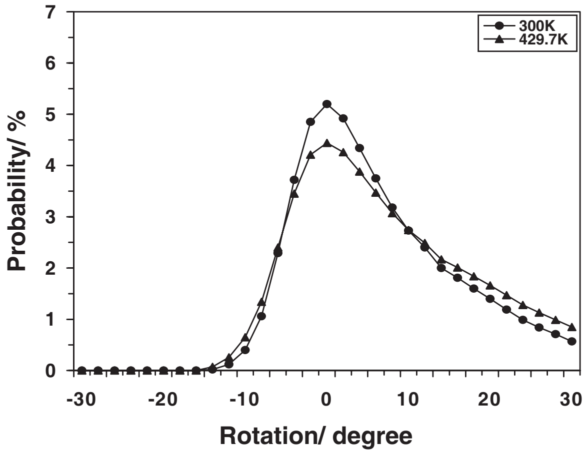

Fig. 6. Variation of probability with respect to rotation about x-axis during terminal interactions at room temperature (300 K) and at smectic-isotropic transition temperature (429.7 K) corresponding to configuration $y(0°)$.

modes of interactions have been considered that provide information about the molecular arrangements inside the bulk materials.

4. Molecular Rigidity and Phase Behaviour

To understand the phase behaviour of the compound, an assumption must be taken into consideration that the flexible alkyl chains in the compound are characterized by a specific disorder mode in each phase. The smectic character of liquid crystals is generally manifested by their rotational/translational freedom about/along axis. In view of this, to examine the results more closely, the molecular rigidity parameters have been calculated with respect to translational and rotational motions during different modes of molecular interactions at room temperature (300 K), at smectic-isotropic transition temperature (429.7 K), and above the transition temperature (500 K).

4.1. Rotational Rigidity

A comparative picture of the rotational rigidity parameter as a function of temperature during stacking, in-plane and terminal interactions between a pair of GAM11 molecules at room temperature (300 K), smectic-isotropic transition temperature (429.7 K), and above transition temperature (500 K) is shown in Table 1. This has been defined as the ratio of probability being at maximum probable point having ±1°-rotations about the z-axis during stacking interactions, while the rotation is extended to the y-axis for in-plane and to the x-axis for terminal interactions. The flexibility of rotation about the z-axis is sufficiently small, which accounts for the smectic character of the GAM11 molecule. Evidently, during the terminal interactions, the molecule can rotate freely about its long molecular axis.

Table 1. Comparative picture of rotational rigidities during stacking, in-plane and terminal interactions between a pair of GAM11 molecules.

	Rotational rigidity		
Temperature / K	Stacking[a]	In-Plane[b]	Terminal[b]
300	0.62	0.61	0.59
429.7 Sm-I	0.60	0.59	0.59
500	0.59	0.58	0.59

[a] rotation about z-axis, [b] rotation about x-axis.

4.2. Translational Rigidity

The translational rigidity parameter as a function of temperature during stacking and in-plane interactions at room temperature (300 K), at smectic-isotropic transition temperature (429.7 K), and above the transition

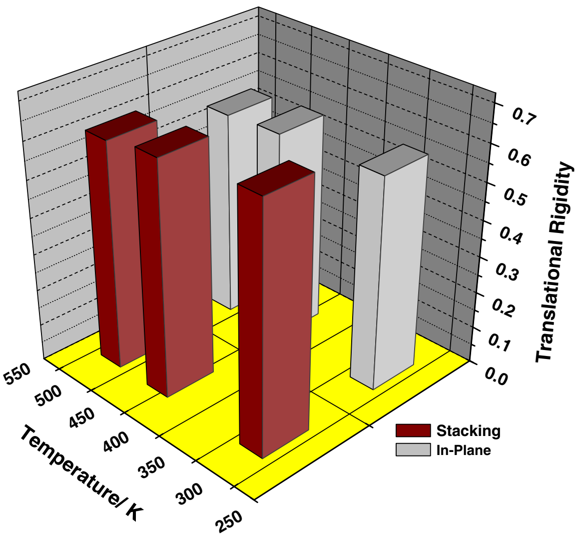

Fig. 7 (colour online). Translational rigidity parameter as a function of temperature during stacking and in-plane interactions at room temperature (300 K), at smectic-isotropic transition temperature (429.7 K), and above transition temperature (500 K).

temperature (500 K) is shown in Figure 7. This has been defined as the ratio of probability being at the maximum probable point having ±0.2 Å displacement along the long molecular axis. Evidently, the translational rigidity along the long molecular axis is 0.64 during stacking interactions at smectic-isotropic transition temperature (429.7 K). However, at room temperature (300 K), the value is 0.67, indicating strong binding at low temperature, which restricts the translational motion in a molecular pair along the planar axis. This ensures the tendency of GAM11 molecules to form a stacked layered structure. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature, this value is 0.58, which reduced to 0.57 at smectic-isotropic transition temperature (429.7 K). It may be noted that, though the freedom is considerable for smaller translation, longer translations are not permitted in general. However, the comparable values in both modes of interactions show that the molecule prefers to form a layered structure at 429.7 K, which accounts for the smectic character of the system.

5. Conclusions

(i) These calculations show that the molecule has a strong capacity of forming a layered structure. A translational motion of a stacked dimer along either of the axes is least probable, while the orientational freedom is completely restricted. All these parameters favour the smectogenic behaviour of the compound in terms of their relative order.

(ii) The estimation of molecular rigidity of a compound provides essential information about the macroscopic behaviour and the other factors responsible to control the equilibrium between the phases of the compound. Further, it explains the smectic behaviour of GAM11 in terms of their relative order. A comparative study on other systems may lead to more general conclusions.

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