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Durga Prasad Ojha[a]; V. G. K. M. Pisipati[a]
[a] Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences, Nagarjuna University, Nagarjuna Nagar -522 510, A.P., India,

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Ordering of fluoro-mesogens: a statistical approach based on quantum mechanics and computer simulation

DURGA PRASAD OJHA and V. G. K. M. PISIPATI*

Centre for Liquid Crystal Research and Education, Faculty of Physical Sciences,
Nagarjuna University, Nagarjuna Nagar -522 510, A.P., India

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Computational analysis of the molecular ordering of nematic *p*-phenylene-4-methoxy benzoyl 4-trifluoromethylbenzoate (FLUORO1) and smectic 4-propyloxyphenyl 4-(4-trifluoromethylbenzoyloxy)benzoate (FLUORO2) mesogens has been carried out with respect to translatory and orientational motions. The net atomic charge and atomic dipole components at each atomic centre of the molecule have been evaluated using the CNDO/2 method. Rayleigh–Schrodinger perturbation theory, along with the multicentred-multipole expansion method, has been employed to evaluate long range intermolecular interactions while a '6-exp' potential function has been assumed for short range interactions. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration at the phase transition temperature using the Maxwell–Boltzmann formula. The flexibility of various configurations has been studied in terms of the variation of probability due to small departures from the most probable configuration. The results obtained enable the determination of the peculiarities of the molecular ordering, as well as the construction of models of the structures of FLUORO1 and FLUORO2 in different modes of interaction. The mesophase nature has been correlated with the parameters introduced in this paper.

1. Introduction

Liquid crystalline materials have been the subjects of extensive study due to the peculiar co-existence of the properties of anisotropic solid and isotropic liquid in a single thermodynamically stable state [1–3]. The majority of mesogenic molecules are composed of an aromatic core with one or two alkyl chains attached [4]. Liquid crystal properties such as the nematic–isotropic transition temperature and the transitions entropy are influenced by the presence of the alkyl chain. In recent years there has been increasing interest in stable phases mediating the transition between different liquid crystalline phases [5–10]. Further, computer simulation is finding an increasingly influential role in understanding the liquid crystal phases [11–14]. However, it is essential to study the simple model in some depth in order to understand the forces responsible for mesophase formation. It is generally agreed that the prime requirement for the formation of a thermotropic liquid crystal is molecular interaction [15].

Recently the role of molecular interactions in mesogenic compounds based on the Rayleigh–Schrodinger perturbation method has been reported by several workers [16–18]. These studies were aimed at computing interaction energy between a molecular pair, and to study the variation of energy with respect to angle and distance between two molecules; their attempts were directed towards explaining the aligned structure or, at best, correlating the minimum energy with observed crystal structure. The interaction energies for a pair of mesogen molecules indicate the preference for a particular configuration over the others depending on their energy values [19, 20]. These values, however, do not reflect the actual relative preference, which can be obtained only through the probability corresponding to each configuration. Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on interaction energy results will provide information regarding the most probable molecular aggregation. Through these computations one can obtain information on dimer complexes; the relative freedom of a molecule in terms of variation in inclination; separation or sliding of one molecule over another, etc.

In this paper, an attempt has been made to identify the characteristic features of fluoro-mesogens in terms of pair energy or configurational probabilities at an intermediate distance of 6 Å for stacking and 8 Å for in-plane

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*Author for correspondence;
e-mail: venkata_pisipati@hotmail.com

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interactions. Similarly, a distance 30 Å has been used 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 short and medium range interactions.

Also, instead of finding the exact minimum energy configuration, an attempt has been made to elucidate the general behaviour of the molecules surrounding a fixed molecule in a particular frame of reference.

An examination of thermodynamic data for the compounds under study indicates that *p*-phenylene-4-methoxybenzoyl 4-trifluoromethylbenzoate (FLUORO1) has a nematic to isotropic transition at 506 K while 4-propyloxyphenyl 4-(4-trifluoromethylbenzoyloxy)-benzoate (FLUORO2) shows a smectic A to isotropic melt transition at 488 K [21].

2. Simplified formula and computational technique

The molecular geometries of FLUORO1 and FLUORO2 have been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [21]. In order to determine the interaction energy between two molecules, it is necessary to compute atomic net charges and dipole moments through an all-valence-electron method. In the present computation, the CNDO/2 method [22] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. The calculations have been carried out in two stages as given below.

2.1. *Computation of interaction energy at various configurations*

A computer program based on a simplified formula for the evaluation of interaction energy between a molecular pair has been used to calculate the energy for fixed configuration. According to the second order perturbation theory as modified for intermediate range interactions [23], the total pair interaction energy of molecules (U_{pair}) is represented as the sum of various terms contributing to the total energy:

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

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

Again, the 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 up to only the dipole–dipole term gives a satisfactory result [24]. The computation of electrostatic term has, therefore, been restricted only upto dipole-dipole energy term.

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

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

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

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 [25].

In this case, the origin on an atom has been chosen close to the centre of mass of the molecule. The X-axis is along the molecular long axis while the Y-axis lies in the plane of the molecule and Z-axis is perpendicular to the molecular plane.

2.2. *Computation of configurational probabilities*

The total interaction energy values obtained through these computations were used as input to calculate the intrinsic probability of each configuration with the help of the Maxwell–Boltzmann formula [26]:

$$P_i = \exp(-\beta\varepsilon_i) / \sum_i \exp(-\beta\varepsilon_i); \quad \beta = 1/kT$$

where P_i is the probability of occurrence of a particular configuration, k is the Boltzmann constant, T is the absolute temperature and ε_i is the relative energy of configuration i to the minimum energy configuration.

3. Results and discussion

The molecular geometries of FLUORO1 and FLUORO2 are shown in figure 1. The results of probability distribution based on interaction energy corresponding to the different modes of interactions are discussed below.

3.1. *Stacking interactions*

In a molecular pair, one of the interacting molecules is fixed in the XY-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 of probability with respect to

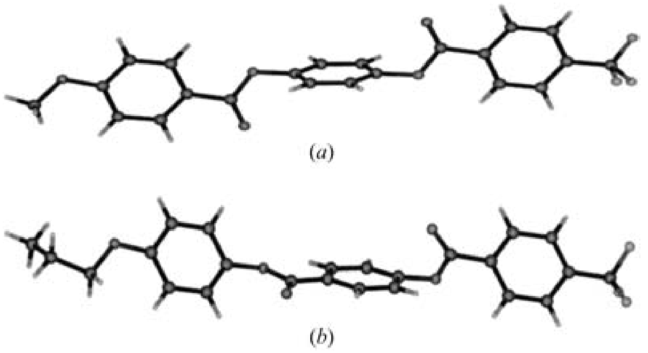

Figure 1. Molecular geometry of (*a*) FLUORO1, (*b*) FLUORO2.

rotation about the Z-axis is shown in figure 2 corresponding to configuration $X(0°)$ $Y(0°)$ at the phase transition temperature. Figure 2 shows that the maximum probability for FLUORO1 is at $-5°$, while for FLUORO2 it is at $-15°$ rotation. The flexibility of rotation is rather small for FLUORO2, 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 minimum energy so obtained is taken as starting point and the entire process is repeated for small intervals. The energy has been minimized with respect to translation and rotation about all axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. It is important to note here that the path of minimization depends strictly on the objective of the computation. The global search for minimum energy configuration, or the study of variation of interaction energy under pre-selected conditions, will have completely different paths, therefore one has to be careful in choosing the specific route.

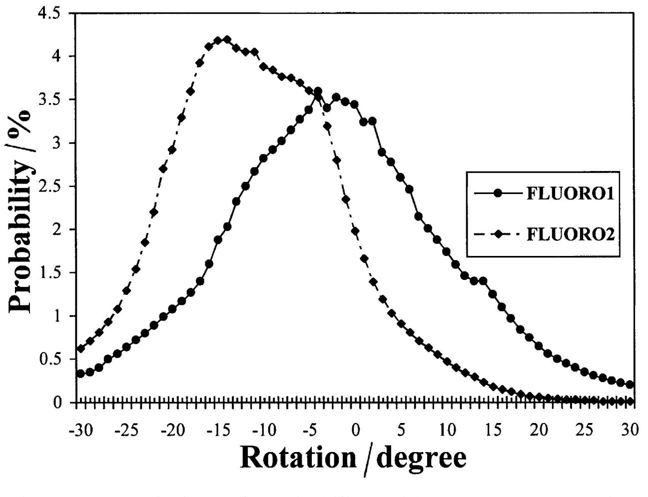

Figure 2. Variation of probability with respect to rotation about the Z-axis during stacking interactions at the phase transition temperature (FLUORO1 at 506 K and FLUORO2 at 488 K).

Having refined the interacting configuration with respect to rotation about the Z-axis at equilibrium, the energy is reduced and the probability is further investigated with respect to translation along the molecular long axis (X-axis) corresponding to configuration $Y(0°)$ $Z(180°)$ (figure 3). It may be observed that the configuration shows a sharp preference towards the minimum energy point. The variation of probability is almost constant in the region of 2.2 ± 0.6 Å for FLUORO1 without any significant change in the energy, hence it is capable of retaining molecular order up to 3 Å against increased thermal agitation.

The variation of probability with respect to rotation about the X-axis corresponding to configuration $Y(0°)$ is shown in figure 4 at the phase transition temperature. The maximum for FLUORO2 is at 11° rotation while for FLUORO1 it is at $-2°$, indicating a slight preference for the aligned structure of this configuration.

3.2. *In-plane interactions*

The interacting molecule has been kept at separation of 8 Å along the Y-axis with respect to fixed one to avoid the possibility of van der Waals contacts, and similar calculations have been performed for in-plane interactions. The effect of translation along the X-axis corresponding to configuration $Y(0°)$ is shown in figure 5 at the phase transition temperature. Since in-plane interactions are weaker than the stacking interactions, a greater freedom corresponding to translation is observed. It is evident from the figure 5 that the maximum probability occurs at an equilibrium position. Having refined the interacting configuration with respect to translation along the X-axis at equilibrium condition, the energy is reduced

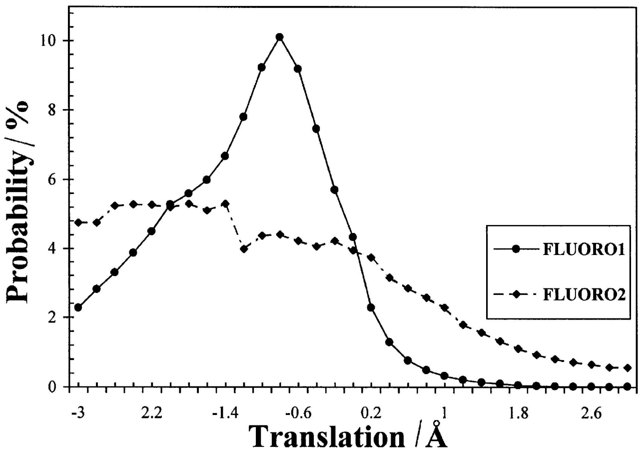

Figure 3. Variation of probability with respect to translation along the X-axis during stacking interactions at the phase transition temperature.

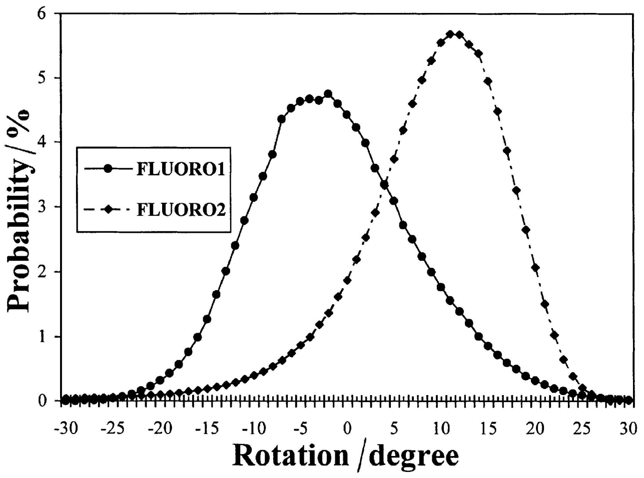

Figure 4. Variation of probability with respect to rotation about the X-axis during stacking interactions at the phase transition temperature.

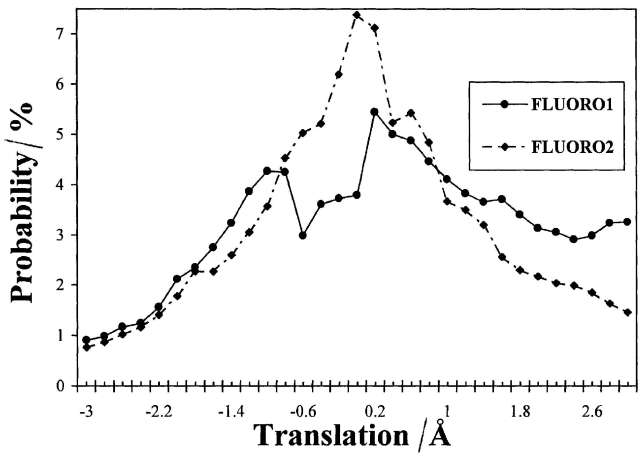

Figure 5. Variation of probability with respect to translation along the X-axis during in-plane interactions at the phase transition temperature.

and the probability is further investigated with respect to rotation about the X-axis. A graphical representation of the probability distribution with respect to rotation about the X-axis corresponding to configuration $Y(0°)$ is shown in figure 6. The significant maximum in probability is observed near the equilibrium point at the phase transition temperature.

Furthermore, it is clear that the rotational freedom is much more pronounced as compared with the stacking interactions. Figure 7 shows the variation of probability with respect to rotation about the Y-axis corresponding to configuration $X(180°)$. Evidently the probability drastically changes in the region of $7° \pm 3°$ for FLUORO2, which restricts the rotational freedom of the molecule along the Y-axis and favours a layered structure in the mesophase.

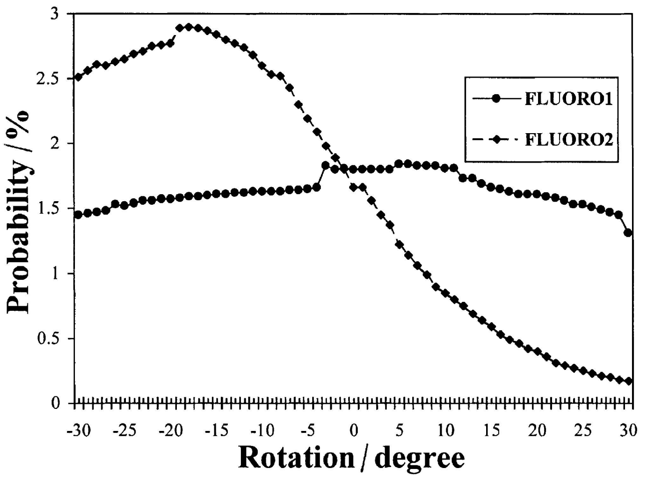

Figure 6. A graphical representation of probability with respect to rotation about the X-axis during in-plane interactions at the phase transition temperature.

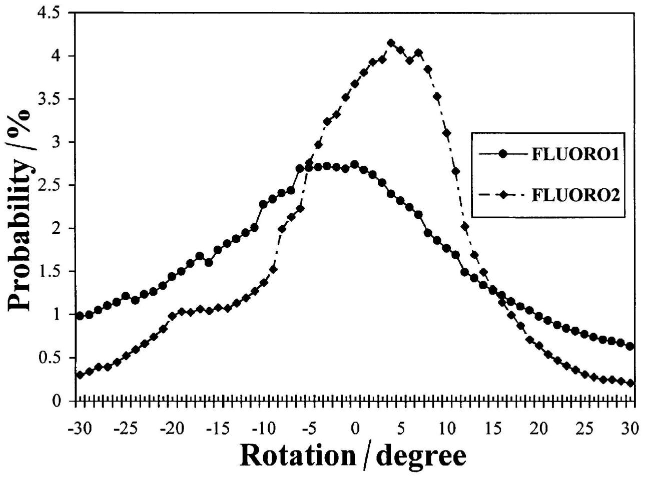

Figure 7. Variation of probability with respect to rotation about the Y-axis during in-plane interactions at the phase transition temperature.

3.3. *Terminal interactions*

To investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the X-axis by 30 Å. Terminal interactions are much weaker than the stacking and in-plane interactions. Rotations about the X-axis (figure 8) show no angular preference. The refined interaction energies corresponding to the different modes of interactions (i.e. stacking, in-plane and terminal) are reported in table 1, with all the contributing terms for comparison. It seems important to note that the largest attractive contribution in stabilizing the stacked, in-plane and terminal interacting pairs of FLUORO1 and FLUORO2 molecules comes from the dispersion forces. Moreover, all possible geometrical arrangements between a molecular pair of

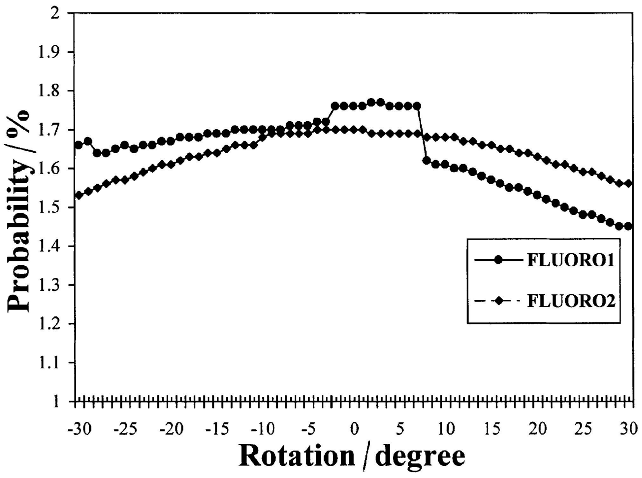

Figure 8. Variation of probability with respect to rotation about the X-axis during terminal interactions at the phase transition temperature.

Table 1. Stacking, in-plane and terminal interaction energy (kcal mol^{-1}) between pairs of FLUORO1 and FLUORO2 molecules after refinement.

Interaction	U_{total}	U_{el}	U_{pol}	U_{disp}	U_{rep}
FLUORO1					
Stacking	−12.566	−0.814	−0.724	−18.414	7.386
In-plane	−4.866	−0.332	−0.566	−6.227	2.259
Terminal	−1.550	−0.567	−0.113	−1.462	0.593
FLUORO2					
Stacking	−14.199	−0.657	−0.731	−19.766	6.954
In-plane	−7.397	−1.269	−0.858	−9.583	4.313
Terminal	−1.747	−0.275	−0.069	−1.849	0.449

fluoro-mesogens have been considered and provide an insight of molecular arrangements inside bulk materials.

It may be concluded from the above discussion that in a molecular assembly a number of local minimum energy configurations exist. Each has an individual importance, as in the case of close molecular packing, and depending on its own spatial position may be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance because while descending from a very high temperature where the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy, and the others have a sequential preference depending on their individual relative probabilities.

The most favourable stacked configuration of pairing for FLUORO2 has been obtained at an interplanar separation of 3.7 Å with energy −14.199 kcal mol^{-1}. This configuration agrees with those obtained from crystallographic studies [21]; see figure 9.

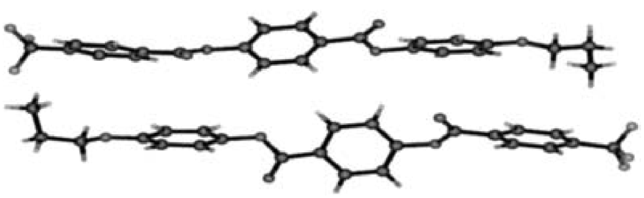

Figure 9. The most favourable stacked configuration of pairing has been obtained for FLUORO2 at an interplanar separation of 3.7 Å with energy −14.199 kcal mol^{-1}.

4. Correlation of the results

In order to examine the results more closely the following parameters have been calculated and an attempt has been made to understand the molecular behaviour in terms of their relative order.

4.1. *Translational rigidity*

This has been defined as the ratio of probability at maximum probable point to that having ±0.2 Å displacement along the molecular long axis. Table 2 shows that the ratio of probability along the molecular long axis is 0.62 at the nematic–isotropic transition temperature (506 K) for FLUORO1. However, at room temperature (300 K), the value is 0.71, indicating a strong binding; with increase of temperature, the molecules obtain sufficient freedom to slide along the molecular long axis. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature this value is 0.59 for FLUORO2, reducing to 0.55 at the nematic–isotropic transition temperature. It may be noted that although the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus in the mesomorphic range, only small movements of the molecules are possible. However, the comparable values in both cases show that the molecule FLUORO1 shows no great preference for forming stacked layers, hence justifying the nematic character.

Table 2. Translational rigidities along the molecular long axis (X-axis) for pairs of FLOURO1 and FLUORO2 molecules.

	Probability ratio	
Temperature/K	Stacking interaction	In-plane interaction
FLUORO1		
300	0.71	0.59
506 N–I	0.62	0.55
550	0.61	0.54
FLUORO2		
300	0.59	0.53
488 SmA–I	0.55	0.52
550	0.55	0.55

Table 3. Comparative pictures of rotational rigidities for pairs of FLUORO1 and FLUORO2 molecules.

Temperature/K	Rotational rigidity Stacking interaction	 In-plane interaction	 Terminal interaction
FLUORO1			
300	0.55	0.52	0.50
506 N–I	0.53	0.51	0.50
550	0.53	0.51	0.50
FLUORO2			
300	0.51	0.52	0.50
488 SmA–I	0.51	0.51	0.50
550	0.51	0.51	0.50

It may be noted that the rigidities decrease with increase of temperature. Furthermore, the nature of the curve in figure 5 shows the tendency of FLUORO2 molecules to form a layered structure at the smectic A to isotropic transition temperature (488 K).

4.2. *Rotational rigidity*

This has been defined as the ratio of probability at maximum probable point to that having $\pm 1^\circ$ rotation about the Z-axis during stacking interactions, while the rotation is extended about the Y-axis for in-plane and X-axis for terminal interactions (table 3). It may, therefore, be concluded that the flexibility of rotation about the Z-axis is rather small (figure 2), which accounts for the smectic character of the FLUORO2 molecule. Table 3 clearly shows that during terminal interactions, the molecules can rotate freely about the molecular long axis.

These two parameters may be of help in understanding the mesogenic character of the molecules in terms of their relative order. A comparative study on other systems may lead to more general conclusion.

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