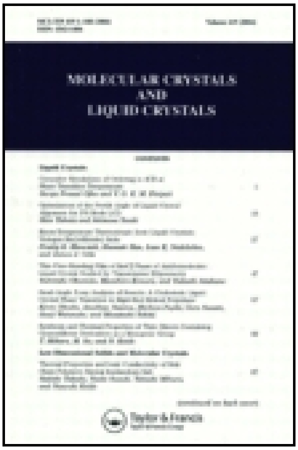

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Ordering of smectogenic compounds--a statistical approach based on quantum mechanics and computer simulation

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ORDERING OF SMECTOGENIC COMPOUNDS— A STATISTICAL APPROACH BASED ON QUANTUM MECHANICS AND COMPUTER SIMULATION

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A statistical analysis of molecular ordering of smectogenic compounds, 3-[2-(perflurooctyl) ethoxy] nitrobenzene (FLUORO1) and ethyl 4-[2-(perfluorooctyl) ethoxy] benzoate (FLUORO2), have been carried out with respect to translatory and orientational motions. The net atomic charge and atomic dipole components at each atomic center of the molecule has been evaluated using the CNDO/2 method. The Rayleigh-Schrodinger perturbation theory, along with the multicentered-multipole expansion method, has been employed to evaluate the long-range intermolecular interactions while "6-exp" potential function is assumed for short-range interactions. The total interaction energy values obtained through these computations were used to calculate the probability of each configuration at its phase transition temperature using the Maxwell-Boltzmann formula. The flexibility of various configurations has been studied in terms of variation of probability due to small departures from the most probable configuration. The results obtained have been correlated with the parameters introduced in this article.

Keywords: fluoro-mesogens; statistical analysis; CNDO/2 method; quantum chemistry; computer simulation

INTRODUCTION

The Liquid crystalline materials are known for their anomalous physical properties near the phase transitions and maintain orientational order in mesophase [1,2]. The phase behavior of liquid crystals is a subject of growing interest from the fundamental and applied points of view [2]. Recently there has been increasing interest in stable phases mediating the

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*Corresponding author. E-mail: venkata_pisipati@hotmail.com transition between different liquid crystalline phases [3–7]. In particular, interest has focused on smectic liquid crystals in which the degree of order within the layers changes, quite often very subtly, form one phase to another. In smectic *A*, for example, the director is parallel to the normal of the layer. Further, the simulation of liquid crystal phase behavior represents a major challenge despite the substantial increase in the availability of computer processing time [8–11]. However, it is essential to study the simple model in some depth in order to understand the forces responsible for mesophase formation. The possibility also exists to extend these simple models by building in realistic features such as molecular flexibility, complicated structural anisotropy, and electrostatic forces. Anisotropy in the molecular interactions is required for the formation of thermotropic liquid crystals [12].

The mesomorphic behavior of liquid crystalline substances rests upon the typical aggregation of molecular clusters. The molecular property, which causes such aggregation, needs intense investigation. The theoretical attempts reported in the literature largely involve evaluation of order parameters, transition temperature, etc. on the basis of a general statistical theory applicable to the nematic and to some extent the smectic liquid crystals where no consideration of actual molecular structure is taken into account. On the other hand, the methods, which consider actual molecular structure, focus their attention to structural properties only.

Calculations of intermolecular interactions of mesogenic compounds, based on the Rayleigh-Schrodinger perturbation theory, have been reported by several workers [13–15]. These studies were aimed at explaining the aligned structure or, at best, correlating the minimum energy with the observed crystal structure. The interaction energies for a pair of mesogens indicate the preference of a particular configuration over the others depending on their energy values. These values, however, do not reflect the actual relative preference, which can be obtained only through their probabilities corresponding to each configuration. It is, therefore, still important to investigate the relative freedom of the molecule apart from the minimum energy configuration in terms of (a) variations in orientation, and (b) translations along the long molecular axis.

In the present article, we report the characteristic features of fluoromesogens in terms of their energy and configurational probabilities between a molecular pair of FLUORO1 and FLUORO2 molecules 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 the 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.

Also, 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 indicates that FLUORO1 and FLUORO2 appears a mesophase, although monotropic, for uni-ring molecules as given below [16]:

FLUORO1 Crystal-328K-(S_A-314K)-Isotropic
FLUORO2 Crystal-353K-(S_A-343K)-Isotropic

THE BASIC FORMALISM AND COMPUTATIONAL TECHNIQUE

The molecular geometry of FLUORO1 and FLUORO2 has been constructed on the basis of published crystallographic data with the standard values of bond lengths and bond angles [16]. In FLUORO1 and FLUORO2, head-to-head arrangements result in the segregation of perfluorochains and the other moieties. The calculations have been carried out in three stages, as outlined below.

Evaluation of Charge and Atomic Dipole Distribution

The simplified formula for interaction energy calculations require the evaluation of atomic net charges and dipole moment components at each atomic center through an all-valence-electron method. In the present computation, the CNDO/2 method [17] 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 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 [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 modifications. According to the second order perturbation theory as modified for intermediate range interactions [18], the total pair interaction energy of molecules (U_{pair}) is represented by

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

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

Again, electrostatic term is expressed as

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

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

In the present computation, the dispersion and short-range repulsion terms are considered together because several semiemperical approaches, viz. 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:

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

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

where $Z = R_{\lambda v}/R^0_{\lambda v}; R^0_{\lambda v} = [(2R^w_\lambda)(2R^w_v)]^{1/2}$, where R^w_λ and R^w_v are the van der Waals radii of atoms λ and v, respectively. The parameters A, B, and γ do not depend on the atomic species. However, $R^0_{\lambda v}$ and factor $K_\lambda K_v$ allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found in Ojha [20] and Ojha and Pisipati [21].

To facilitate these calculations, an orthogonal coordinate system is defined by taking the origin of an atom close to the center of mass of the molecule. The X-axis is along the long molecular axis, while the Y-axis lies in the plane of the molecule and the Z-axis is perpendicular to the molecular plane.

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 Maxwell-Boltzmann formula [21]:

$$P_i = exp(-\beta\varepsilon_i) \Big/ \sum\nolimits_i exp(-\beta\varepsilon_i); \quad \beta = 1/kT,$$

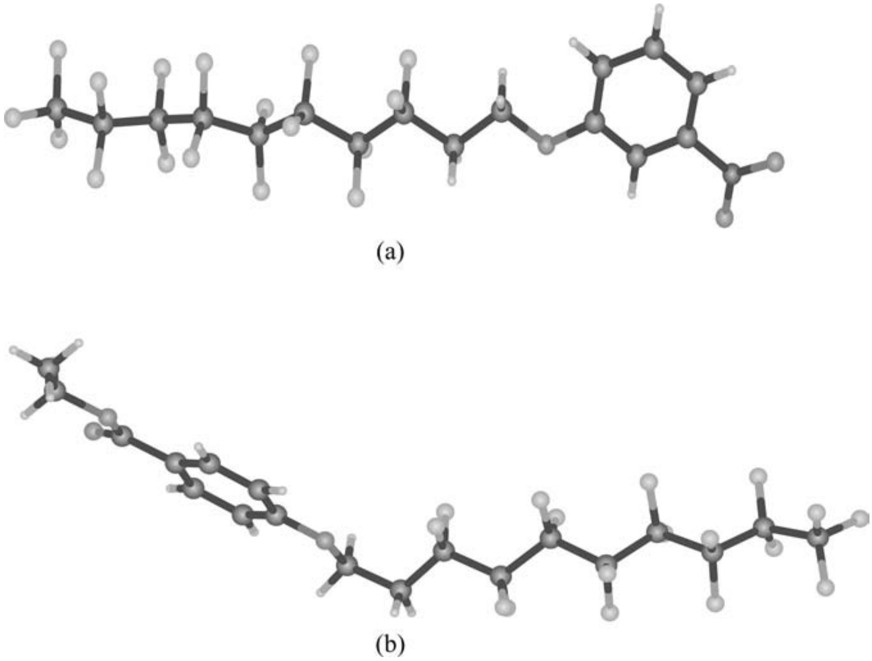

FIGURE 1 Molecular geometry of (a) FLUORO1 and (b) FLUORO2.

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.

RESULTS AND DISCUSSION

The molecular geometry of FLUORO1 and FLUORO2 is shown in Figure 1. Computed atomic net charges and dipole moment components are listed in Table 1. The results of probability distribution based on interaction energy calculations 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 angular dependence of probability with respect to rotation about the Z-axis is shown in Figure 2 corresponding to configuration X(0°) Y(0°) at I-S_A transition temperature. An observation of Figure 2 reveals

TABLE 1 Calculated Atomic Net Charges and Dipole Moments Using the CNDO/2 Method for the Molecule FLUORO1 and FLUORO2

			Atomic dipole components		
S. No.	Atom	Charge	μ_X	μ_Y	μ_Z
FLUORO1 ($C_{16}H_8O_3F_{17}N$)					
1	C	0.063	−0.137	−0.194	0.007
2	C	−0.014	−0.172	0.142	−0.007
3	C	0.026	−0.143	−0.013	−0.001
4	C	−0.051	−0.096	−0.116	0.007
5	C	0.189	−0.138	0.112	0.014
6	C	−0.048	0.225	−0.048	0.002
7	O	−0.226	1.358	0.104	−0.089
8	C	0.159	−0.236	−0.113	0.016
9	C	−0.067	0.138	0.161	−0.027
10	C	0.394	0.341	0.196	−0.026
11	C	0.332	−0.459	−0.009	−0.039
12	C	0.347	0.351	0.142	0.120
13	C	0.351	−0.319	−0.069	−0.218
14	C	0.348	0.218	0.113	0.302
15	C	0.354	−0.153	−0.052	−0.333
16	C	0.308	0.070	0.033	0.379
17	C	0.601	−0.076	0.285	−0.167
18	N	0.461	−0.036	−0.015	0.003
19	O	−0.339	−0.742	1.154	−0.273
20	O	−0.327	1.381	−0.019	0.249
21	F	−0.209	−0.496	−0.200	−0.676
22	F	−0.206	−0.498	−0.050	0.709
23	F	−0.188	0.452	0.135	0.753
24	F	−0.185	0.574	0.114	−0.672
25	F	−0.169	−0.775	−0.054	0.481
26	F	−0.184	−0.156	−0.195	−0.845
27	F	−0.181	−0.009	0.062	0.889
28	F	−0.173	0.836	0.216	−0.289
29	F	−0.173	−0.893	−0.125	0.034
30	F	−0.179	0.279	−0.108	−0.844
31	F	−0.185	−0.447	−0.058	0.752
32	F	−0.169	0.837	0.275	0.241
33	F	−0.171	−0.819	−0.206	−0.299
34	F	−0.167	0.664	0.023	−0.618
35	F	−0.207	−0.641	−0.120	0.562
36	F	−0.197	0.726	0.153	0.484
37	F	−0.173	0.067	−0.782	−0.483
38	H	0.051	0.000	0.000	0.000
39	H	0.052	0.000	0.000	0.000
40	H	0.001	0.000	0.000	0.000
41	H	−0.000	0.000	0.000	0.000

(*Continued*)

TABLE 1 Continued

			Atomic dipole components		
S. No.	Atom	Charge	μ_X	μ_Y	μ_Z
42	H	0.040	0.000	0.000	0.000
43	H	0.019	0.000	0.000	0.000
44	H	0.028	0.000	0.000	0.000
45	H	0.055	0.000	0.000	0.000
FLUORO2 ($C_{19}H_{13}O_3F_{17}$)					
1	C	−0.062	0.062	0.063	−0.019
2	C	0.044	−0.052	0.115	0.006
3	C	−0.074	−0.134	0.036	−0.004
4	C	0.201	0.099	0.210	0.022
5	C	−0.065	0.097	−0.119	−0.005
6	C	0.038	0.130	−0.003	−0.000
7	O	−0.223	0.742	−1.124	−0.132
8	C	0.165	−0.167	0.181	0.014
9	C	−0.088	−0.037	0.051	−0.139
10	C	0.377	−0.185	−0.088	−0.223
11	C	0.344	0.209	0.129	0.351
12	C	0.362	−0.112	−0.189	−0.313
13	C	0.348	0.039	0.202	0.324
14	C	0.349	0.037	−0.208	−0.327
15	C	0.353	−0.111	0.223	0.292
16	C	0.314	0.183	−0.240	−0.256
17	C	0.593	−0.032	0.338	−0.004
18	C	0.387	−0.228	−0.092	0.033
19	O	−0.330	−0.633	1.208	0.093
20	O	−0.255	0.586	−1.166	−0.104
21	C	0.157	0.053	0.239	−0.002
22	C	−0.056	0.166	−0.052	−0.006
23	F	−0.187	0.859	−0.154	0.018
24	F	−0.164	−0.194	0.454	0.759
25	F	−0.178	0.340	−0.533	−0.639
26	F	−0.181	−0.872	0.117	−0.162
27	F	−0.166	0.870	0.041	0.292
28	F	−0.172	−0.548	0.408	0.602
29	F	−0.181	0.664	−0.457	−0.370
30	F	−0.166	−0.752	−0.083	−0.519
31	F	−0.182	−0.778	0.301	0.302
32	F	−0.168	0.664	0.239	0.578
33	F	−0.182	0.826	−0.312	−0.098
34	F	−0.171	−0.492	−0.264	−0.723
35	F	−0.162	−0.897	0.146	0.033
36	F	−0.169	0.395	0.359	0.734
37	F	−0.185	−0.317	−0.420	−0.734

(*Continued*)

TABLE 1 Continued

			Atomic dipole components		
S. No.	Atom	Charge	μ_X	μ_Y	μ_Z
38	F	−0.192	0.853	−0.221	0.106
39	F	−0.191	−0.443	−0.268	0.713
40	H	0.052	0.000	0.000	0.000
41	H	0.059	0.000	0.000	0.000
42	H	−0.001	0.000	0.000	0.000
43	H	−0.003	0.000	0.000	0.000
44	H	0.016	0.000	0.000	0.000
45	H	0.018	0.000	0.000	0.000
46	H	0.027	0.000	0.000	0.000
47	H	0.016	0.000	0.000	0.000
48	H	−0.006	0.000	0.000	0.000
49	H	−0.004	0.000	0.000	0.000
50	H	0.021	0.000	0.000	0.000
51	H	0.022	0.000	0.000	0.000
52	H	0.022	0.000	0.000	0.000

that the maximum probability corresponds to FLUORO1 at 1° and FLUORO2 at −1° rotations. 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 minimum energy so obtained is then taken as the starting point and the entire process is repeated at smaller intervals. The minimum energy has been minimized with respect to translation and rotation about X, Y, and Z-axis. An accuracy of 0.1 Å in translation and 1° 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 the computation. The global search for minimum energy configuration is difficult and time consuming since it would involve many unphysical configurations, which could be avoided by choosing a suitable path of minimization.

Having refined the interacting configuration with respect to rotation about Z-axis at equilibrium, the energy is brought down and the probability is further investigated with respect to translation along the Z-axis corresponding to configuration X(0°)Y(180°). It has been observed that the probability of perpendicular stacking is almost negligible, which agrees with the fact that mesogenic compounds are least expected to have a

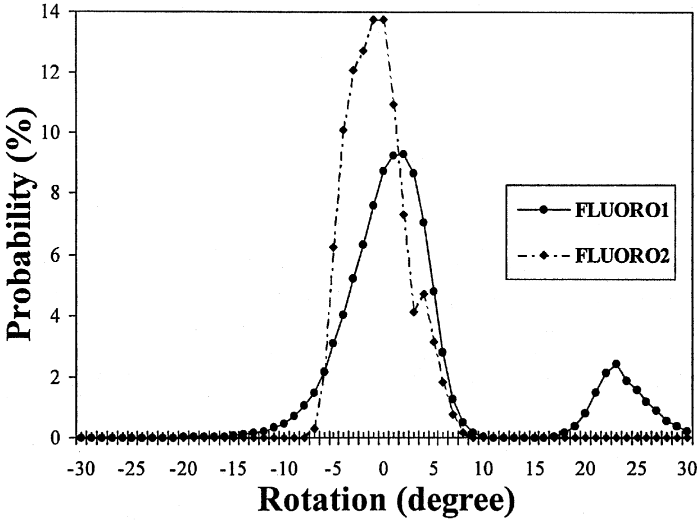

FIGURE 2 Angular dependence of probability with respect to rotation about Z-axis during stacking interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

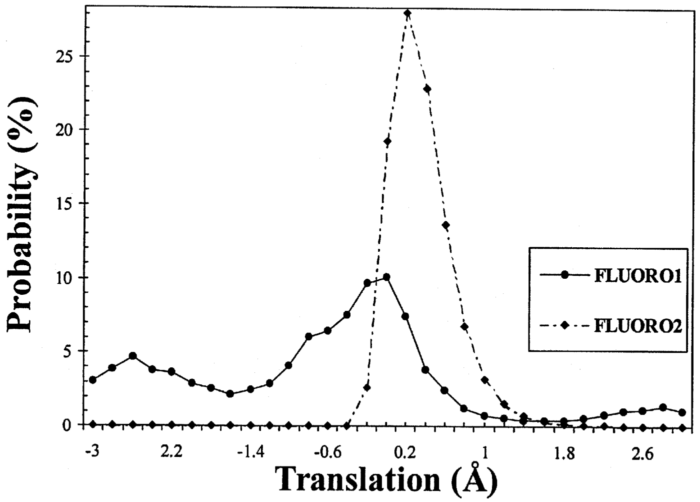

FIGURE 3 Variation of probability with respect to translation along X-axis during stacking interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

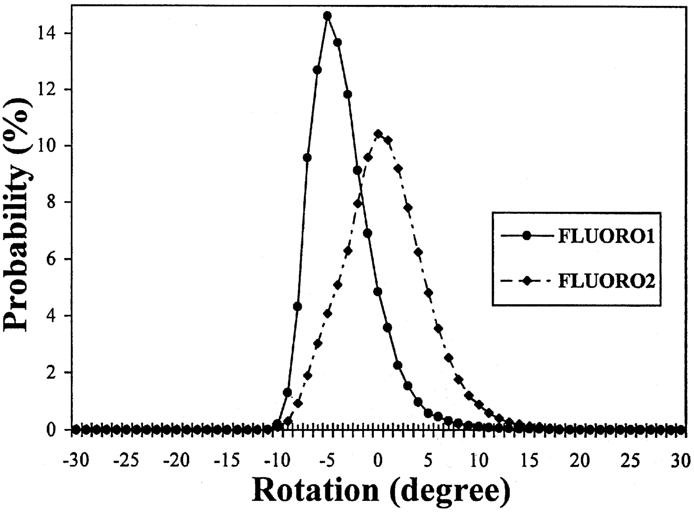

FIGURE 4 Variation of probability with respect to rotation about X-axis during stacking interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

perpendicular stacked configuration. The variation of probability with respect to translation along the long molecular axis (X-axis) corresponding to configuration Y(0°)Z(180°) is shown in 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 1.6 Å ± 0.2 Å without any significant change in the energy, and hence is capable of retaining molecular order upto 3 Å against increased thermal agitation.

The variation of probability with respect to rotation about X-axis corresponding to configuration Y(0°) is shown in Figure 4 at I-S_A transition temperature. The maximum probability corresponds to FLUORO1 at $-5°$ rotations while the maximum probability for FLUORO2 at an equilibrium position indicating a slight preference for aligned structure of this configuration.

In-plane Interactions

To avoid the possibility of van der Waals contacts completely, the interacting molecule has been kept at separation of 8 Å along Y-axis with respect to the fixed one. The similar calculations have been performed for in-plane interactions. The variation of probability with respect to translation along X-axis corresponding to configuration Y(0°) is shown in Figure 5 at I-S_A transition temperature. Since in-plane interactions are weaker than the

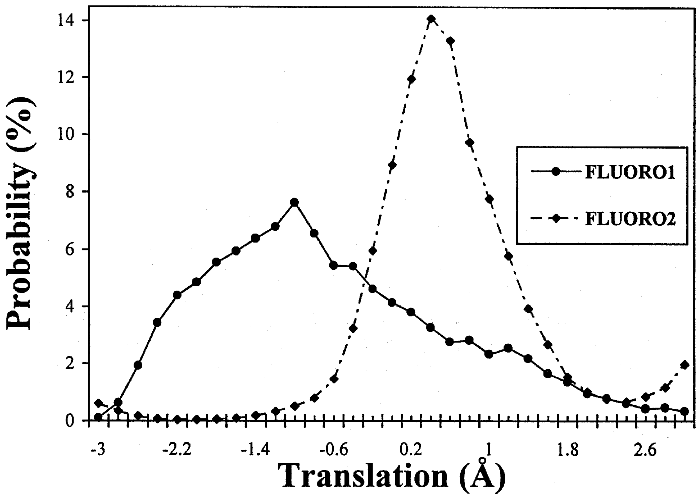

FIGURE 5 Variation of probability with respect to translation along X-axis during in-plane interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

stacking interactions, a greater freedom corresponding to translation is observed. It is evident from the figure that the maximum probability occurs at an equilibrium position. Having refined the interacting configuration with respect to translation along X-axis at equilibrium condition, the energy is brought down and the probability is further investigated with respect to rotation about X-axis. Figure 6 shows the variation of probability with respect to rotation about X-axis corresponding to configuration Y(0°). A pronounced peak exists at an equilibrium point at I-S_A transition temperature, and all the remaining regions have negligible probability as compared to this configuration.

Further, it may be observed that the rotational freedom is much more pronounced as compared to stacking interactions. Figure 7 shows the variation of probability with respect to rotation about Y-axis corresponding to configuration X(180°) at I-S_A transition temperature. Evidently, the probability changes drastically in the range of 3° ± 2° rotations, which restricts the rotational freedom of the molecule along Y-axis and favors an overlapped layered structure in mesophase.

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

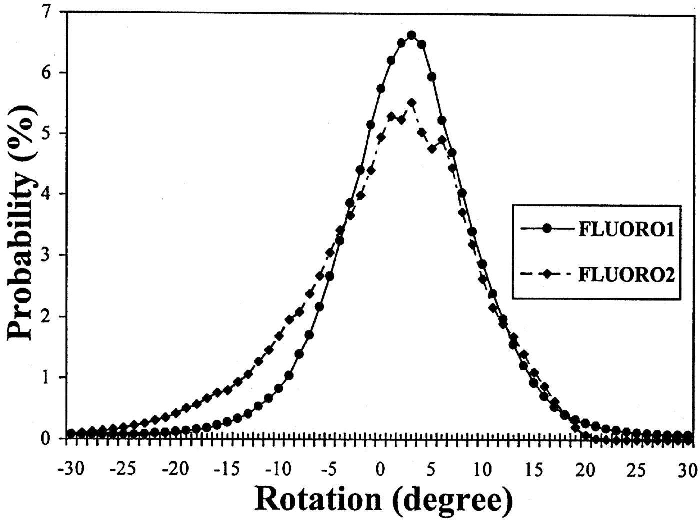

FIGURE 6 Variation of probability with respect to rotation about X-axis during in-plane interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

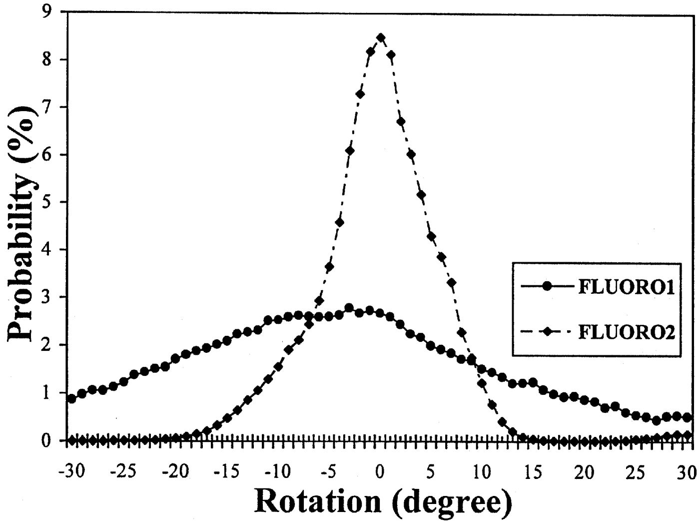

FIGURE 7 Variation of probability with respect to rotation about Y-axis during in-plane interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

away from van der Waals contacts, the interacting molecule has been shifted along the X-axis by 22 Å. The terminal interactions are much weaker than the stacking and in-plane interactions. A graphical representation of probability distribution with respect to rotation about X-axis (Fig. 8) shows no preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis. Although a minimum energy configuration has been marked in this case, too, it has not been emphasized in reporting the results. The various possible geometrical arrangements of a molecular pair during the different modes (i.e., stacking, in-plane, and terminal) of interactions have been considered and provide information about the molecular arrangements inside the bulk materials.

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

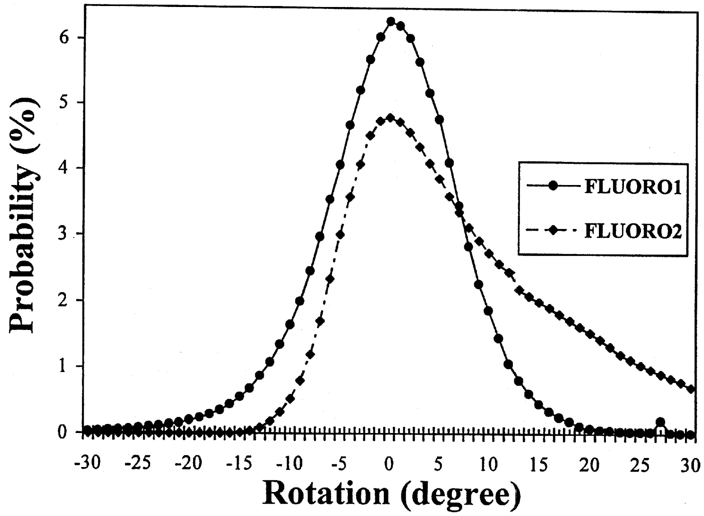

FIGURE 8 Variation of probability with respect to rotation about X-axis during terminal interactions at I-S_A transition temperature (FLUORO1 at 314 K and FLUORO2 at 343 K).

CORRELATION OF THE RESULTS WITH SMECTOGENICITY

The results may closely examine with the following parameters (*viz. Translational Rigidities and Rotational Rigidities*), and attempt has been made to understand the molecular behavior in terms of their relative order.

Translational Rigidities

This has been defined as the ratio of probability being at maximum probable point having ± 0.2 Å displacement along the long molecular axis. Table 2 compares the translational rigidities for stacking and in-plane interactions. It may be noted that the rigidities decrease slowly with the increase of temperature. Further, the nature of curves in Figures 3 and 5 show the tendency of fluoro-mesogens to form a layered structure at isotropic-to-smectic *A* transition temperature.

Rotational Rigidities

This has been defined as the ratio of probability being at maximum probable point having ± 1° rotation about 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 sufficiently small (Fig. 2), which accounts for the smectic character of the molecules. Table 2 clearly shows that during terminal interactions, the molecules can rotate freely about its long molecular axis.

TABLE 2 Translational Rigidities Along the Long Molecular Axis (X-axis) During Stacking and In-plane Interactions Between a Pair of FLUORO1 and FLUORO2 Molecules

	Probability ratio	
Temperature (K)	Stacking interactions	In-plane interactions
FLUORO1		
300	0.59	0.58
314 I-S_A	0.58	0.57
550	0.56	0.55
FLUORO2		
300	0.69	0.56
343 I-S_A	0.66	0.55
550	0.63	0.54

TABLE 3 Comparative Pictures of Rotational Rigidities During Stacking About Z-axis, In-plane About Y-axis, and Terminal Interactions About X-axis Between a Pair of FLUORO1 and FLUORO2 Molecules

	Rotational rigidities		
Temperature (K)	Stacking interactions	In-plane interactions	Terminal interactions
FLUORO1			
300	0.52	0.52	0.51
314 I-S_A	0.52	0.52	0.51
400	0.51	0.51	0.51
FLUORO2			
300	0.52	0.52	0.50
343 I-S_A	0.51	0.51	0.50
400	0.51	0.51	0.50

These calculations show that molecules have a strong capacity of forming a layered structure. Translational motion of a stacked dimer along either of the axes is least probable, while orientational freedom is completely restricted. All of these parameters favor the smectogenic behavior of the compounds in terms of their relative order. A comparative study on other systems may lead to more general conclusions.

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