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Mihir Roychoudhury [a] & Durga Prasad Ojha [a]

[a] Department of Physics, University of Gorakhpur, Gorakhpur, 273009, India

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Theoretical Study of Order in a Liquid Crystal

MIHIR ROYCHOUDHURY and DURGA PRASAD OJHA
Department of Physics, University of Gorakhpur, Gorakhpur-273009, India

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A theoretical analysis has been carried out to determine the configurational preference of a pair of 4-(4′-ethoxyphenylazo) phenyl valerate (EPPV) molecules with respect to translatory and orientational motions. Configuration energy has been computed using modified Rayleight-Schrodinger perturbation method at an interval of 1 Å in translation and 10° in rotations and corresponding probabilities have been calculated using MB statistics. An attempt has been made to identify the most probable configuration at phase transition temperature. Further, the flexibility of various configurations have been studied in terms of variation of probability due to small departures from the most probable configuration. The nature of mesophase has also been correlated with the parameters introduced in this paper.

Keywords: EPPV, nematogen, CNDO/2 method, MB statistics

INTRODUCTION

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 literature largely involve evaluation of order parameters, transition temperature etc. on the basis of a general statistical theory applicable to nematics and to some extent to smectic liquid crystals where almost 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. Thus, for example, Perrin and Berges[1] carried out conformational studies on mesogens. Tokita *et al.*[2] and Sanyal *et al.*[3,4] however, computed interaction energy between a molecular pair to study the variation of interaction energy with respect to angle and distance between two molecules but their attempts were directed towards explaining the aligned structure or at best, correlating the energy minimum with the observed crystal structures. Sanyal *et al.* in their later papers[5–8] attempted to correlate intermolecular interaction with liquid crystallinity but the studies had some inherent limitations. The interaction energies for a pair of mesogens indicate the preference of a particular configuration over others depending on their energy values. These values, however, do not reflect the actual relative preference which can only be obtained through their probabilities corresponding to each configu-

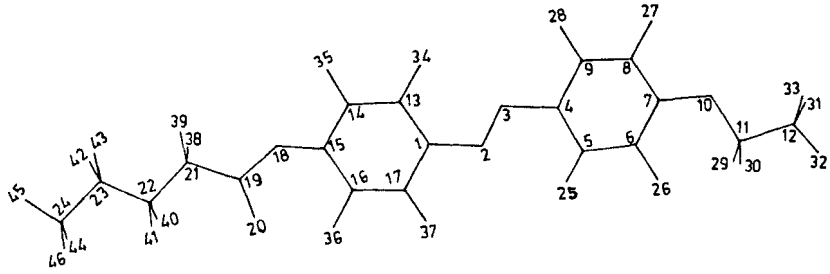

FIGURE 1 Molecular geometry of 4-(4′-ethoxyphenylazo) phenyl valerate along with various atomic index numbers, (scale 1 CM = 1 Å with X-axis along 1 → 2 bond).

ration. Further it is difficult to have a direct correlation between pair energy and liquid crystallinity. It is not straightforward even if one takes the relative probabilities into account. It is, therefore, necessary to identify the characteristic features of liquid crystallinity in terms of the pair energy or configurational probabilities. In the present paper, an attempt has been made to interpret the results of interaction energy calculations on this basis fully for a molecular pair at an intermediate distance, 6 Å for stacking and 8 Å for in-plane interactions. The selections of intermolecular separations have been made to allow the molecule to have full freedom corresponding to rotation and translation relative to each other.

In the present communication, computations have been carried out on the 4-(4′-ethoxyphenylazo) phenyl valerate molecule which forms a nematic mesophase at 352 K and exhibits an isotropic melt at 401 K.[9]

Method of Calculation

The CNDO/2[10] method has been employed to compute the net atomic charges at various atomic centers. Second order perturbation theory as modified by Caillet and Claverie[11,12] has been employed to calculate the total energy (E_{tot}) as a sum of various components:

$$E_{tot} = E_{el} + E_{pol} + E_{disp} + E_{rep}$$

where E_{el}, E_{pol}, E_{disp} and E_{rep}, respectively, represent the electrostatic, polarization, dispersion and repulsion components. Electrostatic energy has been evaluated as a sum of various multipole-multipole interactions acting at different atomic centers as follows:

$$E_{el} = E_{QQ} + E_{QMI} + E_{MIMI} + \ldots$$

where E_{QQ}, E_{QMI}, E_{MIMI} . . . etc. are the monopole-monopole, monopole-dipole, dipole-dipole etc. terms, respectively. The details of the formula may be found in our earlier communications.[3,13,14] The interaction energy values obtained through these computations were used to calculate the probability of each configuration with the help of the Maxwell-Boltzmann formula.[13]

TABLE I

Calculated atomic net charge and dipole moments using CNDO/2 method for the molecule EPPV

Sl. No.	Atom	Charge	Atomic dipole components		
			X	Y	Z
1	C	0.075	−0.013	−0.029	−0.028
2	N	−0.071	−0.859	1.630	0.009
3	N	−0.064	0.863	−1.613	−0.019
4	C	0.059	0.004	0.016	0.021
5	C	0.017	0.081	0.122	−0.003
6	C	−0.051	−0.061	0.128	0.016
7	C	0.185	0.179	0.049	−0.012
8	C	−0.045	−0.075	−0.162	−0.003
9	C	0.011	0.087	−0.076	−0.007
10	O	−0.225	−0.527	−1.255	−0.060
11	C	0.167	−0.080	0.243	0.012
12	C	−0.032	−0.163	−0.070	−0.001
13	C	0.004	−0.089	−0.131	−0.048
14	C	−0.035	0.069	−0.120	−0.016
15	C	0.190	−0.192	0.034	−0.012
16	C	−0.037	0.042	0.185	0.029
17	C	0.010	−0.086	0.090	0.010
18	O	−0.259	0.505	−0.989	0.559
19	C	0.409	0.234	0.095	−0.050
20	O	−0.325	−0.445	1.168	−0.587
21	C	−0.053	−0.013	−0.053	0.019
22	C	0.033	0.031	0.162	−0.037
23	C	0.021	0.016	−0.118	0.012
24	C	−0.006	0.125	0.123	−0.013
25	H	−0.003	0.000	0.000	0.000
26	H	−0.003	0.000	0.000	0.000
27	H	0.009	0.000	0.000	0.000
28	H	−0.007	0.000	0.000	0.000
29	H	−0.024	0.000	0.000	0.000
30	H	−0.024	0.000	0.000	0.000
31	H	0.014	0.000	0.000	0.000
32	H	0.009	0.000	0.000	0.000
33	H	0.014	0.000	0.000	0.000
34	H	−0.001	0.000	0.000	0.000
35	H	0.000	0.000	0.000	0.000
36	H	0.012	0.000	0.000	0.000
37	H	−0.009	0.000	0.000	0.000
38	H	0.023	0.000	0.000	0.000
39	H	0.026	0.000	0.000	0.000
40	H	0.000	0.000	0.000	0.000
41	H	−0.003	0.000	0.000	0.000
42	H	−0.007	0.000	0.000	0.000
43	H	−0.006	0.000	0.000	0.000
44	H	0.002	0.000	0.000	0.000
45	H	−0.004	0.000	0.000	0.000
46	H	0.002	0.000	0.000	0.000

The origin on an atom has been chosen close to the center of mass of the molecule, X-axis along a bond parallel to the long molecular axis, Y-axis in the plane of the molecule and Z-axis perpendicular to the molecular plane. Computations have been carried out by keeping one molecule fixed and placing the other molecule on

TABLE II

Total energy,[a] binding energy,[b] total dipole moment and its components of EPPV molecule; total energy = −230.551 atomic unit, binding energy = −22.964 atomic unit, total dipole moment = 0.684 debyes

Components	X	Y	Z
Densities	−0.029	0.274	−0.265
Sp*	−0.367	−0.571	−0.207
pd**	0.000	0.000	0.000
Total	−0.397	−0.297	−0.472

[a] Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

[b] Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of atomic energies of the constituent atoms.

* Sp, hybridization moment.

** pd, hybridization moment.

both sides (see Figure 2 for definition of sides) during stacking, in-plane and terminal interactions but detailed results have been reported only for one set. However, the salient features of other sets have also been reported. Although, the minimum energy configuration has been marked in each set, it has not been emphasized in reporting the results.

RESULTS AND DISCUSSION

The molecular geometry of EPPV has been shown in Figure 1 with various atomic index numbers. Computed net atomic charges and dipole moments are listed in Table I. The total energy, binding energy, total dipole moment and its components are listed in Table II. The results for intermolecular interaction energy calculations and probability calculations are discussed below.

Stacking Interactions

The variation of various energy components with respect to rotations about Z-axis are shown in Figures 3(a), 3(b) corresponding to configurations X(0°) Y(0°) and X(180°) Y(0°), respectively. An observation of these figures reveals that the dominant component of total energy is the dispersion energy. The contribution of polarization energy is negligible and is almost constant throughout the entire range while the dispersion energy is mainly dependent on the extent of overlap during stacking. Thus, the dispersion energy has two symmetric minima near 0° and 180°. Electrostatic energy, on the other hand, is mainly responsible for the selection of minimum energy configuration for the molecular pair. The magnitude of electrostatic energy term is much less as compared with the dispersion term but the symmetric fluctuation in the electrostatic term is reflected in the nature of variation in the total energy. Thus, the minima for total energy may be observed at 160°

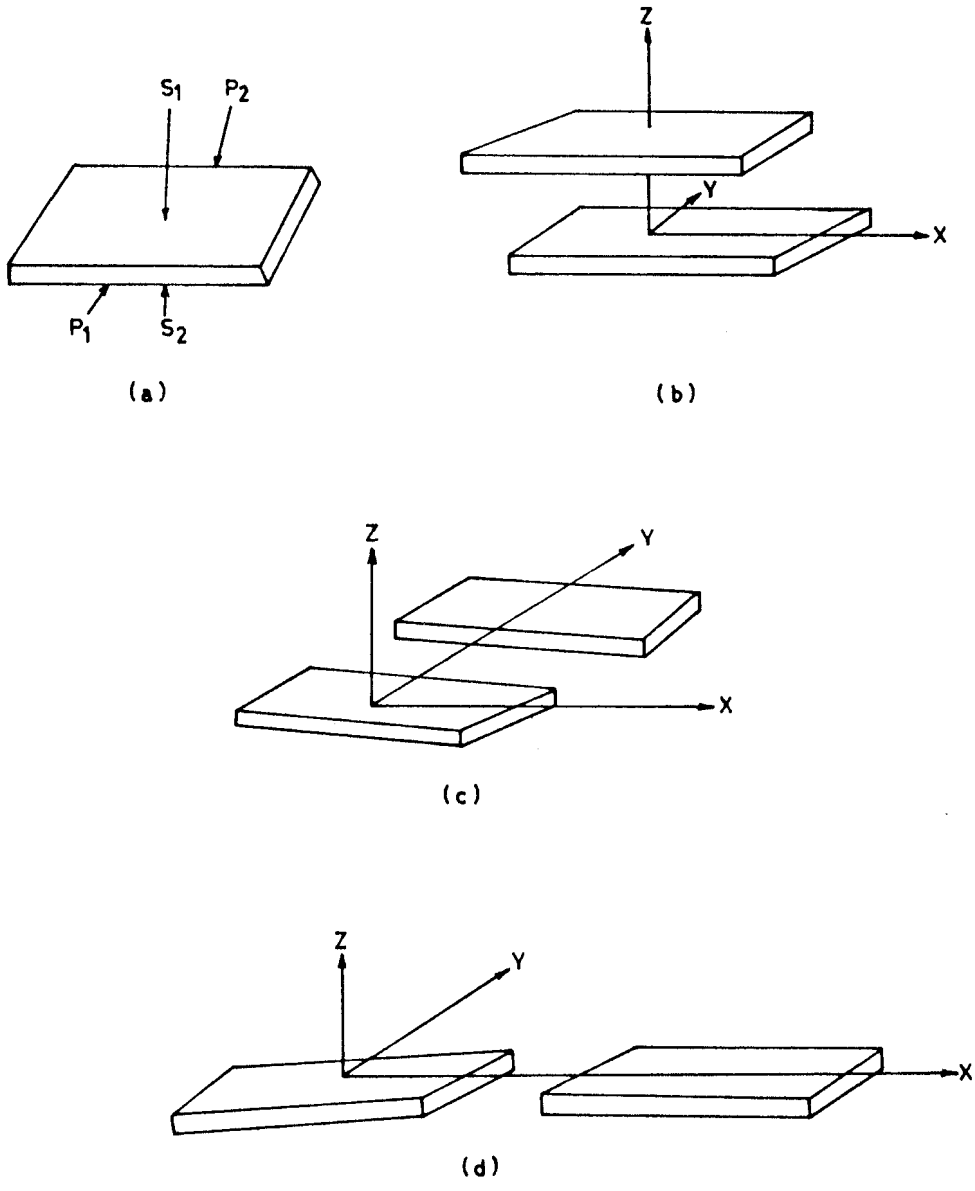

FIGURE 2 The three modes of interactions of a molecular pair; (a) sides (P_1, P_2) and faces (S_1, S_2) of a molecule, (b) Stacking interaction, (c) In-plane interaction, (d) Terminal interaction.

and 340° for X(0°) Y(0°) and 155°, 330° for X(180°) Y(0°). The variation of probability with respect to rotations about Z-axis is shown in Figures 4(a) and 4(b) corresponding to the above mentioned configurations. It is evident from the figures that the maxima for probability may be observed at 160° and 340° for X(0°) Y(0°) and 155° and 330° for X(180°) Y(0°). The study of variation of intermolecular interaction energy with respect to intermolecular separation has also been carried

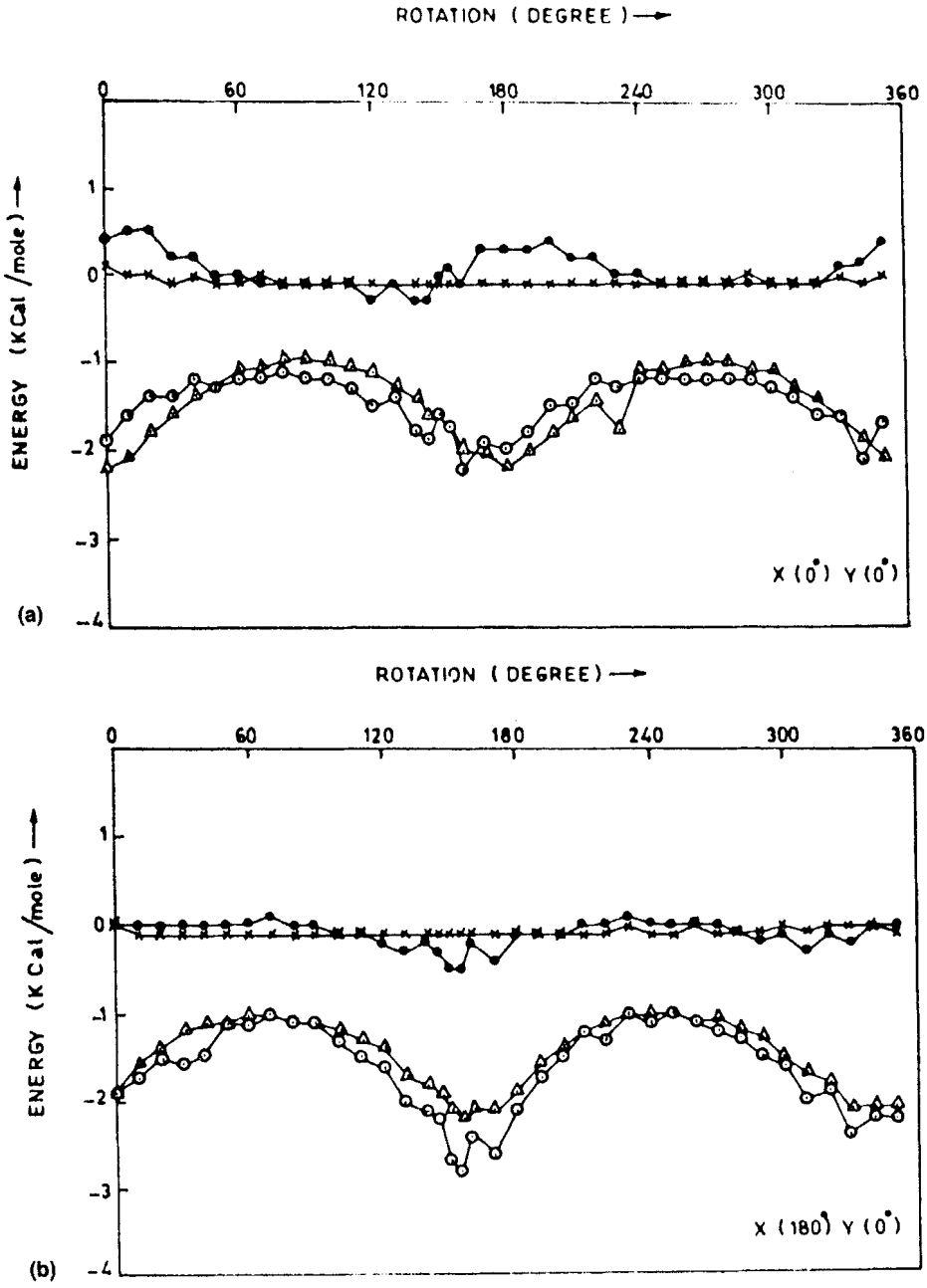

FIGURE 3 Variation of stacking energy components of a pair of EPPV molecules with respect to rotations about Z-axis corresponding to rotational sets. (a) X(0°) Y(0°) (b) X(180°) Y(0°); (· → electrostatic, x → polarization, △ → dispersion and ⊙ → total).

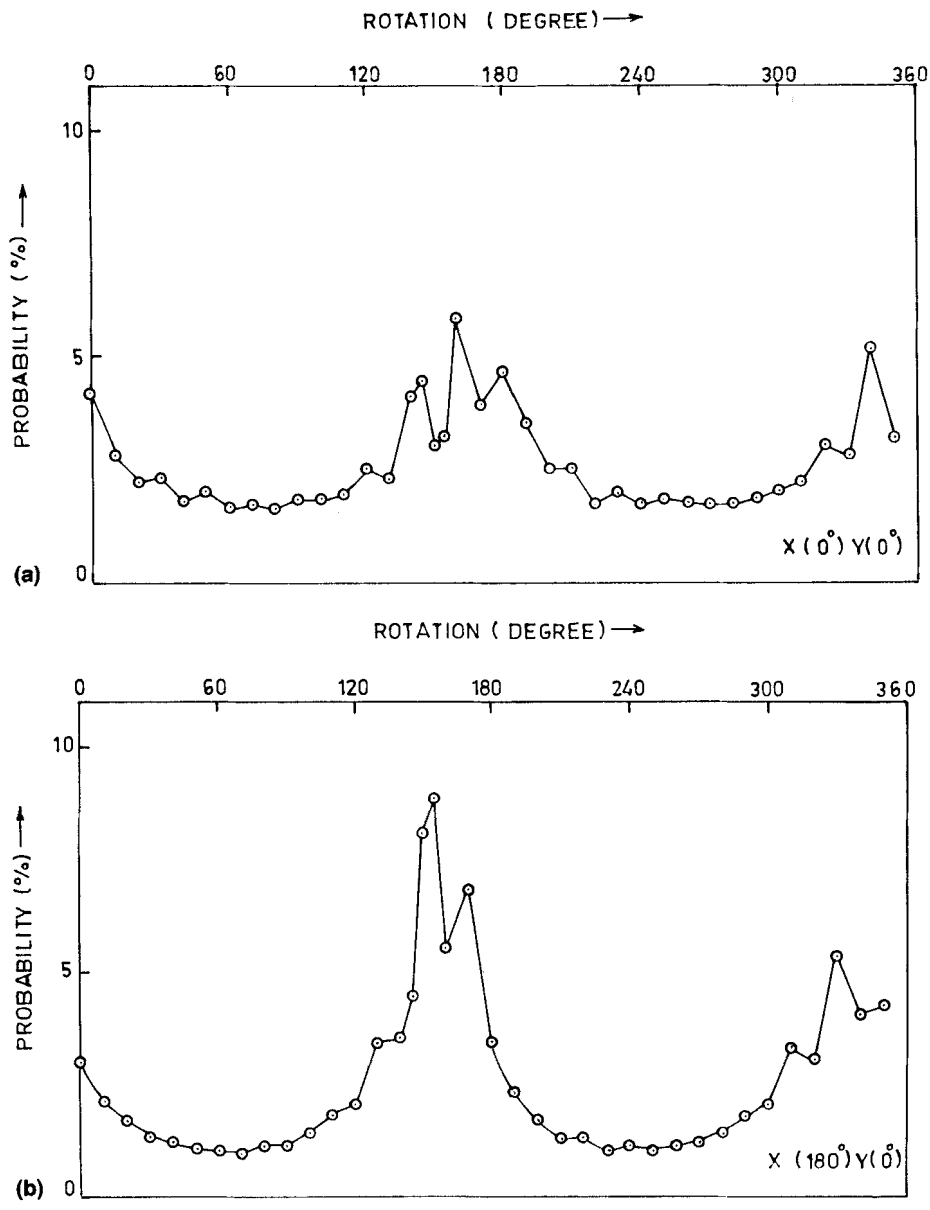

FIGURE 4 Variation of probability during stacking interactions of a pair of EPPV molecules with respect to rotations about Z-axis corresponding to rotational sets. (a) X(0°) Y(0°), (b) X(180°) Y(0°) at 401 K.

out and it has been observed that the polarization and electrostatic components decrease very slowly with respect to decreasing separation and it is almost balanced by the increase in the repulsive energy while the dispersion energy decreases rapidly with respect to decreasing separation. At the lower range of intermolecular separation, the repulsive component increases very rapidly and, in spite of the high

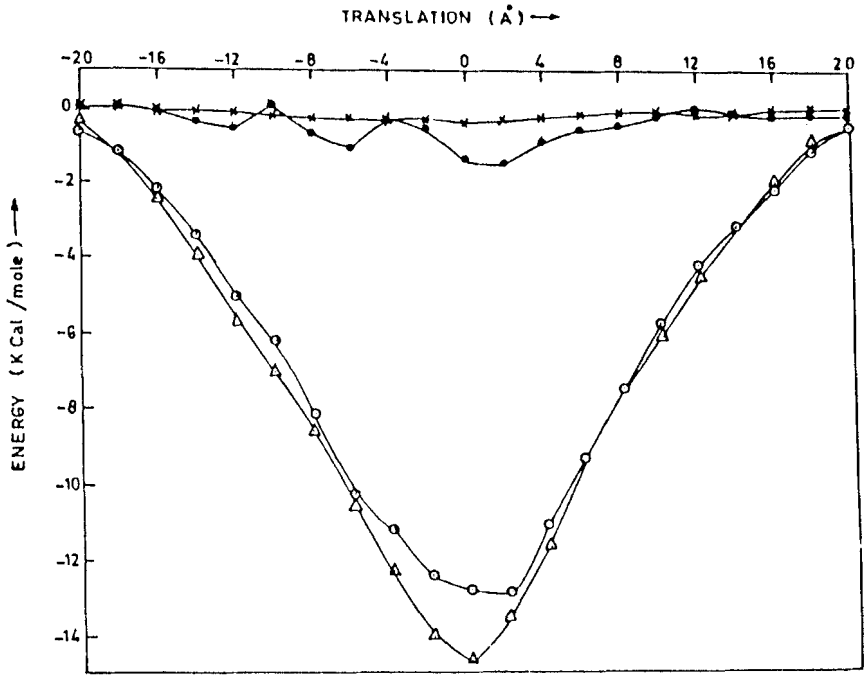

FIGURE 5 Variation of energy components of a pair of EPPV molecules with respect to translation along X-axis. Notations are same as in Figure 3.

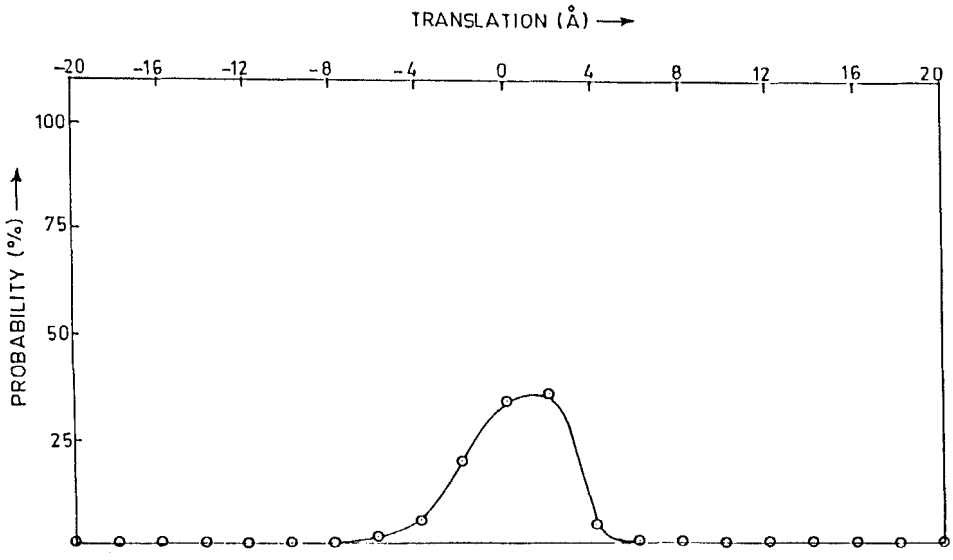

FIGURE 6 Variation of probability during stacking interactions of a pair of EPPV molecules with respect to translation along X-axis at 401 K.

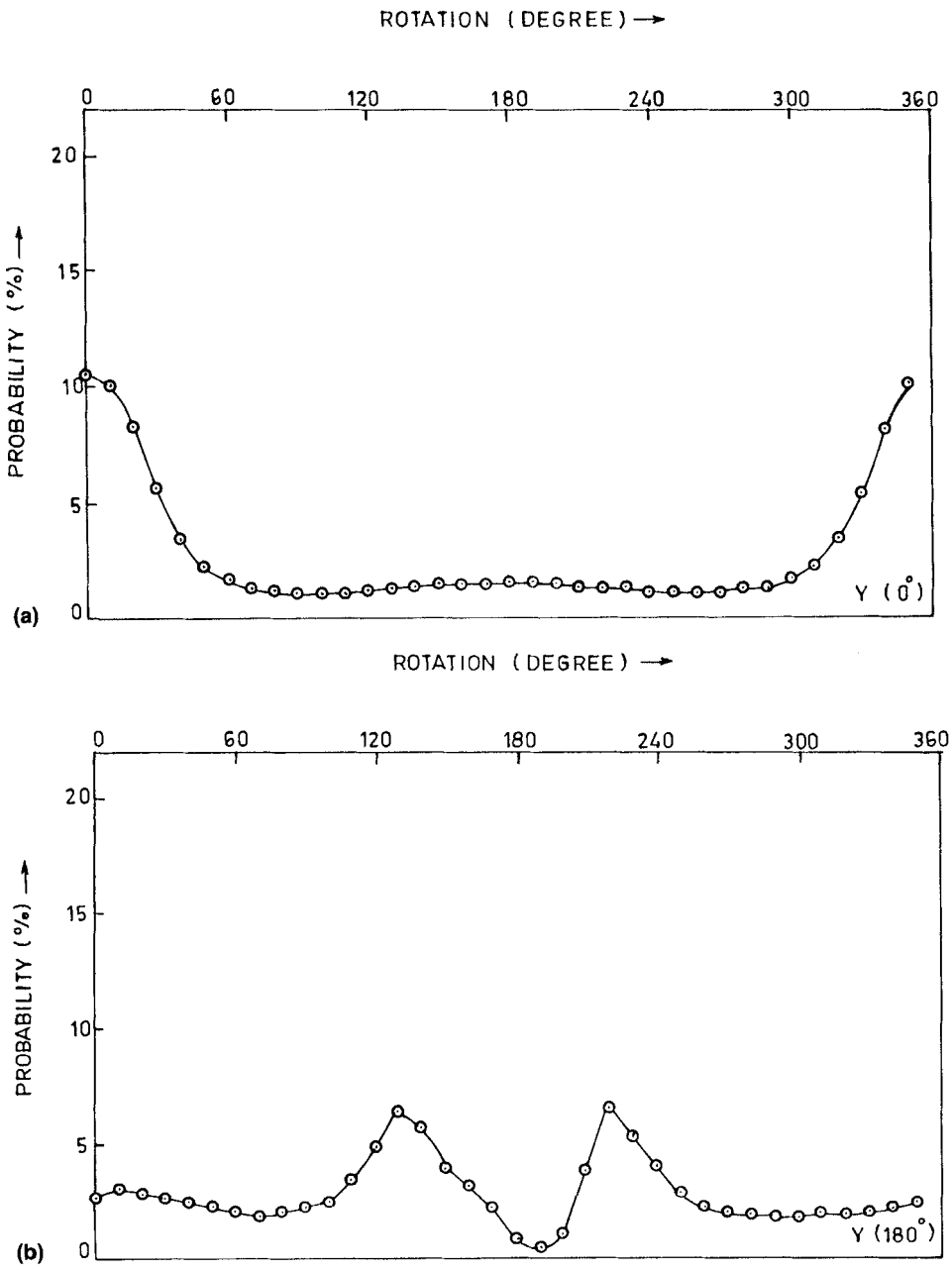

FIGURE 7 Angular dependence of probability during in-plane interactions of a pair of EPPV molecules with respect to rotation about X-axis for (a) Y(0°) and (b) Y(180°) configuration.

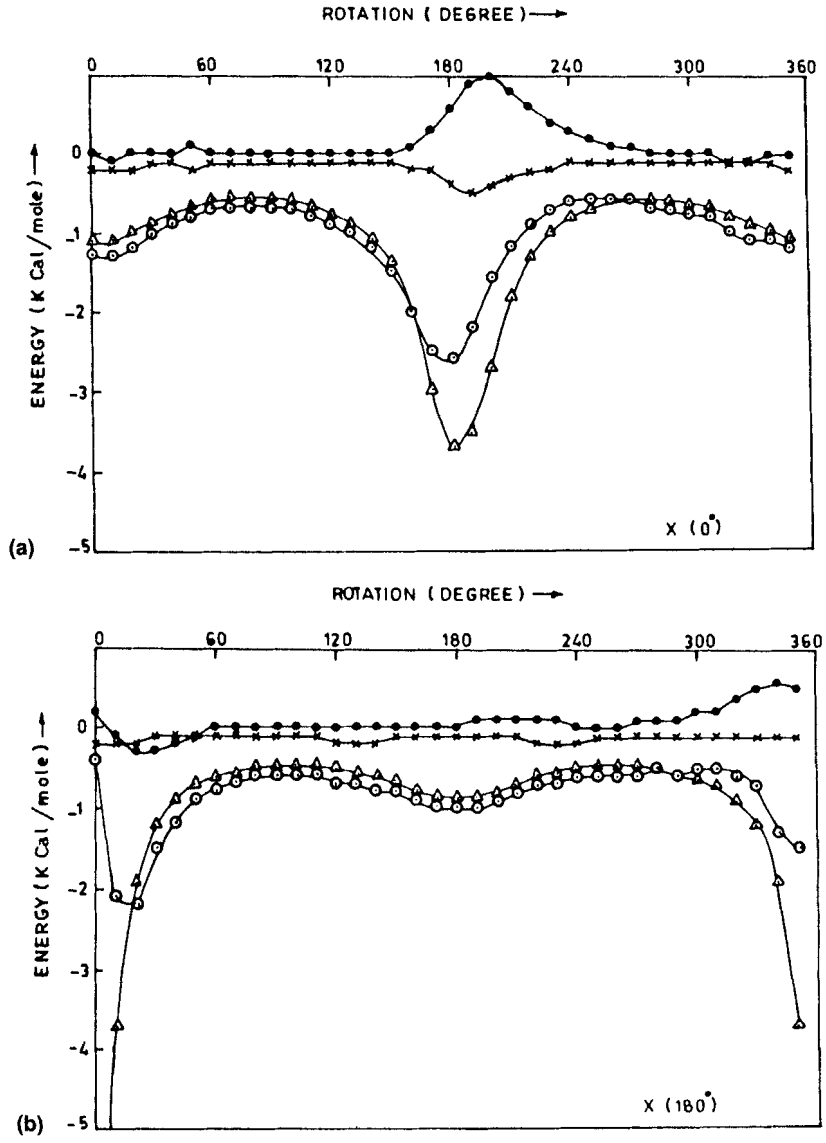

FIGURE 8 Angular dependence ofo in-plane energy components of a pair of EPPV molecules corresponding to configurations (a) X(0°) and (b) X(180°), respectively. Rotation has been given about the Y-axis. Notations are same as in Figure 3.

magnitude of dispersion energy, makes the total energy positive for intermolecular separation 3.25 Å. Having refined the interacting configuration with respect to translation along Z-axis and rotations about Z-axis at the equilibrium condition, the energy is brought down and the probability is further investigated with respect to translation along X-axis. Figure 5 shows the variation of interaction energy components for translation of ± 20 Å along X-axis while the probability distribution is shown in Figure 6. It may be observed that all the components increase in

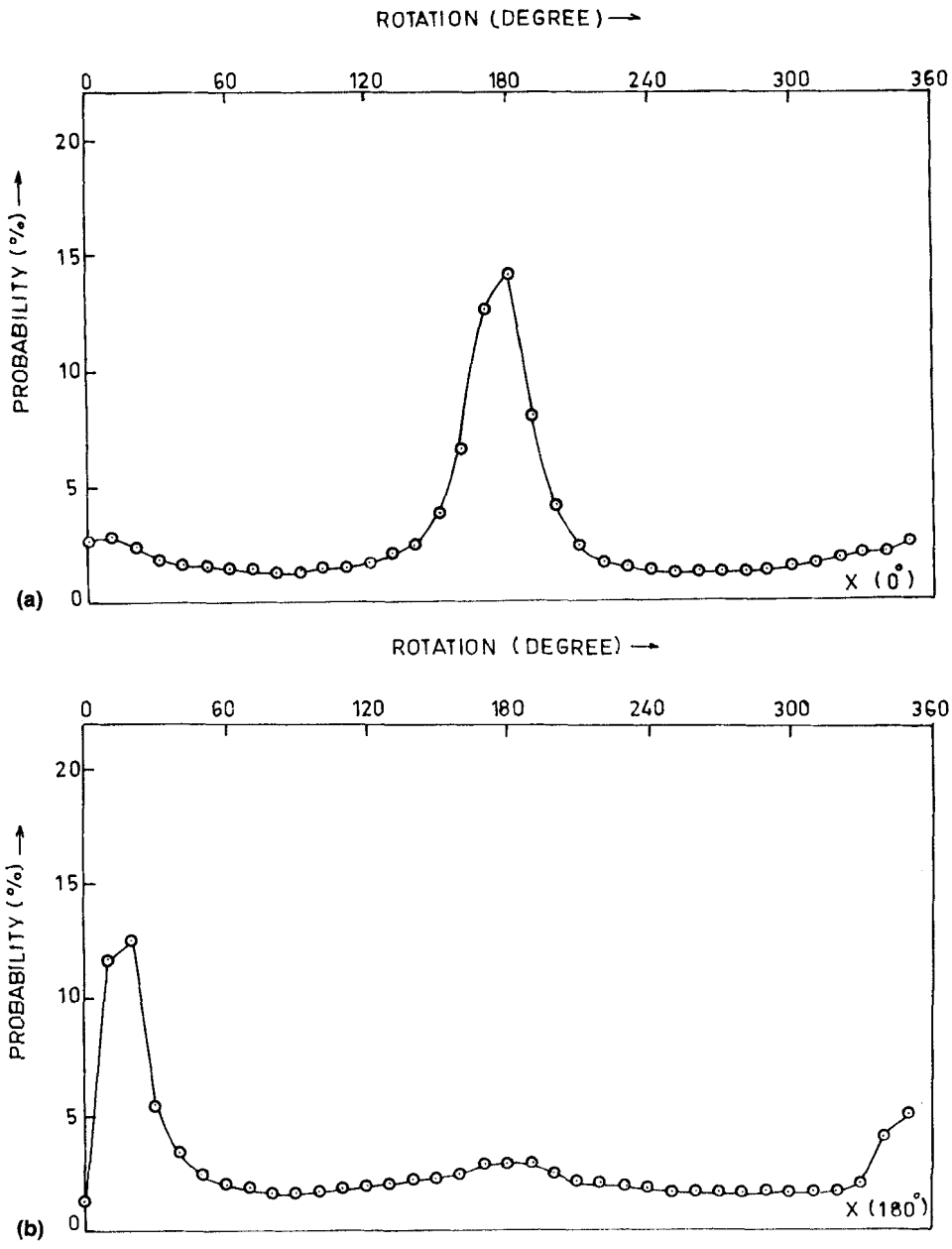

FIGURE 9 Variation of probability during in-plane interactions of a pair of EPPV molecules with respect to rotation about Y-axis for (a) X(0°) and (b) X(180°) at 401 K.

magnitudes with increased overlapping although the extent of increase is relatively lesser for electrostatic and polarization terms. The variation of probability is almost constant for a region ± 2 Å near the equilibrium position which shows that a sliding of one molecule over the other is energetically allowed for a small range which

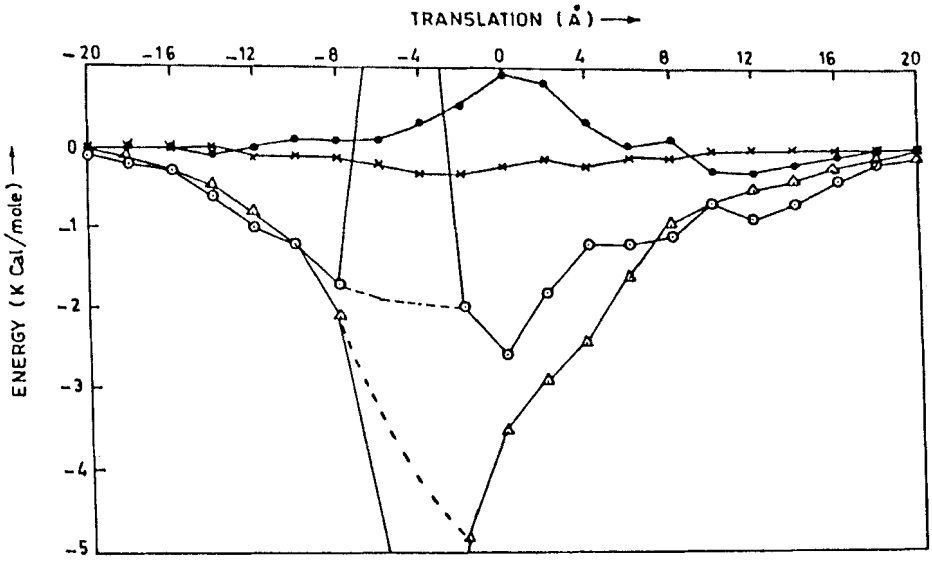

FIGURE 10 Variation of in-plane interaction energy components of a pair of EPPV molecules with respect to translation along X-axis. Notations are same as in Figure 3.

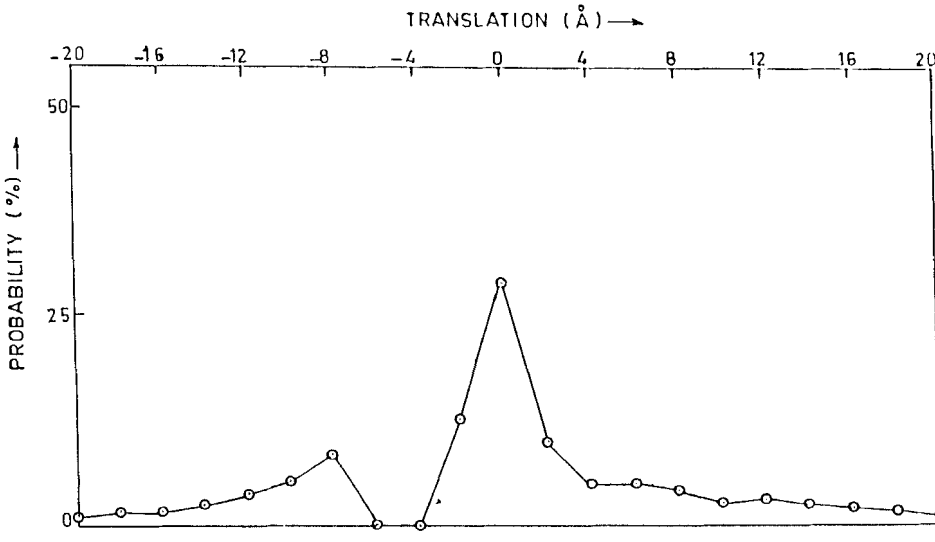

FIGURE 11 Variation of probability during in-plane interaction of a pair of EPPV molecules with respect to translation along X-axis.

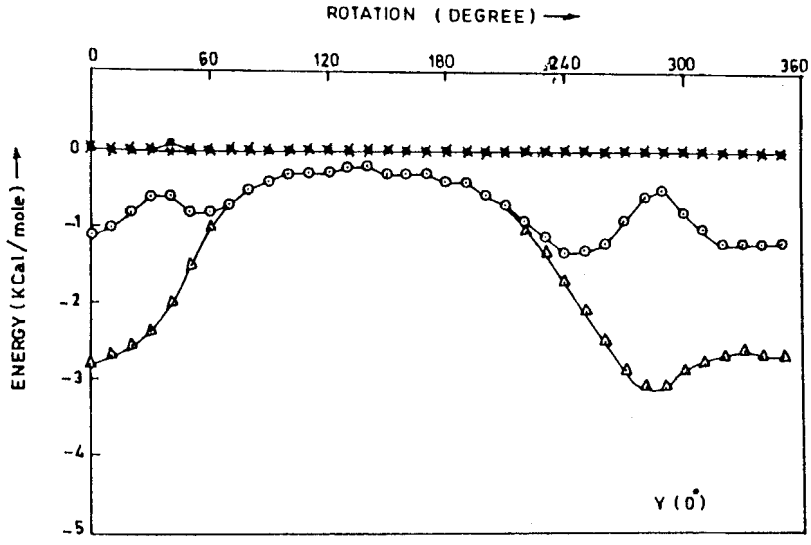

FIGURE 12 Variation of terminal interaction energy components of a pair of EPPV molecules with respect to rotation about X-axis for Y(0°) configuration. Notations are same as in Figure 3.

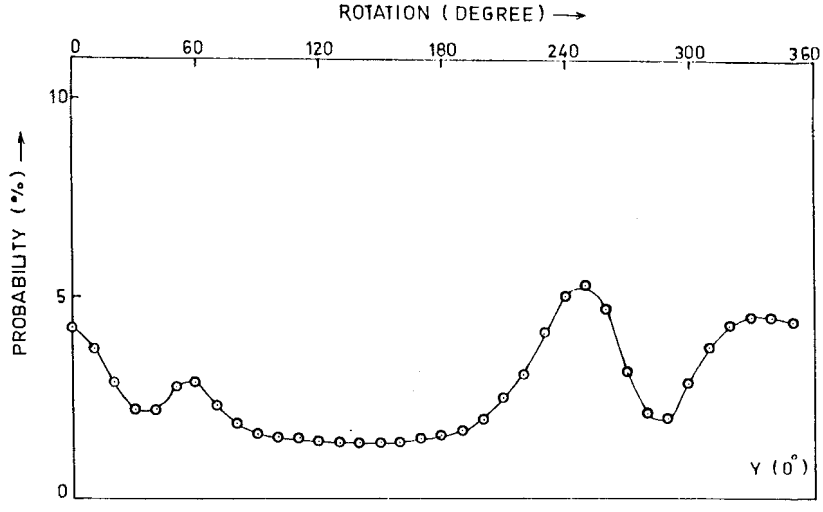

FIGURE 13 Variation of probability during terminal interaction of a pair of EPPV molecules with respect to rotation about X-axis for Y(0°) configuration at 401 K.

may be correlated with the fluidity of compound maintaining its alignment in mesophase.

In-Plane Interactions

Figures 7(a) and 7(b) show the variation of probability with respect to rotation about X-axis for Y(0°) and Y(180°) configuration, respectively. It may be noted that the main attractive part of the energy comes through dispersion term while

TABLE III

Stacking, in-plane and terminal interaction energy values between a pair of 4-(4′-Ethoxyphenylazo) phenyl valerate molecules after refinement. Energy is expressed in kcal/mole

Interaction energy terms	Stacking energy		In-plane energy		Terminal energy	
	Face I	Face II	Side I	Side II	End I	End II
E_{OO}	−0.307	−0.104	−0.042	−0.036	0.026	0.021
E_{QM}	−0.994	−0.059	0.176	−0.052	−0.131	−0.012
E_{MM}	−1.591	−0.974	−0.040	0.205	0.001	−0.019
E_{el}	−2.893	−0.928	0.094	0.117	−0.104	−0.011
E_{pol}	−0.877	−0.568	−0.373	−0.636	−0.034	−0.018
E_{disp}	−30.545	−23.062	−6.498	−6.174	−3.269	−1.697
E_{rep}	19.677	8.168	3.096	2.722	1.313	0.576
E_{tot}	−14.638	−16.390	−3.681	−3.971	−2.093	−1.149

TABLE IV

Comparative probability of all the minimum energy configuration for stacking, in-plane and terminal interactions between a pair of EPPV molecules

Configuration	Separation (Å)	E_{tot} (kcal/mole)	Probability (%)		
			T = 300 K	T = 401 K	T = 433 K
X(0°) Y(0°)*	6 (Z-axis)	−2.166	9.89	11.26	11.56
X(180°) Y(0°)*	6 (Z-axis)	−2.799	28.66	24.98	24.16
X(0°)**	8 (Y-axis)	−2.601	20.54	19.47	19.18
X(180°)**	8 (Y-axis)	−2.195	10.38	11.68	11.95
Y(0°)**	8 (Y-axis)	−2.601	20.54	19.47	19.18
Y(180°)**	8 (Y-axis)	−2.008	7.59	9.25	9.63
Y(0°)[a]	22 (X-axis)	−1.323	2.40	3.91	4.34

* Stacking interaction.
** In-plane interaction.
[a] Terminal interaction.

TABLE V

Translational rigidities along the long molecular axis (X-axis) during stacking and in-plane interactions between a pair of EPPV molecules

Mode of interaction	Probability ratio		
	T = 300 K	T = 401 K	T = 433 K
Stacking	1.02	0.95	0.93
In-plane	1.75	1.28	0.77

the repulsions due to short contacts at 180° for Y(180°) configuration splits the maximum into two parts at approximately ±40° with respect to the 180° position which could be merged during refinements. The details of variations of energy components for rotations with respect to Y-axis are shown in Figure 8 while the variation of probability has been shown in Figure 9 corresponding to configurations X(0°) and X(180°), respectively. The significant maxima in probability is observed

TABLE VI

Comparative picture of rotational rigidities corresponding to most probable configuration during stacking, in-plane and terminal interactions between a pair of EPPV molecules

	Rotational rigidities		
Temperature (K)	Stacking interaction	In-plane interaction	Terminal interaction
300	0.98	0.76	0.57
401	0.83	0.68	0.55
433	0.80	0.67	0.54

near 180° and 0° for the above mentioned configurations. The effect of translation along X-axis has been shown in Figures 10 and 11 where it may be observed that the translational freedom is much more pronounced as compared to stacking (after due consideration of short contacts).

Translation along Y-axis has also been studied and it has been found that minor translation along Y-axis does not alter the total energy very drastically.

Terminal Interactions

Terminal interactions are much weaker as compared to stacking or in-plane interactions. Figures 12 and 13 show the effect of rotation about X-axis for molecules kept at +22 Å separation in X-direction. In this case, the variation in dispersion is asymmetrical and hence a number of minima (maxima of probability) are observed corresponding to various inclinations.

The most prominent energy minima of the above mentioned interactions are further refined and the values thus obtained are listed in Table III with all the contributory terms to enable comparison. The results indicate that due to the planarity of the molecule, the refinement corresponding to stacking energy is maximum and the ultimate magnitude of stacking energy is much larger than in-plane and terminal interaction energies.

A comparative probability of all the minimum energy configurations for stacking, in-plane and terminal interactions at equivalent edge to edge separations are shown in Table IV. It may be observed that configuration X(180°) Y(0°) has maximum relative probability (≈28%) at room temperature (300 K) with an energy −2.799 kcal/mole.

CORRELATION OF THE RESULTS

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

Translational Rigidity

This has been defined as the ratio of probability being at maximum probable point to having ±2 Å displacement along the translational axis. Table V compares the

translational rigidities along long molecular axis (X-axis) for stacking and in-plane interactions. It may be noted that in the case of stacking the rigidity decreases slowly with the increase in temperature while the rapid decrease of the same in case of in-plane interactions indicate that the values obtained at lower temperature (for in-plane interaction) is abnormally high due to a possible contact as referred in Figures 10 and 11.

It may, therefore, be concluded that the molecule is relatively more free for translation during in-plane interactions. However, the comparable values in both the cases show that the molecule does not show extraordinary preference in forming stacked layers hence justifies the nematic character.

Rotational Rigidity

This has been defined as the ratio of probability being at maximum probable point to having $\pm 10°$ rotation with respect to the maximum probable point. Table VI gives the comparison of rotational rigidities in case of stacking, in-plane and terminal interactions. The table clearly shows that during terminal interactions, the molecule can rotate freely about its long molecular axis. Also the rotation is less restricted for rotation about Y in case of in-plane interactions than rotation about Z during stacking. These observations comply with the nematic character of the molecule.

These two parameters may be of help to understand the mesogenic character of the molecule. A comparative study on other systems may lead to more general conclusions.

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