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Intermolecular Interactions in 4,4′-di-*n*-propoxy-azoxybenzene. Part I—Theoretical

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A statistical study of molecular ordering in 4,4′-di-*n*-propoxyazoxybenzene has been carried out on the basis of intermolecular interaction energy calculations. Modified Rayleigh-Schrodinger perturbation treatment has been employed to evaluate the intermolecular interaction energy. CNDO/2 method has been employed to compute the net atomic charge and atomic dipole components at each atomic centre of the molecule. Probability of occurrence of a particular configuration has been calculated using Maxwell-Boltzmann formula. It has been observed that the molecule has a strong preference for stacking through a particular face, while the other configurations such as stacking through the other face, in-plane and terminal interactions show, in general, an aligned structure along its long molecular axis.

Keywords: interaction energy, statistical analysis, DPAB, nematogen, relative probability, stacking

INTRODUCTION

Recently, Sanyal *et al.*[1–3] have reported the results of theoretical investigations on the role of intermolecular interactions in mesogenic compounds. 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. Attempts were also made to correlate the liquid crystalline characters viz. nematic, smectic etc. with the nature of variation of intermolecular interaction energy near the minimum energy configuration. Thus the main emphasis was laid on finding out the minimum energy configuration which, in general for mesogens, is a stacking configuration

showing considerably lower energy value in comparison with the other possible configurations through in-plane or terminal interactions.

One of the limitations of the previous works was that the relative preferences of different configurations were estimated on the basis of interaction energy values which are not directly related quantities. Hence, in order to obtain a quantitative measure for the relative preferences, we have extended the interaction energy calculations to probability calculations. 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. In the present paper, we report the results of our calculations on an enantiotropic liquid crystal, 4,4′-di-*n*-propoxy-azoxybenzene, which shows solid → nematic transition at 116°C and nematic → isotropic transition at 123°C.[4]

METHOD OF CALCULATION

Computations have been carried out in two parts:

(i) Evaluation of intermolecular interaction energy has been carried out using a modified second order perturbation method[5,6] the details of which has already been published elsewhere.[1] The total interaction energy, E_{tot}, betwen a pair of interacting molecules (DPAB) has been computed as a sum of various contributing terms as follows:

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

where, E_{el}, E_{pol}, E_{disp}, and E_{rep} represent the electrostatic, polarization, dispersion and repulsion energy terms respectively. The electrostatic term may be further sub-divided into various components as

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

where E_{QQ}, E_{QMI}, E_{MIMI} etc. respectively represent the monopole–monopole, monopole–dipole, dipole–dipole and other higher order terms corresponding to the higher order multipoles, CNDO/2 method[7] has been employed to compute the net atomic charges and dipoles at each atomic centre.

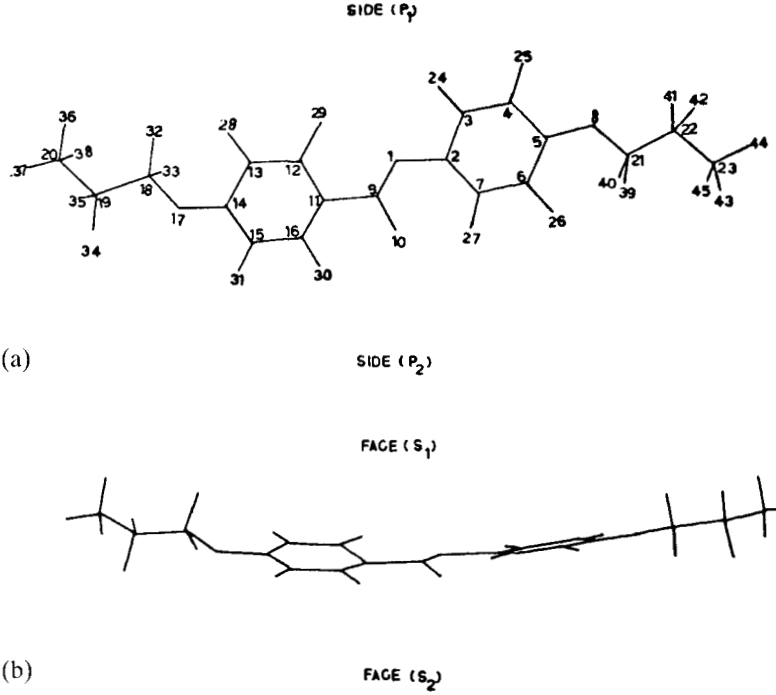
(ii) Probability of occurrence of a particular configuration i has been calculated using Maxwell-Boltzmann formula[9]

$$P_i = \frac{\bar{e}^{\beta\epsilon i}}{\sum_i \bar{e}^{\beta\epsilon i}}$$

where P_i stands for probability, $\beta = 1/KT$ where K is the Boltzmann constant and T, the absolute temperature and ϵ_i represents the energy of the configuration i relative to the minimum energy value in a particular set for which the probability distribution is computed.

The geometry of the molecule was constructed on the basis of the crystallographic data for para-azoxyanisole (PAA)[8] and standard values of bond lengths and bond-angles.

It may be observed from the molecular geometry (shown in Figure 1) that the molecule contains two planar benzene rings joined by a-N = N-bridge with two alkoxy chains at the ends. The X-axis has been chosen along the long molecular axis while the Y-axis perpendicular to it lies in the plane of the molecule and Z-axis lies perpendicular to the plane of molecule. The origin has been chosen at almost



(a)

(b)

FIGURE 1 (a,b) X-Y (Figure 1a) and X-Z (Figure 1b) projections of the molecular geometry of 4,4′-di-*n*-propoxy-azoxybenzene along with various atomic index numbers. X-axis along 1 → 2 bond Y-axis perpendicular to it and in the plane of the molecule and Z-axis perpendicular to the plane of the molecule. Origin is on the atom no. 1. Faces S1 & S2 and sides P1 & P2 refers to the text are shown for clarity.

the midpoint of the molecule. Specifically on the atom no. 1. As mentioned earlier, though the aim of the present investigation is to calculate the probability distribution of different configurations allowing free-rotation and translation of one molecule in the presence of another molecule at a fixed position, the terms like stacking, in-plane or terminal interactions will be used to maintain continuity with our previous works.

(A) Stacking interactions

The interacting molecule has been placed at a separation ± 6 Å along the Z direction with respect to the fixed molecule. 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 range of short and medium range interactions. Rotations about Z- and X-axis have been given at an interval of 10° and probability at each point has been calculated.

(B) In-Plane interactions

The interacting molecule has been kept at separation ± 8 Å along Y-axis with respect to the fixed one. The distances chosen for these calculations are such that the possible van der Waals contacts are avoided. Again, rotation about Y- and X-axis have been given and the corresponding probabilities have been reported.

(C) Terminal interactions

Since the length of a molecule is approximately 20.0 Å, to investigate the terminal interactions away from van der Waals contacts, the interacting molecule has been shifted along the X-axis by ± 22 Å with respect to the fixed one and allowed rotations are along X-, Y- and Z-axes. The probabilities at such points have been examined.

Change in probability corresponding to translations along all the three axes were also studied. All the computations were carried out on a CDC 'Cyber' computer at the TIFR, Bombay.

RESULTS AND DISCUSSION

The molecular geometry of DPAB molecule has been shown in Figure 1 (a, b) with various atomic index numbers. Computed net atomic charges and dipole moments at each of the atomic centres are listed in Table I. The results for probability calculations are discussed below:

TABLE I

Molecular charge distribution on 4,4′-di-*n*-propoxy-azoxybenzene

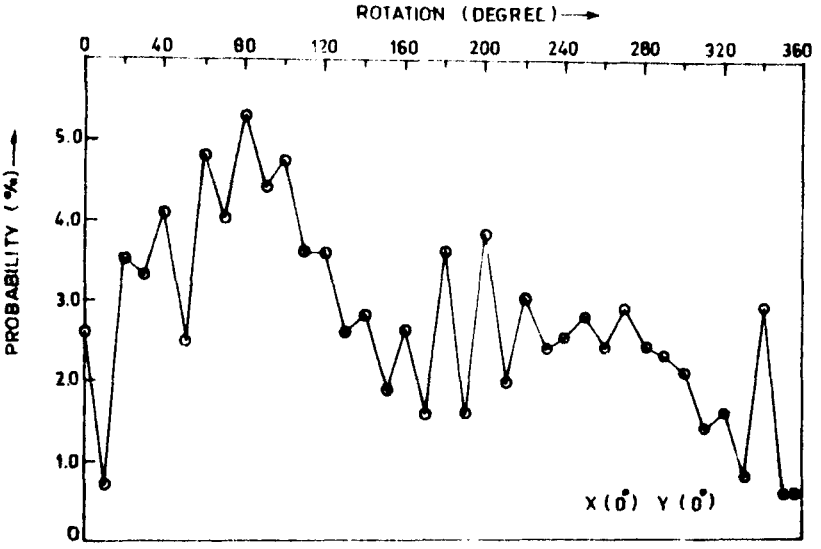
Sl. No.	Atom	Charge	Atomic dipole components		
			X	Y	Z
1	N	−0.188	0.736	−1.709	−0.415
2	C	0.070	−0.042	0.116	0.064
3	C	0.007	0.113	−0.073	0.002
4	C	−0.042	−0.044	−0.173	0.001
5	C	0.180	0.182	0.069	0.017
6	C	−0.057	−0.088	0.137	0.022
7	C	0.007	0.047	0.185	−0.004
8	O	−0.231	−0.390	−1.285	0.009
9	N	0.358	−0.072	0.313	0.074
10	O	−0.429	−0.568	1.198	0.356
11	C	0.025	0.154	−0.025	−0.006
12	C	0.030	−0.048	−0.164	−0.050
13	C	−0.058	0.107	−0.142	−0.059
14	C	0.199	−0.183	−0.042	0.028
15	C	−0.048	0.095	0.154	0.028
16	C	0.034	−0.076	0.192	0.065
17	O	−0.224	0.631	1.089	0.476
18	C	0.155	0.081	−0.205	−0.125
19	C	0.004	0.019	0.143	−0.003
20	C	−0.002	0.139	−0.125	−0.074
21	C	0.155	−0.097	0.208	−0.025
22	C	0.005	−0.004	−0.140	0.020
23	C	−0.005	−0.144	0.110	−0.038
24	H	−0.005	0.000	0.000	0.000
25	H	0.001	0.000	0.000	0.000
26	H	0.004	0.000	0.000	0.000
27	H	0.023	0.000	0.000	0.000
28	H	0.012	0.000	0.000	0.000
29	H	0.014	0.000	0.000	0.000
30	H	0.030	0.000	0.000	0.000
31	H	0.014	0.000	0.000	0.000
32	H	−0.016	0.000	0.000	0.000
33	H	−0.016	0.000	0.000	0.000
34	H	0.010	0.000	0.000	0.000
35	H	0.004	0.000	0.000	0.000
36	H	0.005	0.000	0.000	0.000
37	H	0.002	0.000	0.000	0.000
38	H	−0.001	0.000	0.000	0.000
39	H	−0.018	0.000	0.000	0.000
40	H	−0.019	0.000	0.000	0.000
41	H	0.006	0.000	0.000	0.000
42	H	0.004	0.000	0.000	0.000
43	H	0.003	0.000	0.000	0.000
44	H	0.001	0.000	0.000	0.000
45	H	0.003	0.000	0.000	0.000

(A) Stacking Interactions

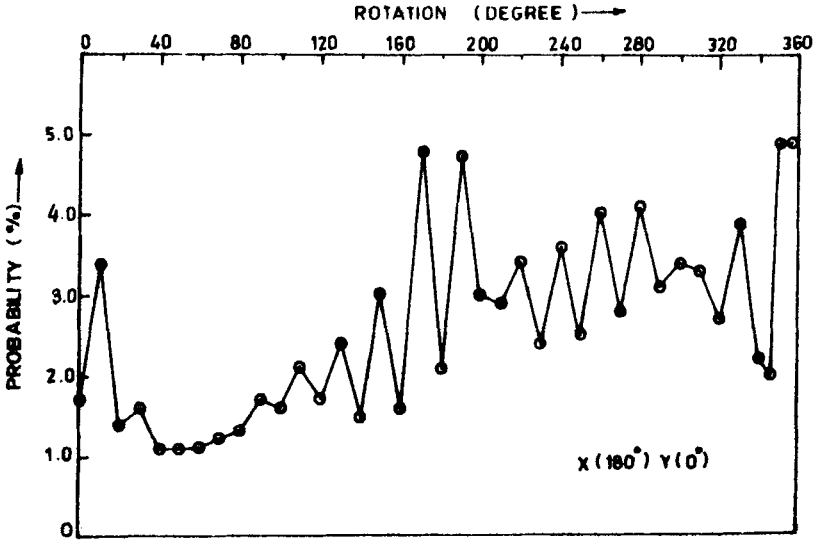
Computations have been carried out on both faces (S1 & S2) of the molecule (see Figure 1 (a, b) for definitions of faces and sides). Figures 2a and 2b show the results obtained for face S1 corresponding to rotations about Z axis and placing the interacting molecule with X(0°) and X(180°) configurations respectively. Similar calculations on face S2 have been shown in Figures 2c and 2d. An observation of these figures reveal that for face S1 there is no major preference for any particular orientation. Probabilities vary from 1–5%, the maximum probability for X(0°) being at 80° while for X(180°) the maxima occur at 0° ± 10° and 180° ± 10° indicating a slight preference for an aligned structure in this configuration. However, for face S2 the situation is quite different (Figures 2c and 2d). A definite preference for an aligned structure is observed. The maximum probability for X(0°) lies between 170°–190° while the next preference is within −10° to +10°. Similarly for X(180°), a very pronounced peak exists at Z = 180° and all the remaining regions have negligible probability as compared to this configuration.

IN-PLANE INTERACTIONS

Similar calculations have been performed for planar interactions on both sides (P1 & P2) of the molecule at an intermolecular separation of 8 Å (see Figure 1 (a) for definition of P1 and P2). Figures 3a–3d show the results corresponding to rotations about Y axis while in Figures 4a–4d, results corresponding to X-rotations have been reported. Table II shows the total probability in a range of ±10° near the maximum probable region for all the configurations of stacking and in-plane interactions at four different temperatures. Results for rotation about the Y axis on both the sides P1 and P2 show that though there is no drastic preference for aligned structure, the smooth rise near 0° and 180° indicates the existence of an aligned structure at low temperature. Probabilities of the minimum energy configuration being in 0° ± 10° with X(0°) are about 9% and 10% for the sides P1 and P2 respectively while for the configuration corresponding to 180° ± 10° is about 16% near transition temperature, which rises up to 19% at room temperature (300°K). Thus for all practical purposes both the sides are equivalent with a reasonably good preference for Y (180°). However, for X(180°) sides P1 and P2 behave in a slightly different way.

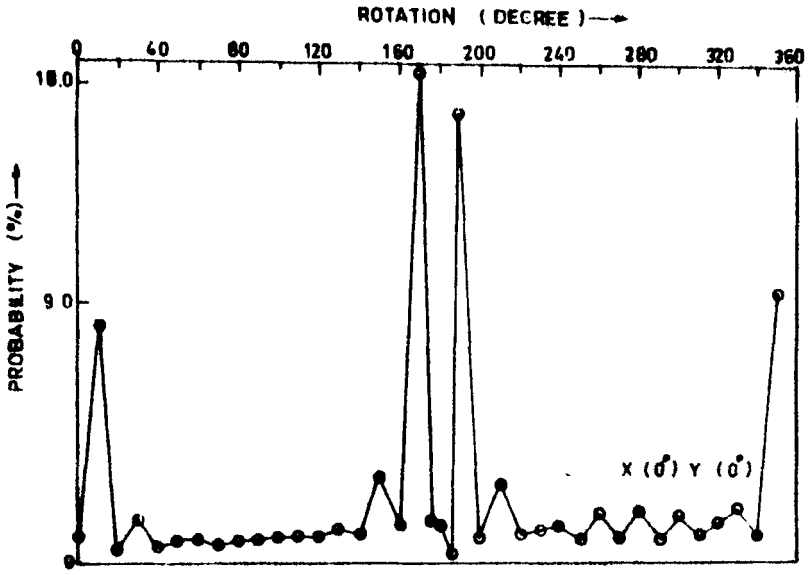


(a)



(b)

FIGURE 2 (a,b) Variation of probability with respect to rotations about Z-axis during stacking interaction through face S1.



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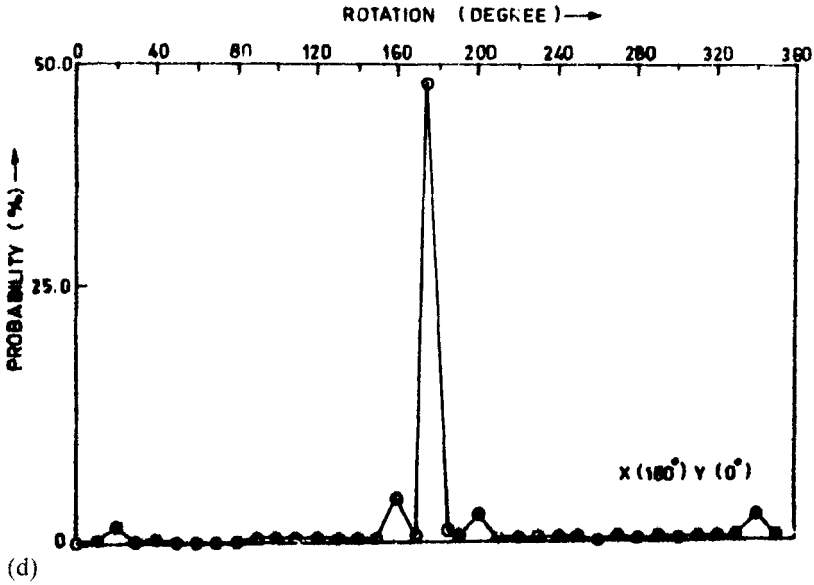
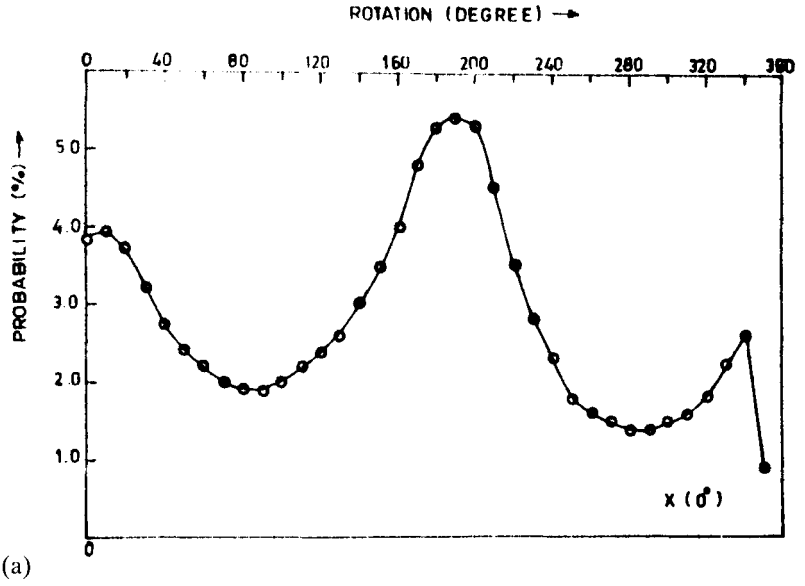
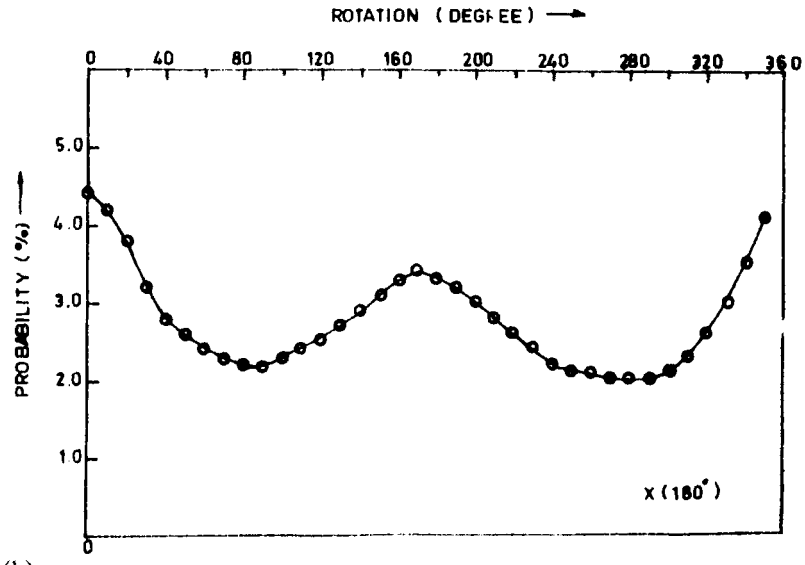


(d)

FIGURE 2 (c,d) Variation of probability with respect to rotations about Z-axis during stacking interaction through face S2.

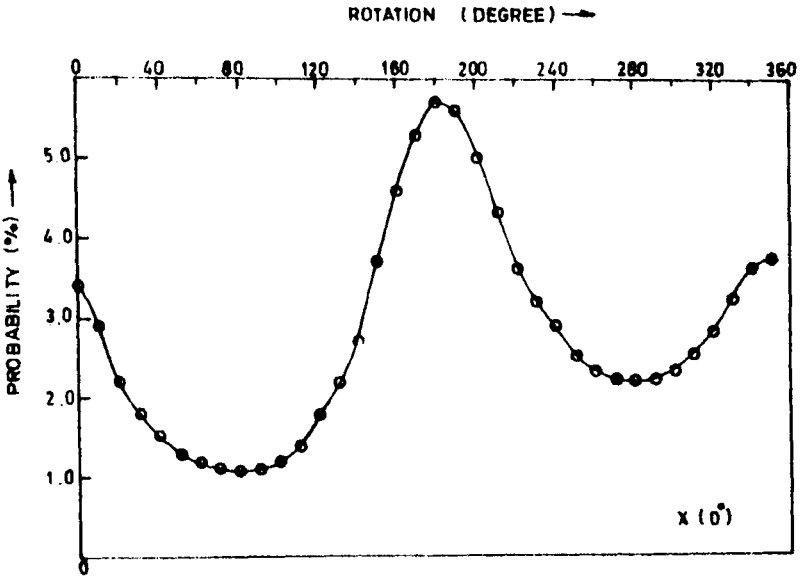


(a)



(b)

FIGURE 3 (a,b) A plot of probability distribution with respect to rotations about Y-axis during in-plane interaction through side P1.



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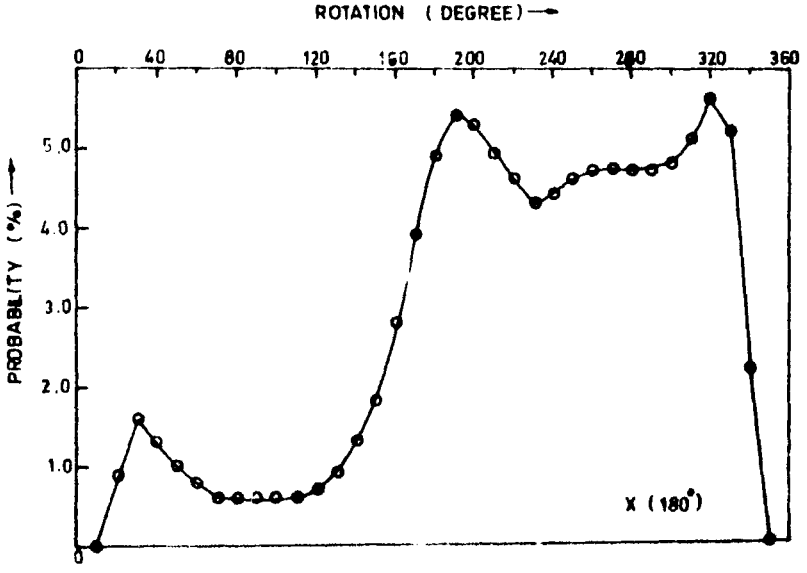
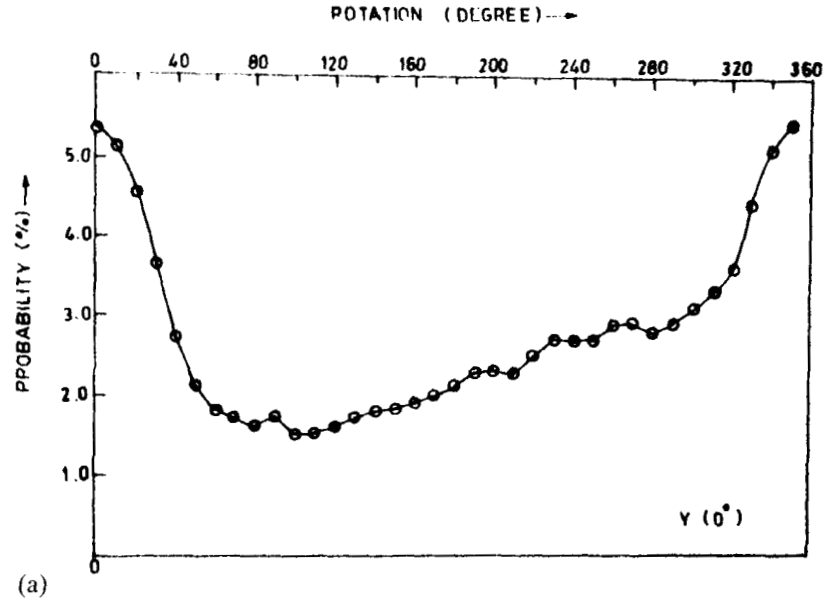
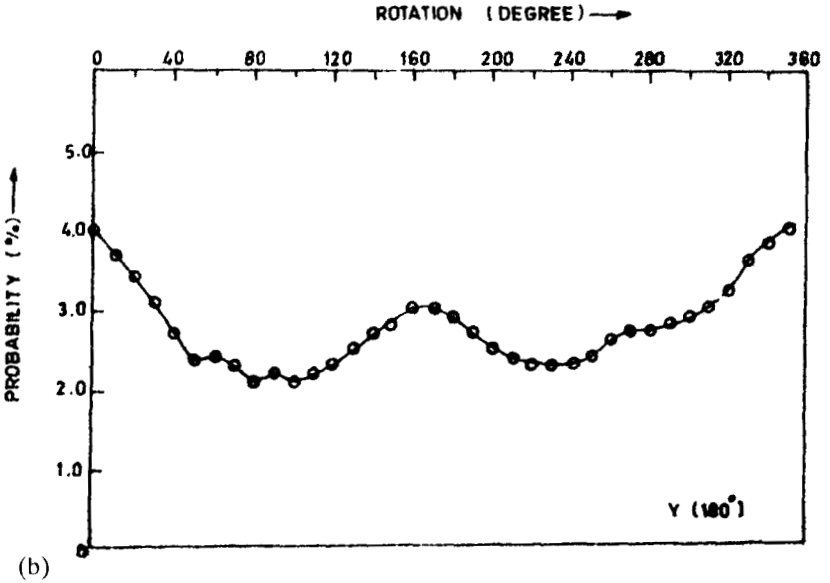


(d)

FIGURE 3 (c,d) Variation of probability with respect to rotations about Y-axis during in-plane interaction through side P2.

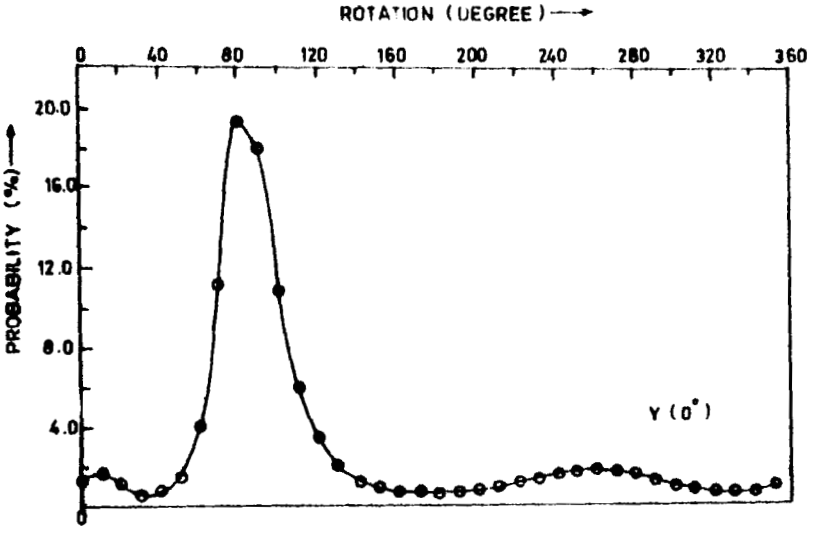


(a)



(b)

FIGURE 4 (a,b) A graphical representation of the probability distribution with respect to rotations about the long molecular axis (X-axis) during in-plane interaction through side P1.



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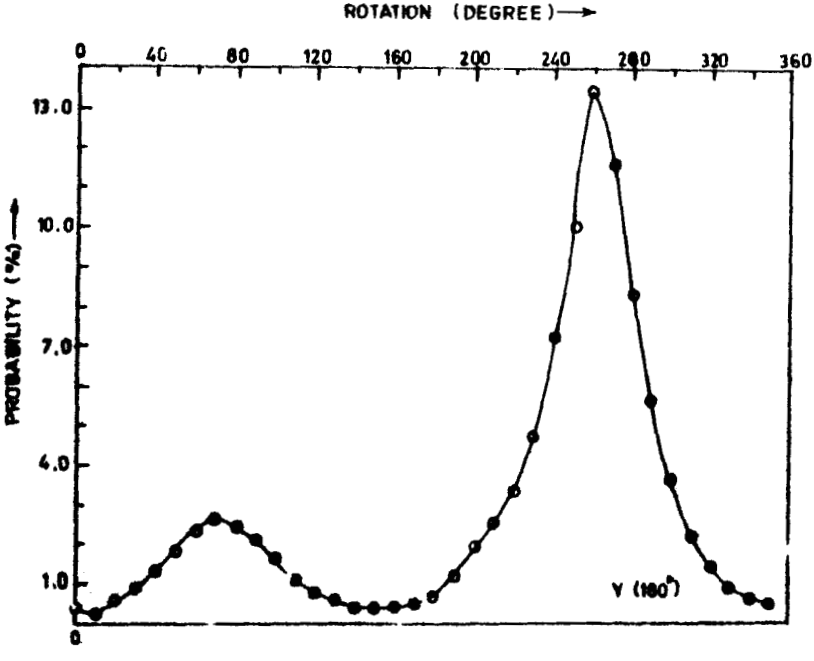

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FIGURE 4 (c,d) Variation of probability with respect to rotations about the long molecular axis during in-plane interaction through side P2.

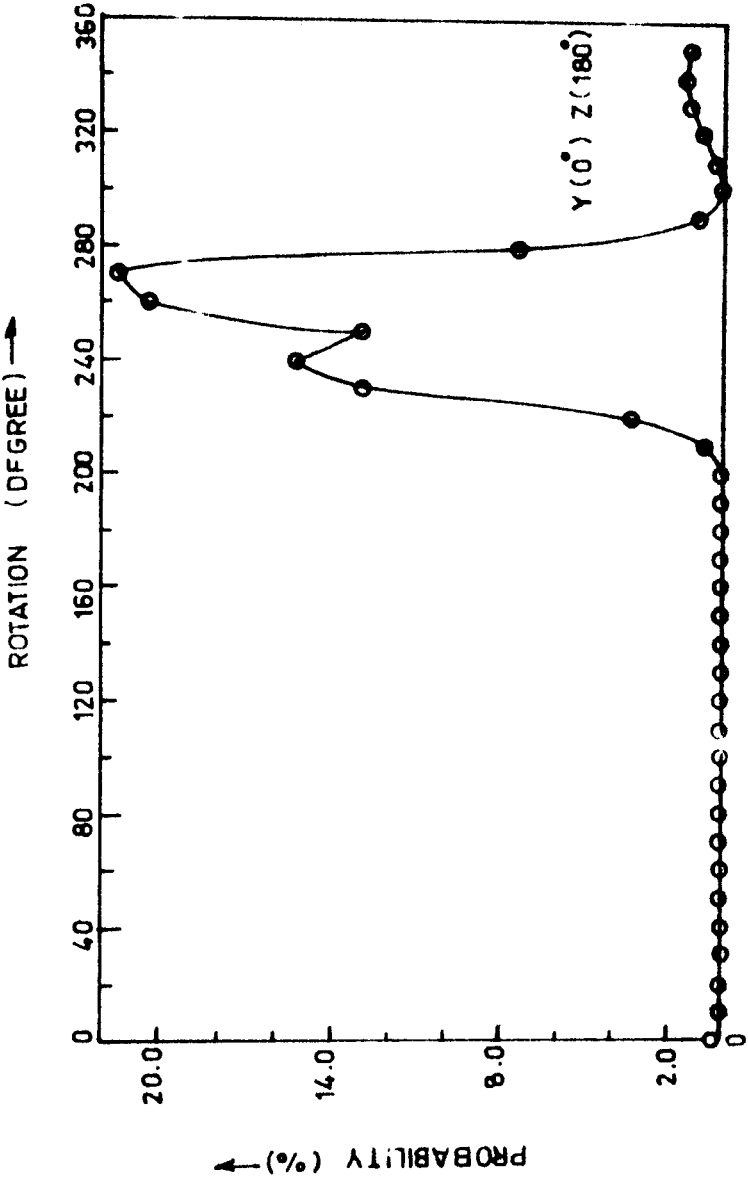


FIGURE 4 (e) Variation of probability with respect to rotations about the long molecular axis (X-axis) during stacking interaction through face S2.

TABLE II

Total probability in a range of ±10° near the maximum probable configuration for stacking and in-plane interactions

Interaction's type	Configuration	Rotation (deg.)	Probability (%) T = 300°K	T = 340°K	T = 396°K	T = 450°K
P1	X(0°)	0 ± 10	8.87	8.75	8.63	8.54
		180 ± 10	18.23	16.88	15.50	15.52
P1	X(180°)	0 ± 10	14.40	13.56	12.71	12.12
		180 ± 10	10.44	10.21	9.97	9.78
P2	X(0°)	0 ± 10	10.08	9.79	9.73	9.83
		180 ± 10	19.73	17.73	16.55	15.42
P2	X(180°)	180 ± 10	15.00	14.61	14.12	13.71
		320 ± 10	17.32	16.60	15.78	15.14
S2	X(0°)Y(0°)	170 – 190	49.94	40.41	36.59	31.98
		350 – 10	21.27	19.86	19.96	18.83
S2	X(180°)Y(0°)	170 – 180	90.62	85.32	77.18	68.96

For P1, the probability at 0° ± 10° is nearly 13% while for 180° ± 10°, it is almost 10% over a large temperature range. For P2, near 180° ± 10°, the probability is nearly 14% but there is no preference near 0°. At close to 320°, the probability rises to 16% and truly speaking, from 180° to 320°, the change in probability is relatively very small. This indicated a finite probability for alignment at low temperatures exists when the thermal agitation does not drastically disturb the molecular alignments. The peculiar behavior of side P2 is further elaborated when the rotation about X-axis is considered.

Rotation about X-axis for Y = 0 or 180° at P1 (Figures 4a, 4b) show clear preference for 0° ± 10° though the difference in energy for different values of X-rotation is very small. Thus, generally, the molecules may be assumed to be capable of free rotations except at lower temperatures where the two molecules prefer being in the same plane. For side P2, however, a different picture is obtained (Figure 4c and 4d). For Y(0°), the preference is for X = 80° ± 10° where the total probability near the transition temperature is about 48% which rises up to 60% at room temperature. Similarly, for Y(180°), the preference is for 260° ± 10° where the probability is 35% rising up to 44% at room temperature. This anomalous behavior is due to an attraction between the oxygen of —N = N— bridge of one mole-

cule with the nitrogen attached to the other molecule through the bridge. This is further explained by Figure 4e when the stacked configuration S2 with Y(0°)Z(180°), one of the molecules is rotated about X-axis and shows about 44% probability in 260°–270° range.

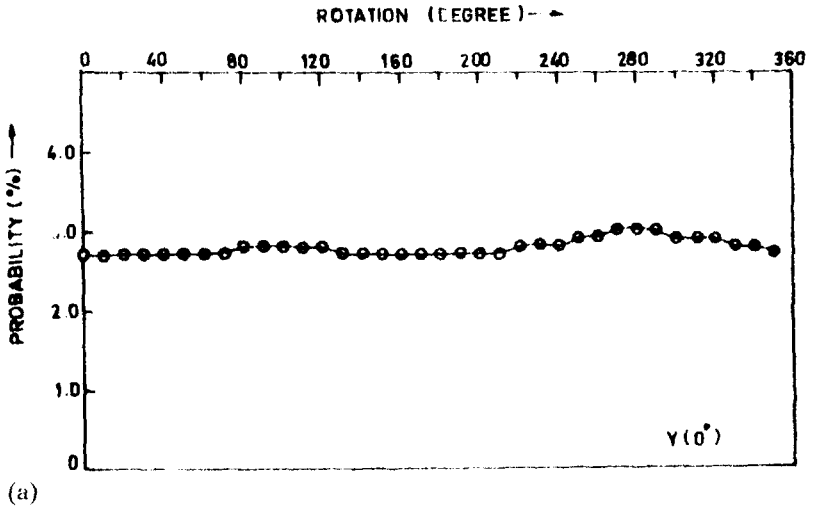
TERMINAL INTERACTIONS

In the absence of strong polar groups at the ends of the molecule, the terminal attraction is very weak (though it is clear that the terminals are not repulsive to each other). Rotations about X-axis (Figures 5a, 5b) show absolutely no preference for any angle *i.e.* the molecules are completely free to rotate about their long molecular axes. However, for rotations about Y-axis, one may observe (Figure 5c, 5d) that there is a slight preference for the molecular axes being on the same line.

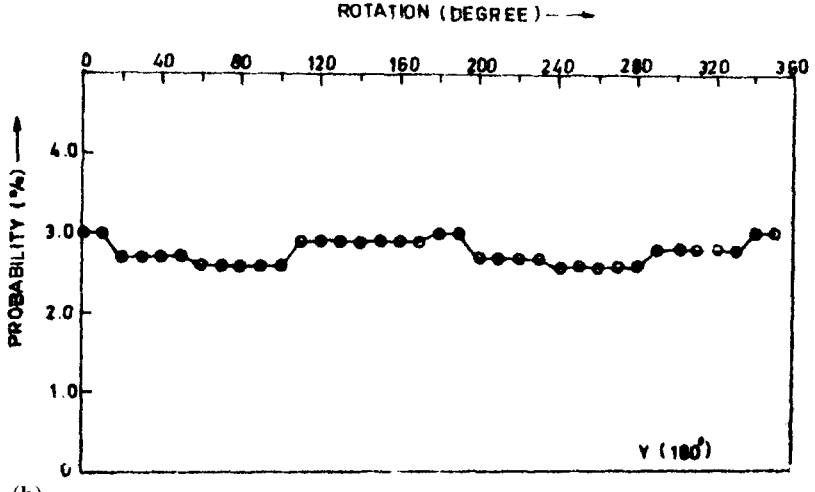
EFFECT OF TRANSLATION

The nematic character of a liquid crystal is generally manifested by its translational freedom along the long molecular axis. Therefore, for stacked and in-plane interactions, translations towards both the directions have been allowed at an interval of 2 Å and the corresponding change in probabilities have been reported.

Figures 6a, 6b show the results obtained for stacking interactions at faces S1 and S2 respectively. It may be observed that stacking interactions have lesser translational freedom. Table III shows that the ratio of probability of being at maximum probability point to having ± 2 Å displacement is 1.94 for S2 and 1.28 for S1 at nem. $\rightarrow$ isotropic transition temperature. However, at room temperature these values are respectively 2.94 and 1.73 indicating a very strong binding at lower temperatures but with the increase in temperature, the molecules obtain sufficient freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planar interactions. Thus, for side P1 even at room temperature this ratio is only 0.65 which reduces to 0.44 at the transition temperature. Similarly, for P2, the ratio at room temperature is 1.24 which reduces to 1.10 at transition temperature. It may however be noted that (see Figures 6c and 6d) though the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus in the mesomorphic range, small movements along the sides (or at best along surface S1) of the molecules are only possible.



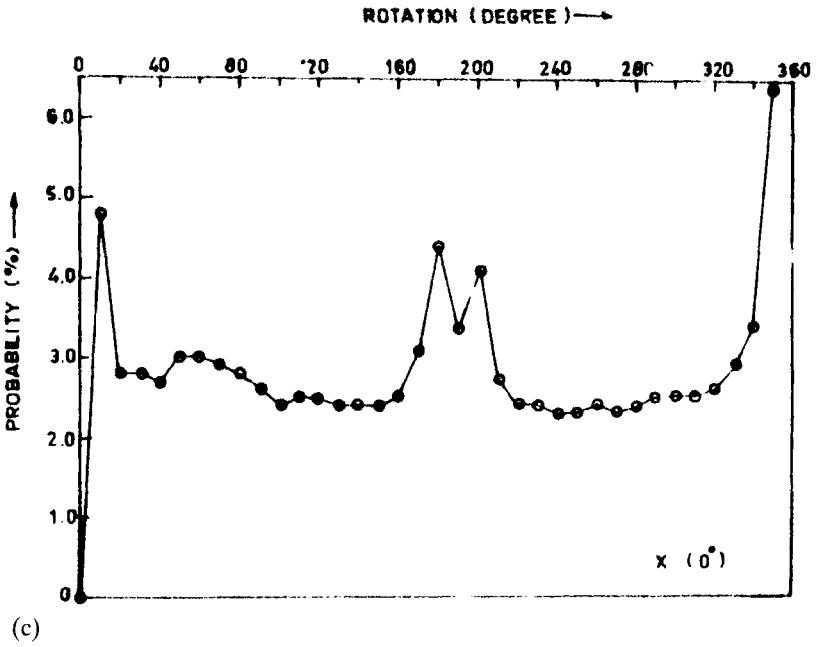
(a)



(b)

FIGURE 5 (a,b) Variation of probability with respect to rotations about the long molecular axis (X-axis) during terminal interactions.

It is clear from the above discussion that isolated consideration for any particular degree of freedom manifests, in general, a preference for an aligned structure with some allowance of deviation from its minimum energy (or maximum probable) configuration. Also, each configuration has its own minimum energy structure for every degree



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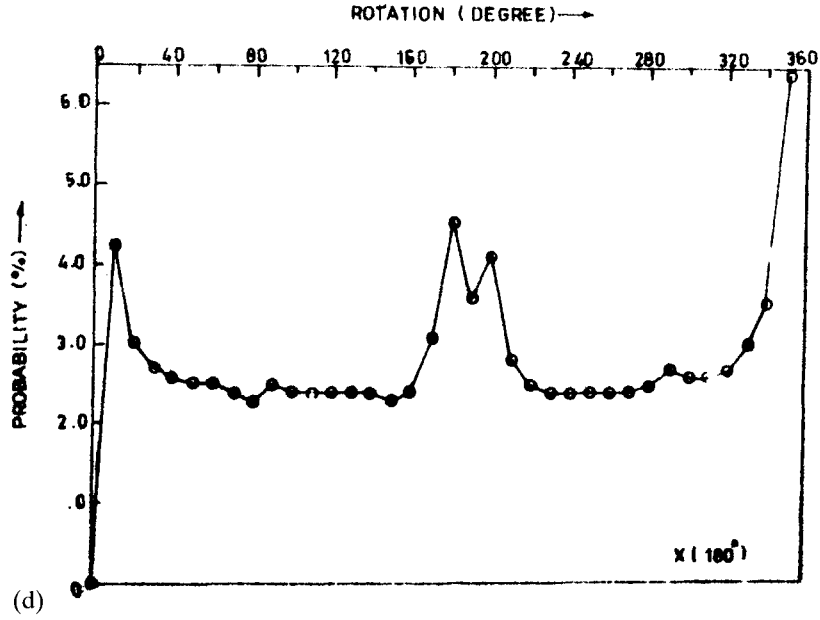


(d)

FIGURE 5 (c,d) Variation of probability with respect to rotations about Y-axis during terminal interactions.

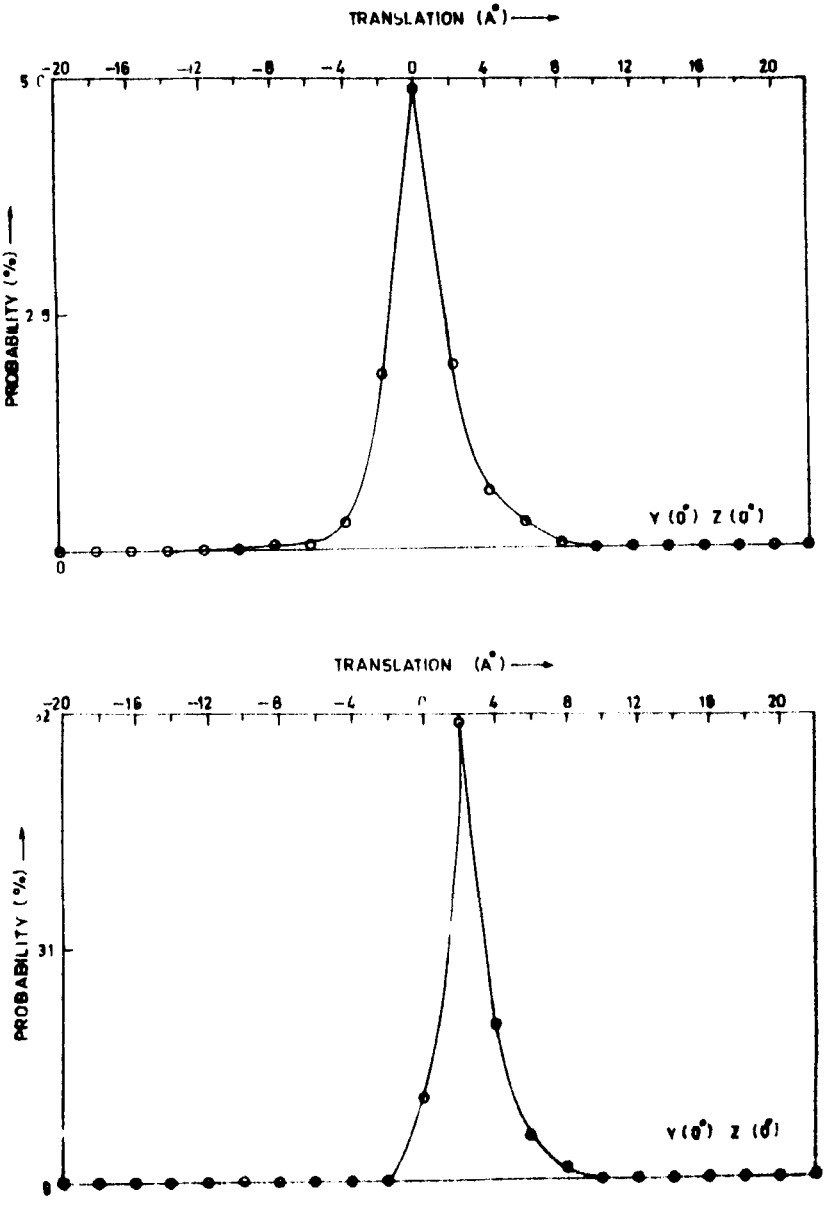
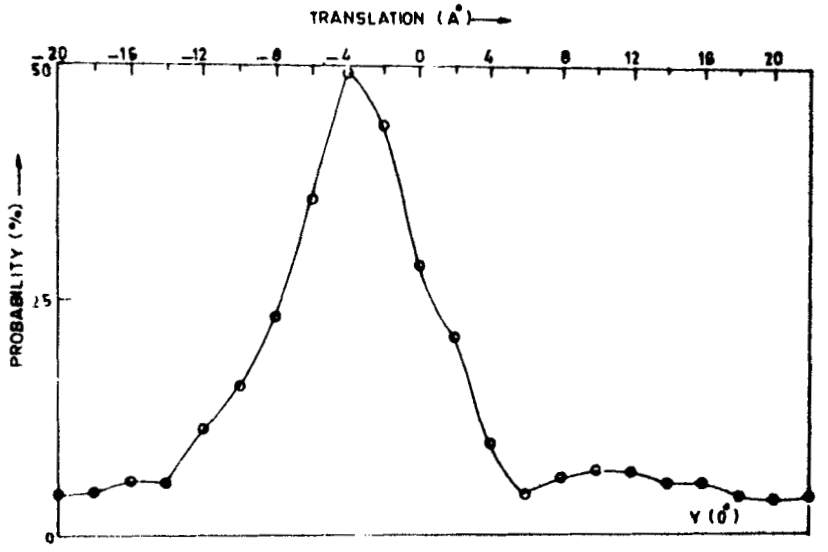
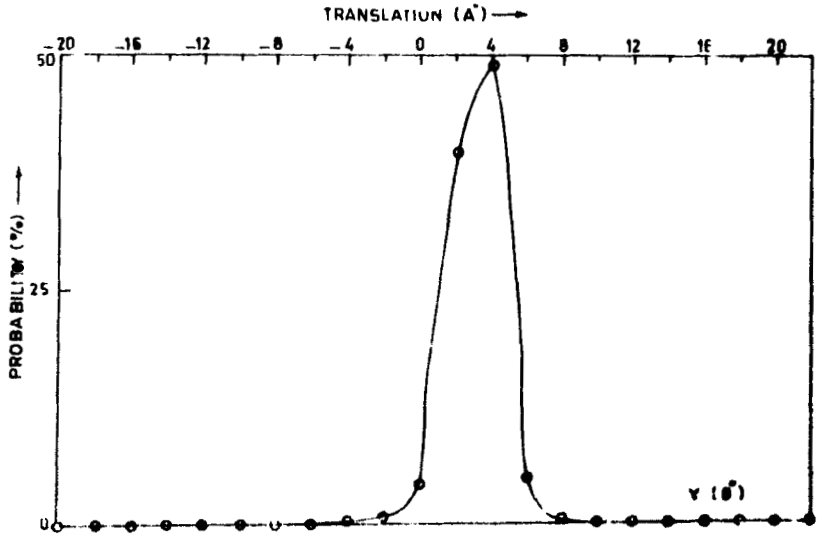


FIGURE 6 (a,b) Variation of probability with respect to translation along the long molecular axis during stacking interactions through faces S1 & S2 respectively.



(c)



(d)

FIGURE 6 (c,d) Variation of probability with respect to translation along the long molecular axis during in-plane interactions through sides P1 & P2 respectively.

TABLE III

Ratio of probability of being at maximum probability point to having ±2 Å displacement along the long molecular axis for stacking and in-plane interactions.

Interaction's type	Configuration	Probability (%)			
		T = 300°K	T = 340°K	T = 396°K	T = 450°K
P1	Y(0°)	0.65	0.47	0.44	0.42
P2	Y(0°)	1.24	1.17	1.10	1.04
S1	Y(0°)Z(0°)	1.73	1.49	1.28	1.14
S2	Y(0°)Z(0°)	2.94	2.41	1.94	1.66

of freedom. Thus in a molecular assembly, a number of local minimum energy configurations exist; all of them have their own importance as in the case of a close molecular packing, any molecule, 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 coming down from a very high temperature when the molecules have a completely disordered distribution, the global minimum has the maximum probability of occupancy and the other minima have a sequential preference depending on their individual relative probability. Table IV gives the compatative probabilities for all the observed minima in different configurations. It may be observed that stacking through S2 with X(180°)Y(0°) has maximum relative probability (almost 90%) while X(0°)Y(0°) for S2 has the next highest probability than S2 but slightly higher than for planar associations. In-plane interactions through both the sides are almost equivalent but are of importance only after stacking is complete.

CONCLUSION

These calculations provide an insight of the molecular arrangements inside a bulk of material. The major alignment seems to come through stacking at S2 surface with X(180°)Y(0°) which is a fairly rigid configuration over a wide temperature range. All other configurations such as stacking through S1 or in-plane interactions on both the sides show a preference for an aligned structure but they are much less rigid and at higher temperature show gradual increase in the freedom for deviating from the minimum energy configuration by translating along the long molecular axis or to a smaller extent by orientational changes.

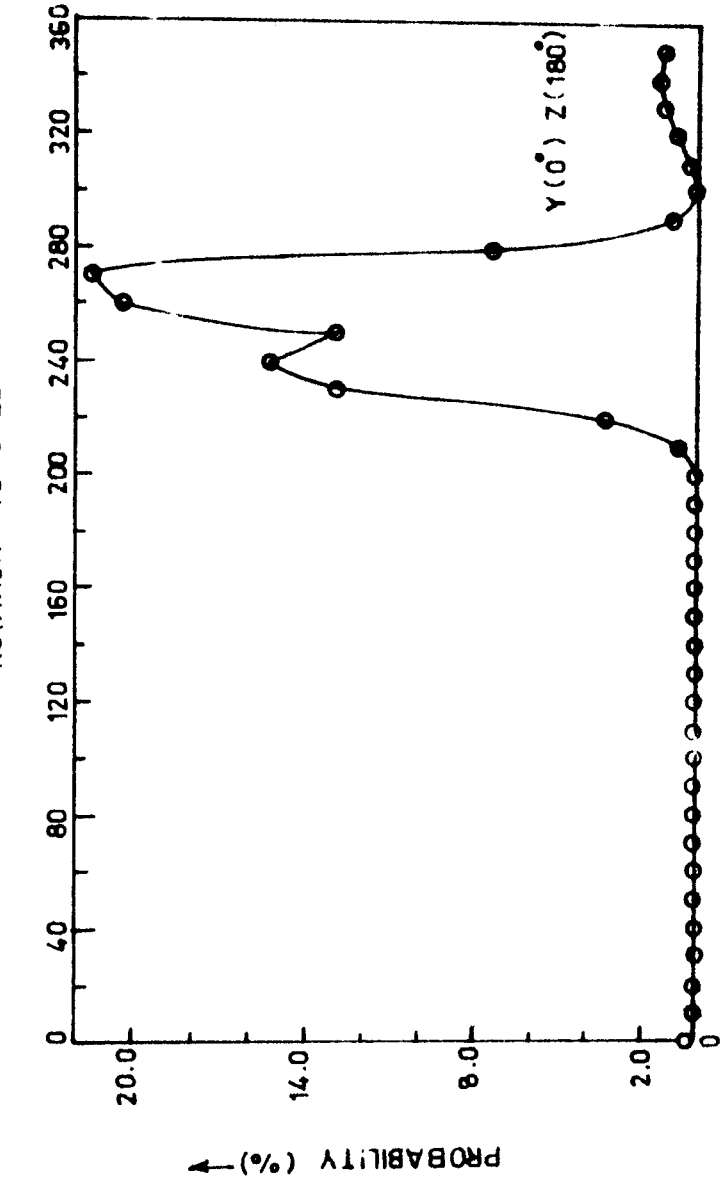


FIGURE 4 (e) Variation of probability with respect to rotations about the long molecular axis (X-axis) during stacking interaction through face S2.

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