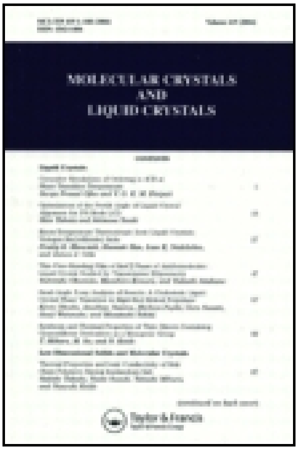

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Molecular Interactions between a Pair of Ethyl para-azoxybenzoate (EPAB) Molecules: A Smectogenic Liquid Crystal

Nitish K. Sanyal [a] , Sugriva Nath Tiwari [a] & Mihir Roychoudhury [a]

[a] Department of Physics, University of Gorakhpur, Gorakhpur, 273001, India

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Molecular Interactions between a Pair of Ethyl para-azoxybenzoate (EPAB) Molecules: A Smectogenic Liquid Crystal

NITISH K. SANYAL, SUGRIVA NATH TIWARI and MIHIR ROYCHOUDHURY

Department of Physics, University of Gorakhpur, Gorakhpur 273001, India

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A theoretical study of molecular ordering in Ethyl para-azoxybenzoate has been undertaken. Modified Rayleigh-Shrodinger perturbation treatment has been employed to evaluate the stacking and in-plane lateral interactions between a pair of EPAB molecules. CNDO/2, an all valence electron method, has been used to compute the net atomic charges and dipoles at each atomic centre. Results have been discussed to enunciate the role of various molecular forces in stabilizing the interacting configurations in the maintenance of molecular ordering. An attempt has also been made to correlate the results with experimental evidences.

Keywords: inter-molecular interactions, multicentred-multipole method, smectogenic liquid crystals.

INTRODUCTION

Ethyl para-azoxybenzoate (EPAB) transforms at about 90°C to a high-temperature polymorph (solid II), melts to a smectic mesophase at 114°C and becomes an isotropic liquid at 120°C.[1] The low temperature form (solid I) of the enantiotropic smectogenic liquid crystal, EPAB, has been studied by crystallographic methods by Krigbaum and Barbar[1] while the high temperature crystallographic studies (solid II) has been extensively discussed by Krigbaum and Taga.[2] It has been established that EPAB exists in four different rotational conformers viz cis-cis, cis-trans, trans-cis and trans-trans. Solid I is presumed to exist predominantly in the cis-cis form which is known to be a high energy conformer. The high temperature polymorph (solid II), is composed of a mixture of trans-cis and cis-trans conformers. However, in both the cases (solid I and solid II) molecular planarity of EPAB molecules, is always noticed.[1,2]

It is evident that intermolecular forces are of immense importance in determining the positional and orientational order of mesomorphic compounds. The melting point, the temperature at which an ordered geometrical arrangement collapses and gives rise to the disordered isotropic melt, and also the temperatures at which profound but peculiar (mesomorphic properties) type of changes are noticed, depend to a very large extent on the nature of intermolecular interactions existing within the system. The cycle of mesomorphism (heating or cooling) and the transition temperature are governed by the intermolecular forces which act between the planes and ends of the molecules. Also, the nature of mesomorphism, its ranges and thermal stability etc. of the systems are justified by the extent to which the forces like dipole-dipole, induced dipole and van der Waal's etc operate to maintain regular molecular arrangement against the disturbing influence of thermal agitations caused by increased temperature. The significant role of intermolecular forces in the case of mesomorphic compounds, have been extensively discussed in numerous books and research articles.[3-11]

In the earlier communications,[12,13] second order perturbation treatment (Rayleigh-Schrodinger) together with CNDO/2 method, were employed to study Anisaldehyde azine[12] and Biphenyl-4-carboxylic acid.[13] A comparative study of the persistence of electrostatic forces during hydrogen bonding (dimer formation) and stacking of biphenyl systems were also reported.[13]

In the present paper, an extensive study of the molecular interactions in the smectogenic liquid crystal, ethyl p-azoxybenzoate, has been presented. All the possibilities of in-plane lateral interactions which are often considered to be largely responsible for smectogenic behaviour of compounds, has been explored to obtain the lowest energy configuration. The stacking interactions between a pair of EPAB molecules, have also been evaluated corresponding to 0° and 180° of rotations about the long molecular axis and about an axis perpendicular to it. The variations of various components of interaction energy viz electrostatic, polarization, dispersion and repulsion along with the total energy as a function of inter-molecular separation, orientation and inversion, have been calculated and represented graphically. In fact, the repulsion energy has not been shown but it can be estimated and its nature can be very easily obtained from the sum of the dispersion and repulsion energy curve. This has been done because of the fact that the expression due to Kitaigorodskii[14,15] has been used to evaluate dispersion and repulsion energy terms together. Only lowest energy configurations have been reported and has been compared with crystallographic studies.

METHOD OF CALCULATION

Second order perturbation treatment applicable for intermediate range[16,17] has been used to evaluate the intermolecular interaction energy between a pair of EPAB molecules for both, stacking and in-plane interactions. According to this, the total energy (E_{TOT}) is expressed as

$$E_{TOT} = E_{EL} + E_{POL} + E_{DISP} + E_{REP}$$

where E_{EL}, E_{POL}, E_{DISP} and E_{REP} are the electrostatic, polarization, dispersion and repulsion terms respectively. Again, electrostatic term may be split as

$$E_{EL} = E_{QQ} + E_{QMI} + E_{MIMI} + ---$$

where E_{QQ}, E_{QMI}, and E_{MIMI} etc represent the monopole-monopole, monopole-dipole, dipole-dipole and other higher order terms due to higher multipoles. On the basis of a comparative study of theoretical calculations and experimental observations, it has been found that computations upto dipole-dipole term are sufficient to evaluate the electrostatic energy with reasonable accuracy as the higher order terms have a very minor contribution to the total electrostatic energy and at the same time involves a complicated conceptual and computational excercise.[17] Therefore, the computation was restricted upto dipole-dipole term only. The detailed formalism may be found elsewhere.[12]

An all valence electron method,[18] CNDO/2, has been employed to compute the net atomic charges and atomic dipoles at each of the atomic centres. The crystallographic data for the molecular geometry of EPAB, has been taken from literature[1] in the cis-cis conformer only.

All the computations were carried out on a CDC 'Cyber' computer at Tata Institute of Fundamental Research, Bombay.

ENERGY MINIMIZATION

Energy optimization is carried out for both, stacking and in-plane interactions separately. Both, lateral and angular variations are made in one of the molecules with respect to the other which is kept fixed. In this system, X- and Y-axes are defined as the long molecular axis and an axis perpendicular to it such that the molecular plane lies in the (XY) plane. The Z-axis is chosen perpendicular to (XY) plane and passing through the centre of gravity of the molecule, which is taken as origin.

STACKING ENERGY

The interplanar distance between a pair of molecules are varied from 3.5 Å to 6.0 Å at an interval of 0.5 Å and energies have been computed for four distinct rotational sets namely X(0°)Y(0°); X(0°)Y(180°), X(180°)Y(0°) and X(180°)Y(180°). The minimum energy configuration, thus located, is chosen as starting point and four fixed rotations about Z-axis viz 0°, 90°, 180° and 270° are given. Corresponding to each of the rotations, the other molecule is slided along the X-axis (long molecular axis) starting from −12.0 Å to 12.0 Å and again energies are computed at an interval of 2 Å. Taking the configuration with minimum energy, further rotations about Z-axis are given at an interval of 10°. Rotations, both, clockwise and anti-clockwise, ranging upto ± 70°, are made and energies are evaluated. The final configuration with the lowest energy, is obtained by refining the minimum energy configuration at shorter intervals e.g. 1° in rotation and 0.1 Å in translation (sliding).

IN-PLANE INTERACTIONS

During the in-plane interaction energy calculations, one of the molecules is translated along ±Y-axis and starting from ±3.0 Å to ±11.0 Å, energies are evaluated at an interval of 1.0 Å corresponding to the four rotational sets viz X(0°)Y(0°), X(0°)Y(180°), X(180°)Y(0°) and X(180°)Y(180°). This gives a minimum energy configuration which is chosen as starting point for further optimization. Also, the interacting molecule is slided with respect to the fixed one along the X-axis, starting from −26 Å to 28 Å at an interval of 1 Å and energies are computed for each point and a minimum energy configuration is obtained. This is further refined to finally obtain the lowest energy configuration.

Accuracies upto 0.1 Å in translation (sliding) and 1° in rotation, are achieved. Only the lowest energy configurations have been reported in the present paper.

RESULTS AND DISCUSSION

The molecular geometry of EPAB molecule has been shown in Figure 1 along with various atomic index numbers. Net atomic charge and the corresponding dipoles at each atomic centre, have been listed in table I while the total energy, binding energy and of distribution of the dipole moment have been presented in table II.

Figure 2 (a to d) shows the dependence of stacking energy on interplanar distance between the two stacked EPAB molecules corresponding to four different rotational sets namely X(0°)Y(0°), X(0°) Y(180°), X(180°)Y(0°) and X(180°)Y(180°) respectively. It is evident from Figure 2 that electrostatic energy decreases with increasing intermolecular separation except in the case shown in Figure 2d where it increases with the increase in separation. The electrostatic contribution to the total energy, is repulsive for the two cases shown in Figure 2a and 2b respectively while negligible contribution is observed for the rotational set X(180°)Y(0°) shown in Figure 2c. However, a small but significant elecrostatic contribution is noticed corresponding to X(180°)Y(180°) shown in Figure 2d. This implies that electrostatic energy is largely affected by axial rotations. Polarization energy is always weak and shows nearly the same nature in all the four cases. The dispersion energy exhibits a continuous and rapid decrease with

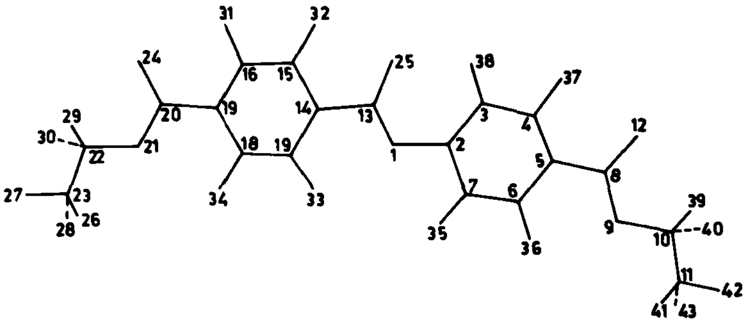


FIGURE 1 Molecular geometry of Ethyl para-azoxybenzoate (EPAB) alongwith various atomic index numbers.

TABLE I

Molecular charge distribution on Ethylpara-azoxybenzoate molecule

Sl. No.	Atom	Charge	Atomic dipole components X	Y	Z
1	N	−0.166	0.656	1.786	0.002
2	C	0.095	−0.029	−0.123	−0.013
3	C	−0.021	0.041	−0.240	−0.001
4	C	0.032	−0.095	−0.161	−0.007
5	C	−0.042	−0.067	0.016	0.007
6	C	0.027	−0.044	0.150	0.002
7	C	−0.009	0.094	0.111	0.002
8	C	0.396	0.188	−0.190	−0.026
9	O	−0.252	0.900	0.937	0.022
10	C	0.156	−0.233	0.081	−0.102
11	C	−0.033	−0.041	−0.026	0.181
12	O	−0.326	−0.917	−1.021	−0.039
13	N	0.354	−0.019	−0.446	0.003
14	C	0.068	0.112	0.035	0.015
15	C	0.002	−0.093	−0.263	−0.008
16	C	0.042	0.086	−0.139	0.004
17	C	−0.040	0.131	0.009	−0.037
18	C	0.036	0.108	0.139	0.013
19	C	−0.008	−0.045	0.223	0.000
20	C	0.400	−0.183	−0.132	0.007
21	O	−0.254	−0.646	1.139	0.030
22	C	0.184	0.222	−0.130	0.011
23	C	−0.018	0.072	0.223	−0.019
24	O	−0.317	0.649	−1.211	−0.060
25	O	−0.445	−0.495	−1.266	−0.009
26	H	0.010	0.000	0.000	0.000
27	H	0.014	0.000	0.000	0.000
28	H	0.011	0.000	0.000	0.000
29	H	−0.015	0.000	0.000	0.000
30	H	−0.017	0.000	0.000	0.000
31	H	0.002	0.000	0.000	0.000
32	H	0.042	0.000	0.000	0.000
33	H	0.021	0.000	0.000	0.000
34	H	0.004	0.000	0.000	0.000
35	H	−0.004	0.000	0.000	0.000
36	H	−0.004	0.000	0.000	0.000
37	H	0.008	0.000	0.000	0.000
38	H	0.039	0.000	0.000	0.000
39	H	−0.010	0.000	0.000	0.000
40	H	−0.004	0.000	0.000	0.000
41	H	0.019	0.000	0.000	0.000
42	H	0.012	0.000	0.000	0.000
43	H	0.012	0.000	0.000	0.000

separation in all the cases. At shorter distances, the drop in dispersion energy is sharp but at the same time repulsion energy arising due to short range "exchange" type of forces becomes more dominant and,

TABLE II

Total energy, binding energy and total dipole moment distribution of Ethylpara-azoxybenzoate

Total Energy = −256.9198 A.U.
Binding Energy = −21.8892 A.U.
Total Dipole Moment = 2.7254 Debyes

Components	X	Y	Z
Densities	−1.55169	−1.94030	−0.14498
S.P.	0.35108	−0.50080	−0.02069
P.D.	0.00000	0.00000	0.00000
Total	−1.20060	−2.44110	−0.16567

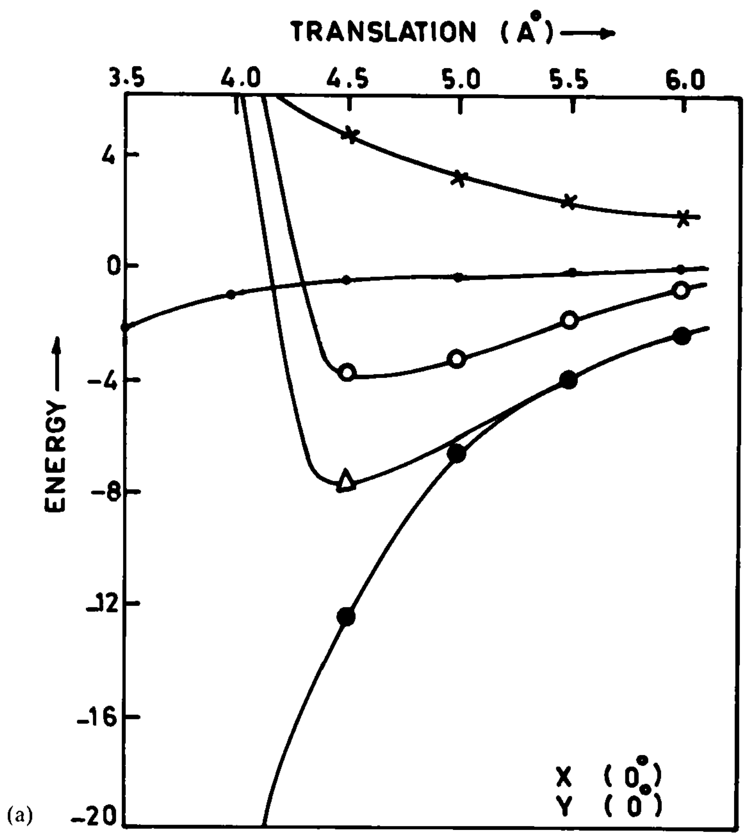


FIGURE 2 (a to d): The variation of stacking energy components with respect to interplanar separation for various rotational sets mentioned in the respective figures [X → electrostatic, • → polarization, ● → dispersion, ▲ → dispersion + repulsion and ⊙ → total stacking energy] in KCal/mole.

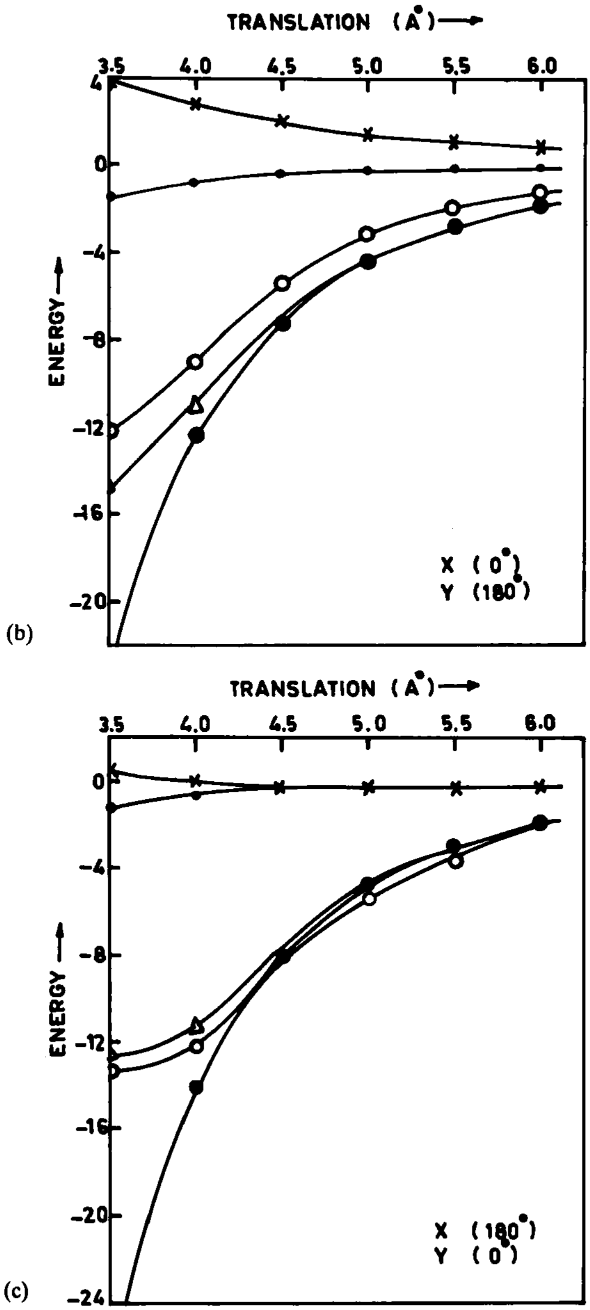


FIGURE 2 *continued*

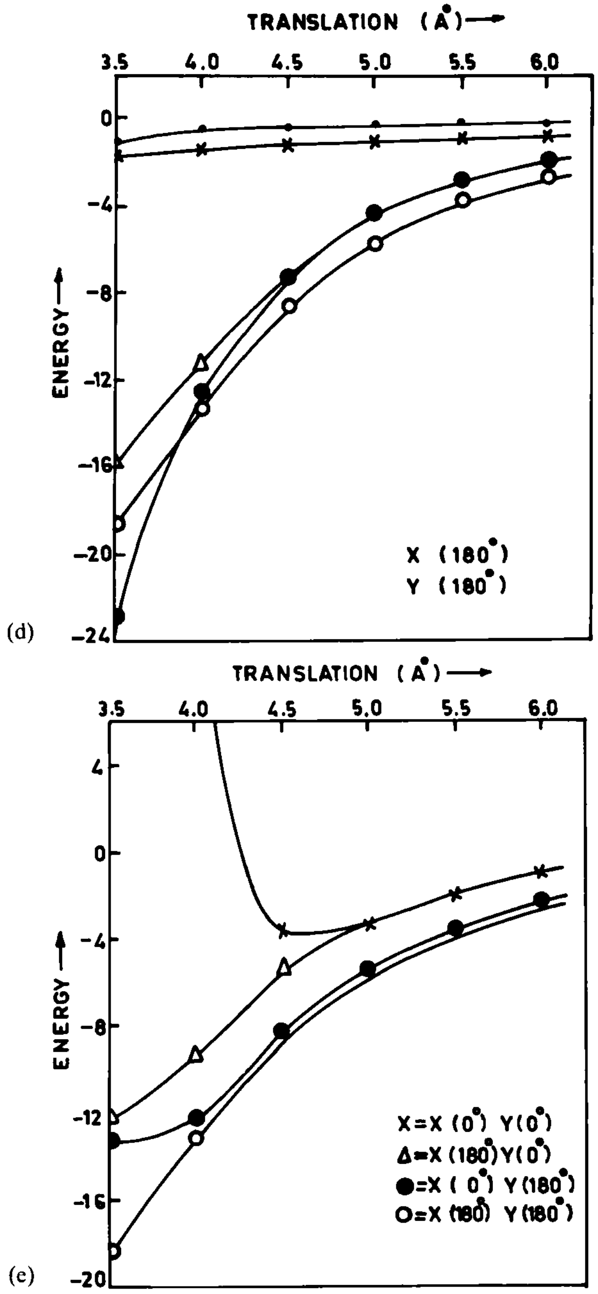
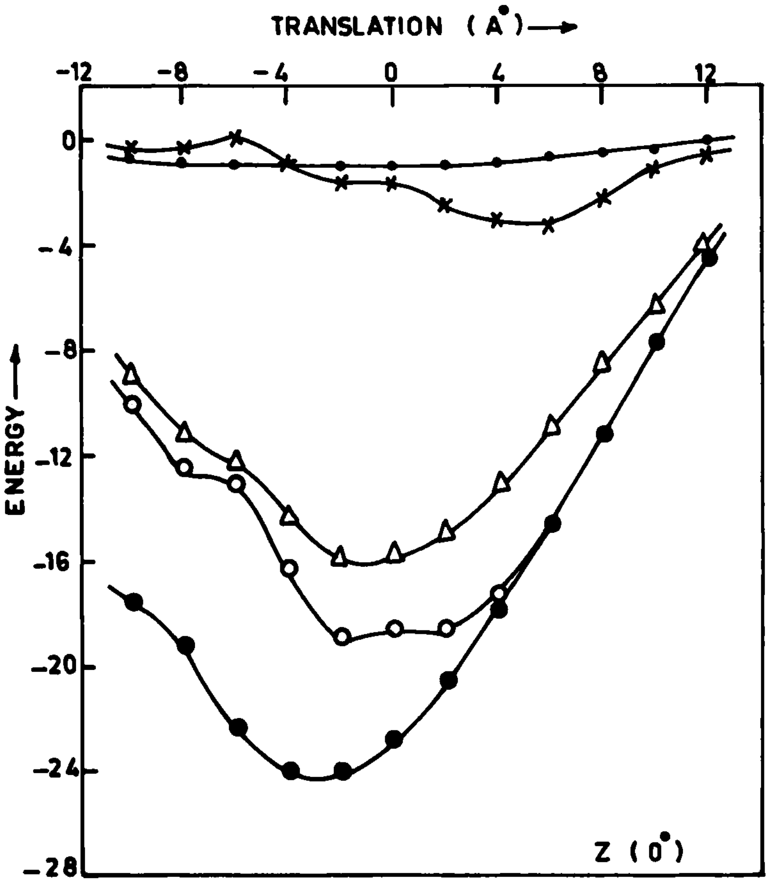


FIGURE 2e: A plot of the total stacking energy values as a function of interplanar separation (Energy in KCal/mole).

therefore, a definite value of the total energy results. The repulsion energy has not been plotted explicitly as it can be easily recognized by the curve due to the Kitaigorodskii term which shows a gross similarity with the total energy curve in all the cases. As indicated in Figure 2e, except for X(0°)Y(0°) which selects its minimum at 4.5 Å, the remaining three configurations show their energy minima at 3.5 Å. However, energetically the most favourable complex is obtained due to X(180°)Y(180°) which has been further analyzed.

The variation in the stacking energy with respect to translation along the X-axis, has been shown in Figure 3 (a to d) for four pre-selected rotations about the Z-axis viz 0°, 90°, 180°, 270°. It is noticed



(a)

FIGURE 3 (a to d): The variation of stacking energy components with respect to sliding along the long molecular axis for four fixed rotations about the z-axis. Energy is in KCal/mole (X → electrostatic, • → polarization, ● → dispersion, ▲ → dispersion + repulsion and ⊙ → total energy).

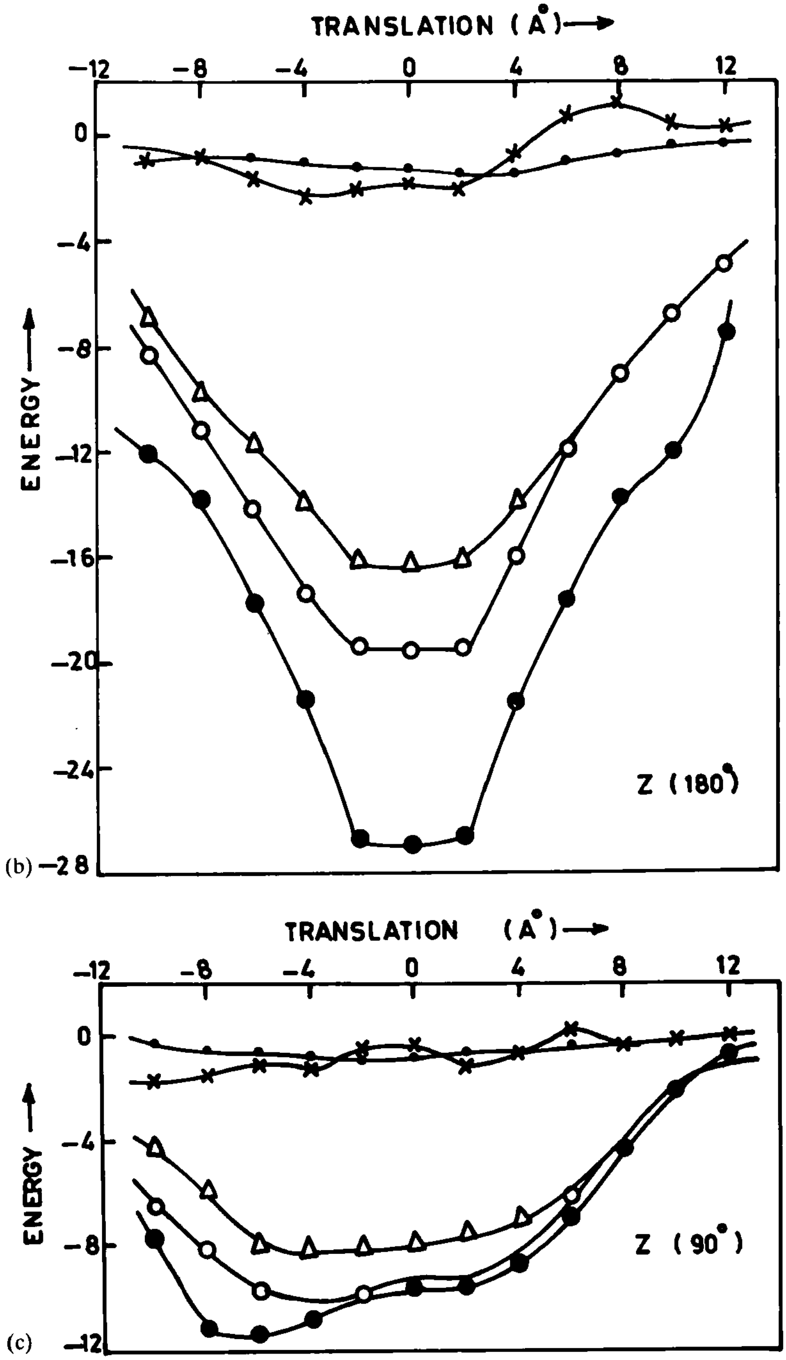


FIGURE 3 *continued*

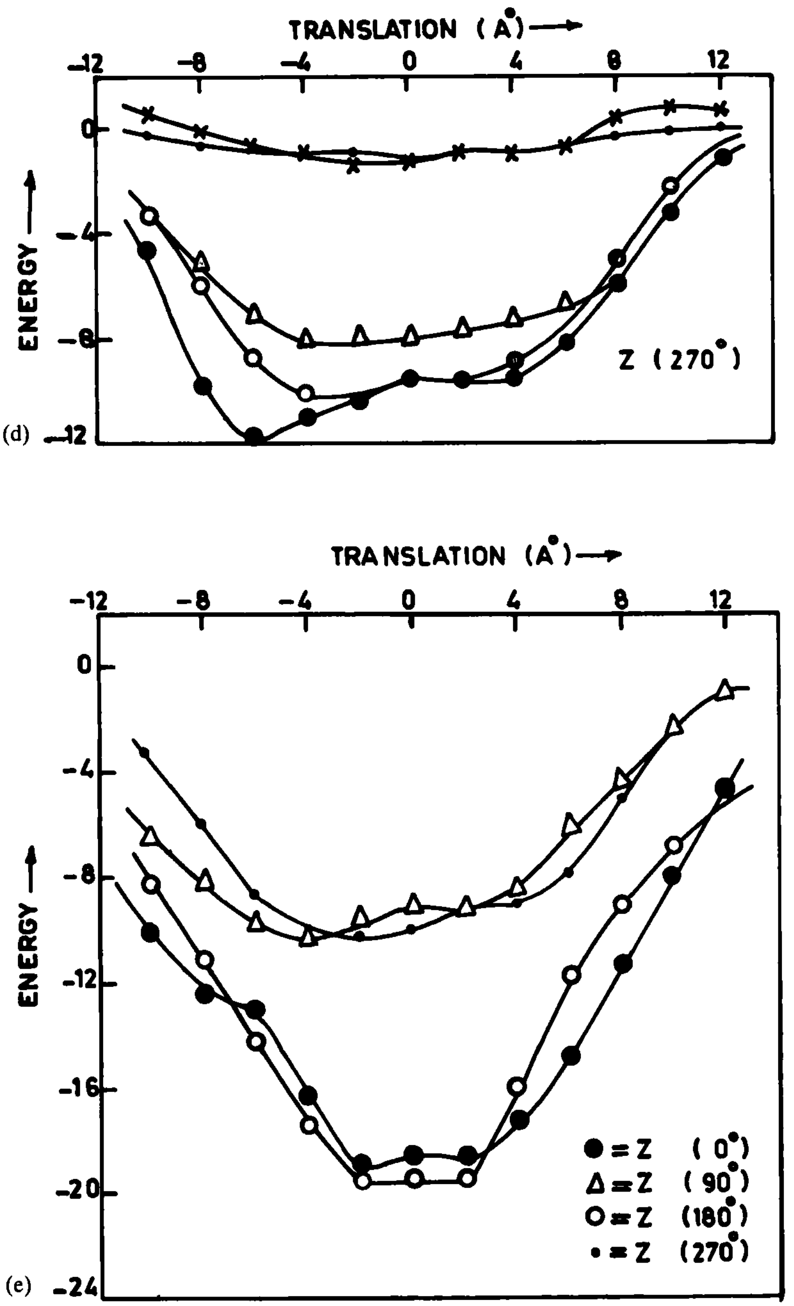


FIGURE 3e: The variation of the total stacking energy with respect to sliding along the long molecular axis.

that polarization energy, though persists over a long range, has a very small contribution to the total energy. Electrostatic energy assumes both, attractive and repulsive nature and its contribution is relatively insignificant. Also, the total energy curve shows a gross similarity with either dispersion energy curve or the curve due to Kitaigorodskii term. This implies that dispersion energy term plays a dominant role during sliding. As evident from Figure 3 (a and b), the total energy curve maintains a constant nature with respect to translation upto 4.0 Å (±2 Å back and forth from the minimum energy point). This constant region is also supported by the individual values for dispersion and dispersion plus repulsion energy components of interaction energy. However, the configuration due to Z(180°) which has a slightly lower value as compared to others, is selected for further study. Figure 3e indicates that the total energy of stacking for the cases Z(90°) and Z(270°) shown in Figure 3 (c and d), is nearly half as compared to that obtained for Z (0°) and Z (180°). This feature seems to be noteworthy because it is always less likely that two molecules of any mesomorphic compound may be stacked perpendicularly.

The angular dependence of the stacking energy components for rotations about z-axis, has been shown in Figure 4. It is noticed here that polarization energy is nearly independent of rotation while the electrostatic component shows a miminum corresponding to the total energy. Again, as discussed earlier (Figure 3) the three curves viz., dispersion, dispersion + repulsion and the total energy curves are similar in nature which implies that dispersion energy plays the most significant role in stabilizing the stacked complexes. As indicated by total energy curve, the energies at 0° (minimum) and 10° are nearly equal. This implies that EPAB molecules may possess orientational flexibility of 10° with respect to each other at the expense of a small energy.

The lowest energy configuration resulting from stacking interactions, is shown in Figure 5a with an energy −20.08 KCal/mole. The two molecules are stacked one above the other at 3.40 Å such that one of the molecules has been rotated by 180° about all the three (X,Y,Z) axes. The lowest in-plane energy configuration having energy −4.98 KCal/mole, is shown in Figure 5b. The various energy components have been given in table III. It is evident from table III that dispersion energy component largely contributes in both, stacking as well as in-plane interactions. These lowest energy configurations thus obtained are in agreement with those obtained by crystallographic studies.[1]

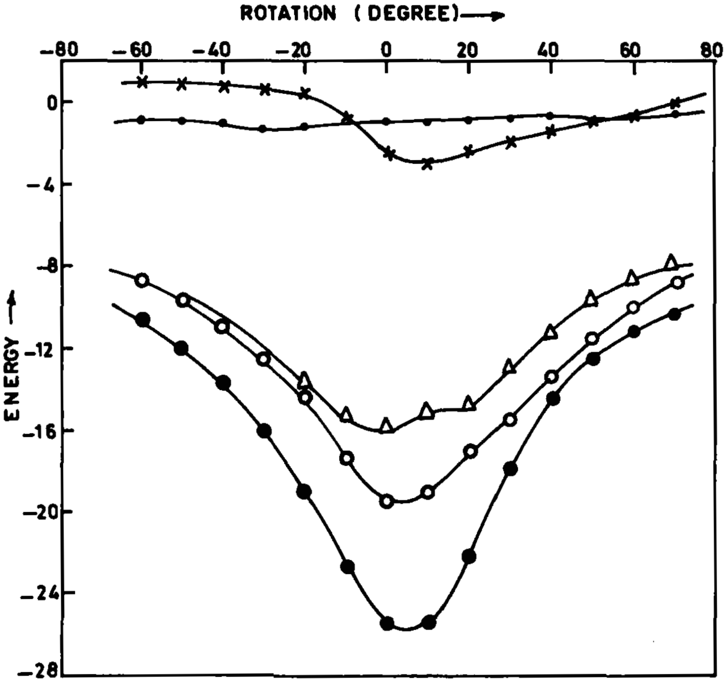


FIGURE 4 A graphical representation of the dependence of stacking energy on the rotations about the z-axis. Notations are same as in Fig 2 and 3 and energy is in KCal/mole

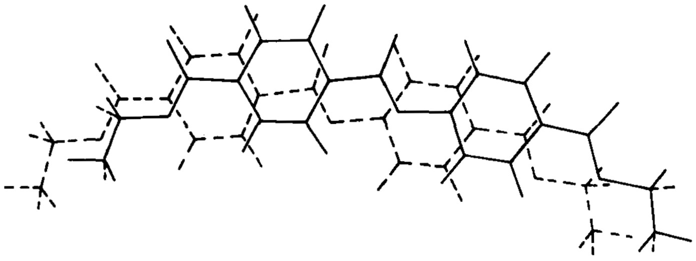


FIGURE 5a The stacked pair of EPAB molecules with lowest energy of −20.08 KCal/mole and interplanar separation 3.4 A° such that one of the molecules has been rotated by 180° about all the three (x,y & z) axes.

The interaction energy can be correlated with mesomorphic behaviour of the system. When the solid crystals of EPAB molecules are heated, the attractions between the planes of the molecules (stacking) are affected to some extent, although these attractions are strong enough (− 20.08 KCal/mole) to retain the laminar arrangement. Since

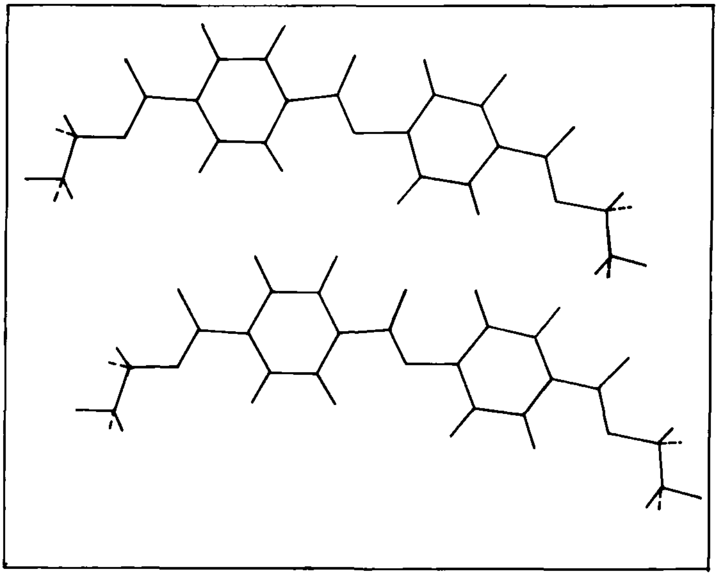


FIGURE 5b The lowest energy configuration obtained from in-plane interactions with an energy −4.98 KCal/mole.

TABLE III

Stacking and in-plane interaction energy values between a pair of EPAB molecules (Energy in KCal/mole).

Interaction energy terms	Stacking	In-plane
E_{QQ}	1.5139	−0.2013
E_{QMI}	−1.3887	−0.0798
E_{MIMI}	−3.0541	0.4394
E_{EL}	−2.9289	0.1583
E_{POL}	−1.3287	−1.0509
E_{DISP}	−29.8657	−7.1412
E_{REP}	14.0455	3.0566
E_{TOT}	−20.0779	−4.9772

EPAB molecules are associated with the two ethyl groups attached to both the ends of the molecules, the terminal (end to end) attractions will be less significant. The strong attractions between the stacked complexes, the significant contribution due to in-plane interactions to the total packing energy of the system and the weaker terminal attractions, all favour the smectic mesophase of the system at higher temperature. Also, EPAB molecules have an orientational freedom of 10° (Figure 4) with nearly same energy values for Z (0°) and Z

(180°) as evident from Figure 3a and Figure 3b respectively. This implies that a slight increase in the temperature will equally favour both the stacking patterns corresponding to X (180°) Y (180°) Z (0°) and X (180°) Y (180°) Z (180°). At very high temperatures, thermal vibrations will overcome the intermolecular attractions eventhough the system is capable of retaining order over a small but significant range of 4 Å (Figure 3a and 3b). An all around disruption of these intermolecular attractions will result at still higher temperatures. Thus at the melting point (120°C) of the system, the dispersion forces which are mainly responsible for stability of the stacked complexes tend to vanish as intermolecular separation rapidly increases (Figure 1) and the layer structure passes into an isotropic melt state.

Acknowledgments

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