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Molecular ordering in para-azoxyanisole (PAA), a nematogenic liquid crystal, has been studied with the help of intermolecular interaction energy calculations. Modified Rayleigh-Schrödinger perturbation theory with multicentered-multipole expansion method has been employed to evaluate the intermolecular interactions between a pair of PAA molecules. Both, stacking and in-plane interactions between a molecular pair have been considered. Results obtained, have been discussed in the light of experimental as well as other theoretical observations.

Keywords: nematogenic liquid crystal, multicentered-multipole expansion method, short-range interactions, semi-empirical methods.

INTRODUCTION

Para-azoxyanisole, the first homologue of 4,4'-di-*n*-alkoxyazoxybenzene series, is one of the most widely studied systems.^{1–7} In view of the key role of molecular interactions in mesogenic compounds, semi-empirical potential energy calculations have been emphasized by several workers^{8–10} to examine from an energetic point of view the (i) internal distortions and (ii) possibilities of motion in aromatic core as well as in the terminal alkyl chains of mesomorphic compounds. Berges and Perrin have employed PCILO (Perturbational Configuration Interaction of Localized Orbitals) and INDO (Intermediate Neglect of Differential Overlap) methods to analyze the influence of

the conjugation between the oxygen lone pairs and the benzene ring on the internal rotations in para-azoxyanisole¹¹ and several other systems.^{12–14} In addition to conformational studies, there has always been an advocacy for a detailed analysis of pair interactions between the molecules of a crystal lattice as it is presumed to offer a better understanding of the mesomorphism.¹³ In this context, it seems pertinent to quote the work carried out by Tokita et al.¹⁵ on a couple of pure model nematogens who used Rayleigh-Schrödinger perturbation theory with Lennard-Jones potential to evaluate intermolecular interactions between a molecular pair and found their results partially in agreement with molecular field theory.^{16–18} However, it must be mentioned here that instead of Lennard-Jones potential, Buckingham '6-exp' type of potential functions are believed to be more suitable to deal with molecular packing.^{19–21} In earlier communications,^{22–27} we have reported interaction energy studies on some mesogenic and non-mesogenic compounds with a view to search a possible correlation between mesomorphism and molecular interaction picture.

The present paper incorporates the results of interaction energy calculations between a pair of para-azoxyanisole molecules. An examination of the thermodynamic data²⁸ has revealed that PAA transforms to a nematic mesophase at 118.2°C and exhibits an isotropic melt at 135°C.

THEORETICAL METHOD

Second order perturbation theory as modified by Caillet and Claverie^{29–32} for intermediate range interactions, has been employed to evaluate pair interactions between the molecules of PAA. The total interaction energy (E_{TOT}) is expressed as:

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

where E_{EL} , E_{POL} , E_{DISP} and E_{REP} represent electrostatic, polarization, dispersion and repulsion energy components respectively.

Again, electrostatic term is expressed as:

$$E_{\text{EL}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}} + \dots$$

where E_{QQ} , E_{QMI} and E_{MIMI} etc. are monopole–monopole, monopole–dipole and dipole–dipole etc. terms respectively.³³ In fact, the inclusion of higher order multipoles does not affect significantly

the electrostatic interaction energy and the calculation of electrostatic energy component only up to dipole–dipole term gives satisfactory results.³⁴ The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term. The details of the formalism may be found in one of our previous papers.³⁵

The crystallographic data from literature³⁶ has been used to construct the molecular geometry of PAA while CNDO/2 method³⁷ has been used to compute the net atomic charge and dipole moment components at each atomic centre of the molecule.

Energy minimization has been carried out separately for both, stacking and in-plane interactions. In this process, one of the molecules is kept fixed throughout the computation while the position of the other molecule is varied in all respects (lateral and angular) with respect to the fixed one. Here, *X*- and *Y*-axes are defined as the long molecular axis and an axis perpendicular to it lying in the molecular plane. The *Z*-axis is chosen perpendicular to the molecular plane (*XY*) and passing through the centre of gravity of the molecule, which is taken as the origin of the coordinate system. Accuracies up to 0.1 Å in translation (sliding) and 1° in rotation, have been achieved.

All the calculations reported in this paper, have been carried out on CDC 'Cyber-170' computer at TIFR, Bombay.

RESULTS AND DISCUSSION

The molecular geometry of PAA has been shown in Figure 1 along with various atomic index numbers while the CNDO charges and dipoles are listed in Table I. The total energy, binding energy, total dipole moment and its components are listed in Table II.

The variation of the total stacking energy as a function of interplanar separation between two PAA molecules corresponding to four

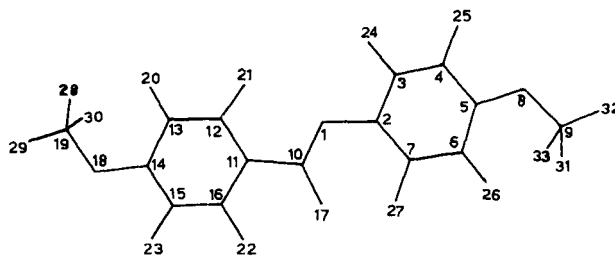


FIGURE 1 Molecular geometry of *p*-azoxyanisole along with various atomic index numbers (Scale 1 CM = 1 Å with *X*-axis along 1 → 2 bond).

TABLE I
Molecular charge distribution of para-azoxyanisole

Sl. No.	Atom	Charge	Atomic dipole components		
			<i>X</i>	<i>Y</i>	<i>Z</i>
1	N	-0.187	0.736	-1.709	-0.415
2	C	0.072	-0.042	0.116	0.064
3	C	0.007	0.116	-0.074	0.003
4	C	-0.041	-0.040	-0.142	0.001
5	C	0.183	0.203	0.071	0.021
6	C	-0.056	-0.087	0.142	-0.021
7	C	0.007	0.049	0.187	-0.004
8	O	-0.216	-0.364	-1.307	0.065
9	C	0.127	-0.233	0.199	-0.048
10	N	0.358	-0.074	0.313	0.074
11	C	0.026	0.152	-0.025	-0.007
12	C	0.030	-0.051	-0.165	-0.051
13	C	-0.057	0.104	-0.147	-0.061
14	C	0.202	-0.208	-0.039	0.025
15	C	-0.047	0.092	0.159	0.036
16	C	0.034	-0.080	0.193	0.065
17	O	-0.428	-0.568	1.198	0.356
18	O	-0.209	0.569	1.197	0.303
19	C	0.129	0.222	-0.236	-0.095
20	H	0.014	0.000	0.000	0.000
21	H	0.015	0.000	0.000	0.000
22	H	0.031	0.000	0.000	0.000
23	H	0.015	0.000	0.000	0.000
24	H	-0.004	0.000	0.000	0.000
25	H	0.002	0.000	0.000	0.000
26	H	0.006	0.000	0.000	0.000
27	H	0.024	0.000	0.000	0.000
28	H	-0.008	0.000	0.000	0.000
29	H	0.004	0.000	0.000	0.000
30	H	-0.008	0.000	0.000	0.000
31	H	-0.010	0.000	0.000	0.000
32	H	-0.003	0.000	0.000	0.000
33	H	-0.010	0.000	0.000	0.000

distinct sets of rotation viz. $X(0^\circ) Y(0^\circ)$, $X(180^\circ) Y(0^\circ)$, $X(0^\circ) Y(180^\circ)$, $X(180^\circ) Y(180^\circ)$, has been shown in Figure 2(a). It is clear from this figure that optimum interplanar separation between a pair of stacked PAA molecules, instead of being constant for all the rotational sets, exclusively depends upon the rotations given in one of the molecules about *X* and *Y*-axes with respect to the other. The complexes corresponding to $X(0^\circ) Y(0^\circ)$ and $X(180^\circ) Y(0^\circ)$, are more stable as compared to others. A deep and sharp minimum is observed for the rotational set $X(0^\circ) Y(0^\circ)$ where two molecules of PAA are exactly overlapped one above the other with their planes separated by 4.0 Å.

TABLE II

Total energy,^a binding energy,^b total dipole moment and its components of PAA molecule

Total energy = -188.796 atomic unit

Binding energy = -17.144 atomic unit

Total dipole moment = 1.422 debyes

Components	<i>X</i>	<i>Y</i>	<i>Z</i>
Densities	-1.510	0.692	0.470
sp*	0.498	-0.069	0.312
pd**	0.000	0.000	0.000
Total	-1.012	0.623	0.782

^aTotal energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

^bBinding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

*sp hybridization moment.

**pd hybridization moment.

The various interaction energy components for this case has been depicted in Figure 2(b) as an illustrative example. As observed here, the electrostatic component, which decreases with increasing separation, has no significant contribution to the stacking interactions as it is always repulsive. Polarization energy is very weak though persists over a long range. Dispersion energy, which has a major contribution to the total energy, plays a decisive role. At shorter distances below 4.0 Å, the dispersion energy rapidly decreases which is compensated by simultaneous increase in the short-range 'exchange' type of forces (repulsion component). The total energy curve exhibits a gross similarity with the Kitaigorodskii curve. This indicates that only short-range forces such as dispersion and repulsion solely confer the stability to the interactions in a pair of PAA molecules. Further, it is obvious that dispersion forces are the only major attractions which act between the planes of PAA molecules and account for a specific stacked geometry. The repulsion component has not been plotted explicitly. It can be easily obtained with the help of dispersion and Kitaigorodskii curves since dispersion and repulsion terms are evaluated together using Kitaigorodskii type of formulae.³⁸⁻⁴⁰

The variation of interaction energy with respect to sliding along the long molecular axis (*X*) has been shown in Figure 3(a) corresponding to the minimum energy stacking pattern: *X*(180°) *Y*(0°).

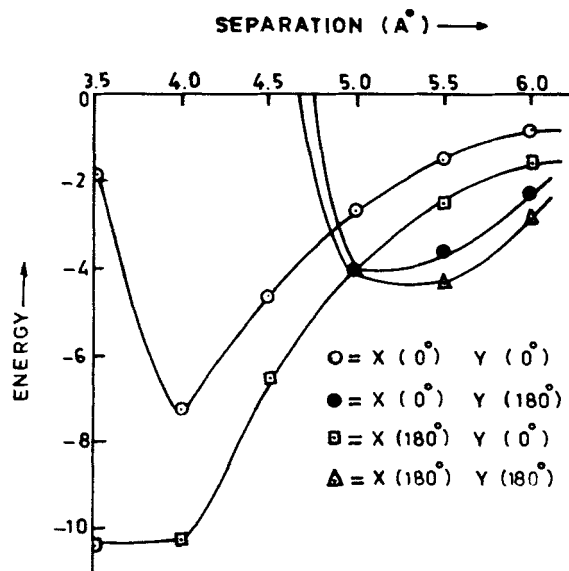


FIGURE 2(a) Variation of total stacking energy with respect to interplanar separation. Energy is expressed in kcal/mole.

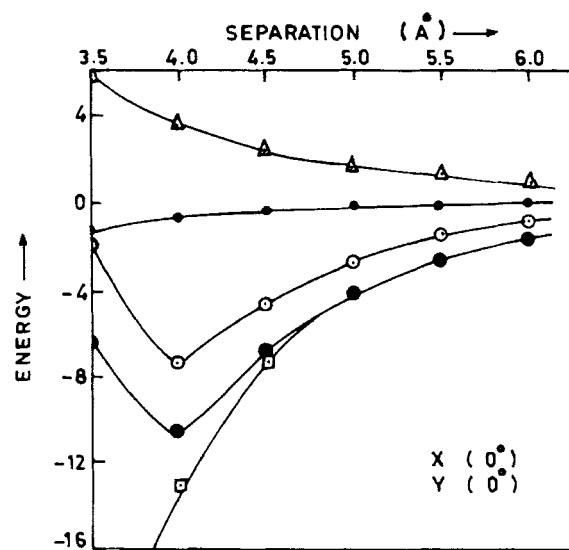


FIGURE 2(b) Variation of stacking energy components as a function of interplanar separation corresponding to the rotation set $X(0^\circ) Y(0^\circ)$. Energy is expressed in kcal/mole. [$\Delta \rightarrow E_{EL}$, $\bullet \rightarrow E_{POL}$, $\square \rightarrow E_{DISP}$, $\bullet \rightarrow E_{DISP} + E_{REP}$, $\circ \rightarrow E_{TOT}$].

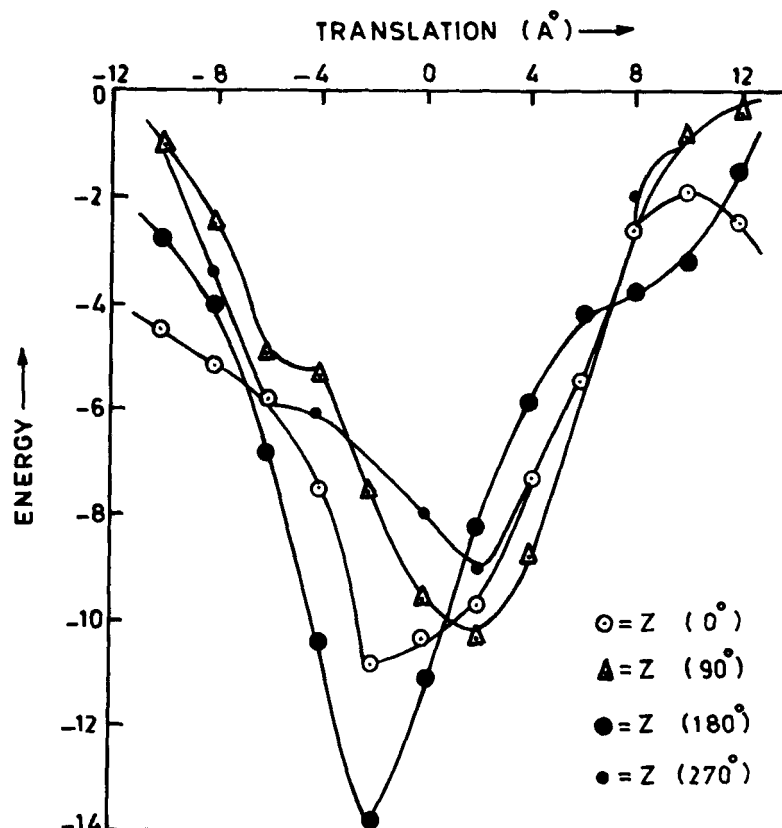


FIGURE 3(a) Variation of total stacking energy with respect to translation along molecular axis corresponding to minimum energy rotational set $X(180^\circ) Y(0^\circ)$. The interplanar separation is 3.5 Å. Energy is expressed in kcal/mole.

As mentioned in Figure 3(a), four fixed rotations, namely $Z(0^\circ)$, $Z(90^\circ)$, $Z(180^\circ)$, $Z(270^\circ)$ are given in one of the molecules of the stacked pair and sliding energies are calculated for each case separately. Here, most stable configuration corresponds to $Z(180^\circ)$ with an energy -14.0 kcal/mole instead of $Z(0^\circ)$ which has obviously a higher energy. The rotations, $Z(90^\circ)$ and $Z(270^\circ)$ give energetically less probable stacked geometries. This appears to be realistic also since the possibility of stacking between a pair of molecules at right angles to one another, capable of mesophase formation, is highly improbable. Various components of the stacking energy have been plotted in Figure 3(b) and 3(c) respectively for $Z(0^\circ)$ and $Z(180^\circ)$. From both the figures, it is evident that electrostatic and polarization components

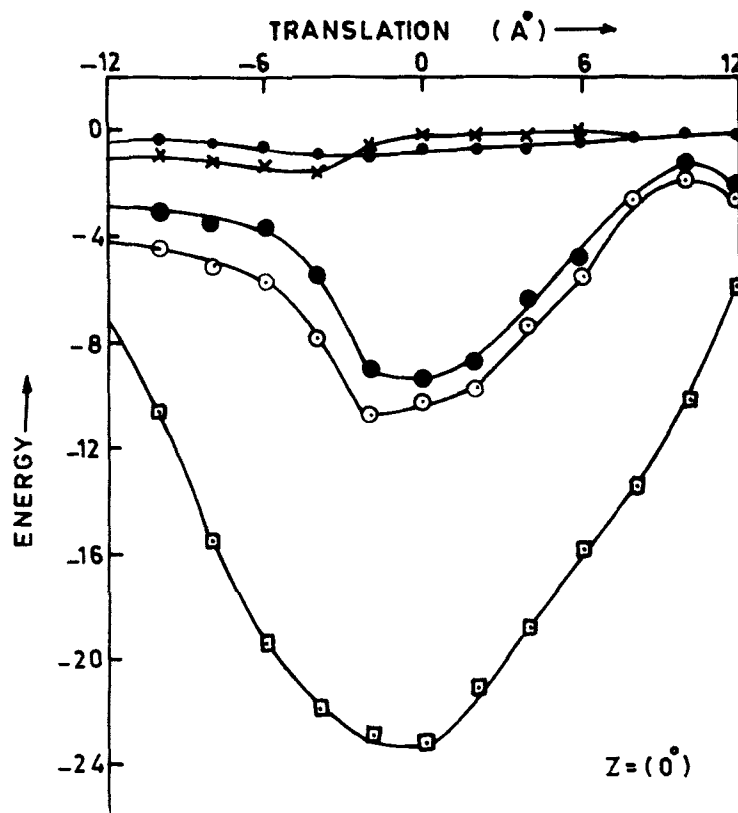


FIGURE 3(b) Variation of stacking energy components with respect to translation along the long molecular axis. Energy is expressed in kcal/mole. [$\times \rightarrow E_{EL}$, $\bullet \rightarrow E_{POL}$, $\square \rightarrow E_{DISP}$, $\circ \rightarrow E_{TOT}$].

are weak and are less significant. Dispersion component is mainly responsible for the attractions between the planes of the PAA molecules though the exact optimum point is always located by Kitaigorodskii energy curve which has a gross similarity with the total energy curve. The total energy curve shows a deep and sharp minimum (Figure 3b). Any deviation from the optimum position will, therefore lead to energetically less favourable stacking geometry. However, it is interesting to note that even in the range of $\pm 2.0 \text{ \AA}$, the stability of the stacked geometry is greater (Figure 3c) as compared to the other cases shown in Figure 3(a) which correspond to rotations $Z(0^\circ)$, $Z(90^\circ)$ and $Z(270^\circ)$. In other words, the stacked pair of PAA molecules can slide one above the other in the range of $\pm 2.0 \text{ \AA}$ without any significant change in the energy and, hence, is

capable of retaining molecular order up to 4.0 \AA against increased thermal agitations. Thus, it is established that energetically most stable complex results when one of the stacked molecules is rotated by 180° both about X - and Z -axes, i.e. due to the stacking pattern $X(180^\circ) Y(0^\circ) Z(180^\circ)$.

The variation of stacking energy components with respect to translation along Y -axis has been graphically represented in Figure 3(d). Similar to the cases discussed in foregoing paragraphs (Figures 2(b), 3(b), 3(c)), the gross nature of various components remains unchanged in this case too. However, it may be seen from the total energy curve that an energy barrier of approximately 6 kcal/mole is noticed for translations within the range of $\pm 2.0 \text{ \AA}$. This implies

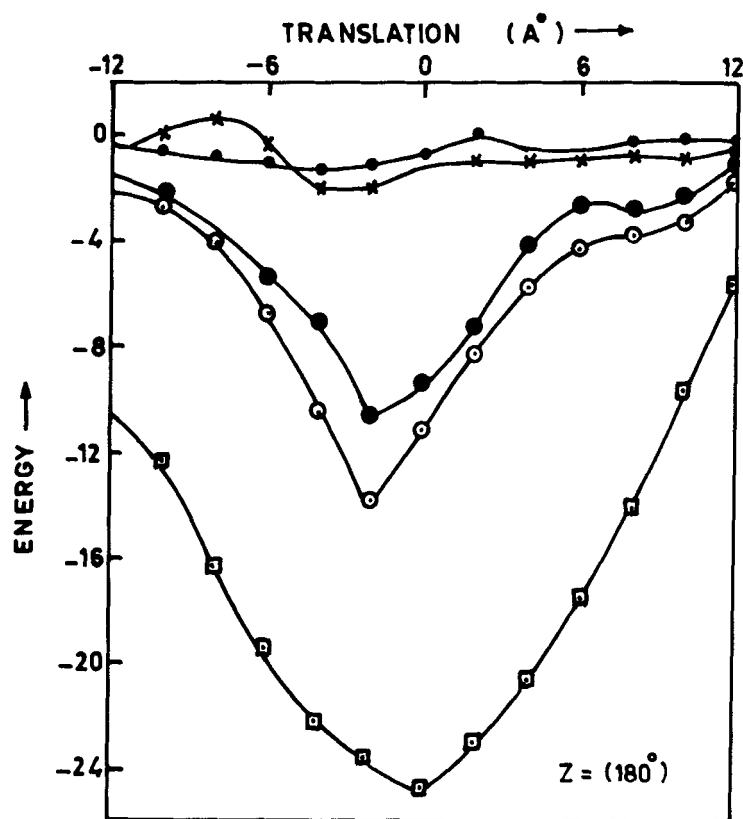


FIGURE 3(c) Variation of stacking energy components with respect to translation along the long molecular axis. Energy is in kcal/mole. Notations are same as in Figure 3(b).

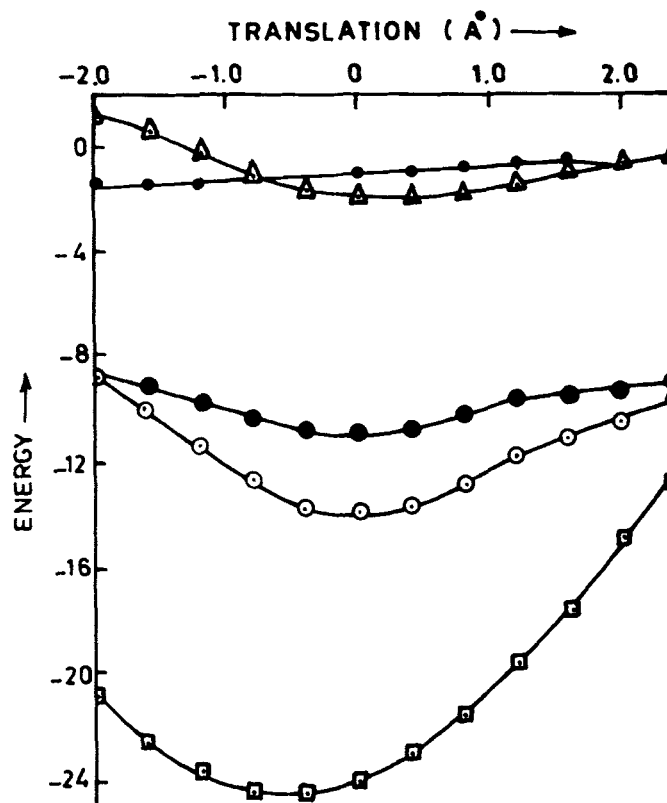


FIGURE 3(d) Variation of stacking energy components with respect to translation along an axis perpendicular to the long molecular axis and lying in the molecular plane. Energy is in kcal/mole. Notations are same as in Figure 2(b).

that the possibility of one of the molecules of the stacked pair to slide along the Y -axis, is very much restricted.

It may be observed from Figure 4, representing the angular dependence of the energy of stacked complexes, that polarization is nearly independent of rotations and has a small contribution to the total energy while the electrostatic component largely depends on the angle of rotation as it bears both, attractive and repulsive, nature and has a very little contribution to the stacked pair at optimum position. The dominating role of the dispersion energy is obviously marked although the optimum angle is always governed by Kitaigorodskii term. There is a gross similarity between the curves representing the total and Kitaigorodskii energies. The minimum energy configuration always corresponds to parallel orientation. It is also observed that

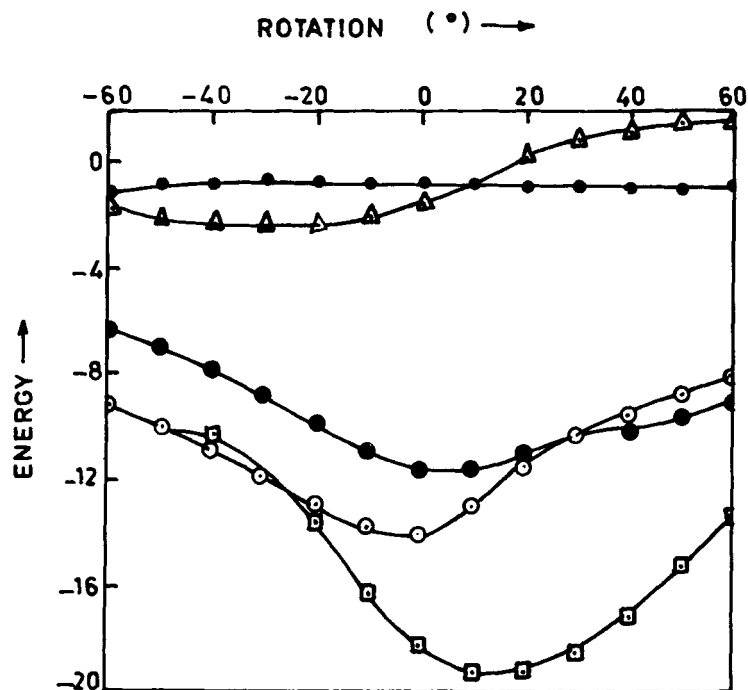


FIGURE 4 Angular dependence of stacking energy. Energy is in kcal/mole. Notations are same as in Figure 2(b).

the total energy gradually increases with rotational angle for clockwise rotations. For rotations, -20° to $+10^\circ$, an energy difference of only 2 kcal/mole is observed implying that at increased thermal agitations, the stacked PAA pair may get orientated with respect to each other. The maximum angle of relative orientation will normally be 30° which however, at very high temperatures may be something more.

The energy corresponding to the optimum angle obtained initially, located at 0° (Figure 4), has been further refined with accuracies 1° in rotation and 0.1 \AA in translations. The final lowest energy stacked geometry, has been shown in Figure 5(a) having an energy -14.43 kcal/mole. The in-plane lowest energy configuration has been presented in Figure 5(b) which bears an energy -3.07 kcal/mole. These configurations are in agreement with those from crystallographic studies.³⁶ The details of the stacking energy as well as in-plane energy, are listed in Table III. It seems important to note again that the largest attractive contribution in stabilizing the stacked as well as in-plane interacting pair of PAA molecules comes from the dispersion forces. This also supports the earlier observations.^{41,42}

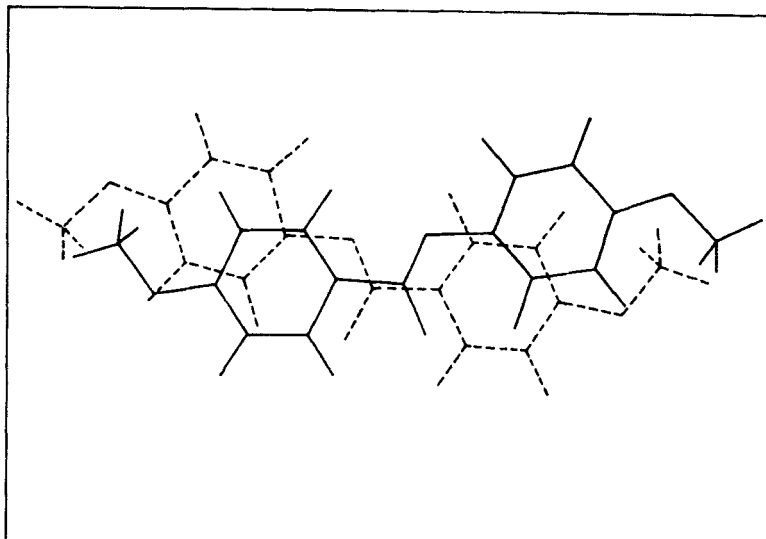


FIGURE 5(a) Minimum energy stacked complex for a pair of PAA molecules. Here, one of the molecules has been rotated by 180° about both X and Z -axes and is optimized at 3.60 \AA with an energy -14.34 kcal/mole .

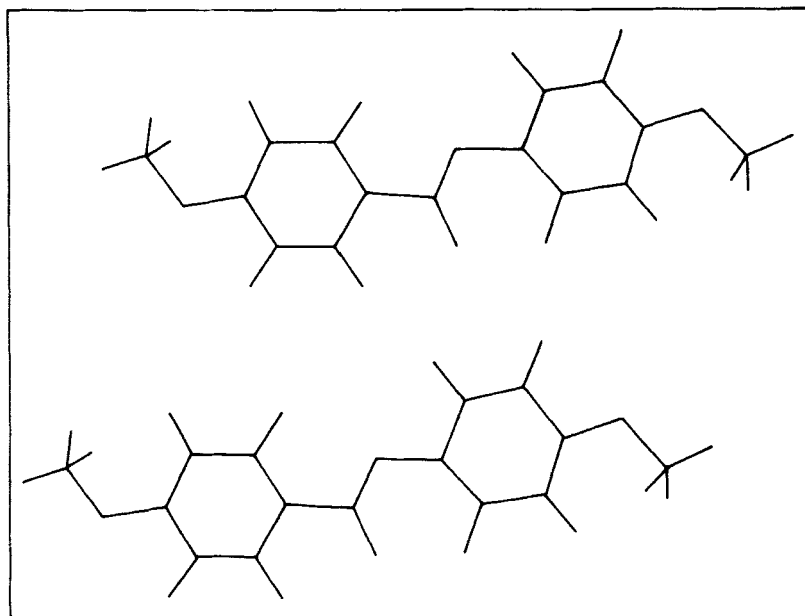


FIGURE 5(b) Minimum energy in-plane configuration for a pair of PAA molecules. Obviously both the molecules are exactly similar, separated by 6.90 \AA , with an energy -3.07 kcal/mole .

TABLE III

Stacking and in-plane interaction energy values between a pair of para-azoxyanisole molecules. Energy is expressed in kcal/mole

Interaction energy terms	Stacking	In-plane
E_{QQ}	-0.83	0.38
E_{QMI}	0.47	-0.05
E_{MIMI}	-1.55	-0.08
E_{EL}	-1.91	0.25
E_{POL}	-1.02	-0.68
E_{DISP}	-20.20	-4.18
E_{REP}	8.70	1.54
E_{TOT}	-14.43	-3.07

The inter-molecular interaction energy calculations may be reasonably correlated with the mesomorphic behaviour of the system. When the solid crystals of PAA molecules are heated, thermal vibrations disturb the molecular ordering of the strongly packed geometrical arrangement of PAA molecules. Consequently, the attractions between the pair of molecules which largely consists of the dispersion forces, tend to get weaker at higher temperatures and hence, the possibility of relative movement in a molecular pair along the long molecular axis is considerably enhanced (Figure 3). As indicated in Figure 3(d), the freedom of the molecules in a stacked pair to slide along an axis perpendicular to the long molecular axis (Y-axis) is energetically restricted while terminal attractions are quite insignificant due to the presence of methoxy groups at both the ends (Figure 1). These results favour the nematogenic behaviour of the system at higher temperatures because the molecules of para-azoxyanisole are capable only of sliding along the long molecular axis with a maximum relative orientation of 30° . At very high temperatures, an all round breaking of the dispersion forces results and as shown in Figure 2(a), all the possible stacking geometries (even perpendicular stacking) will be equally favoured instead of only an imbricated structure of PAA molecules. This will ultimately cause the system to pass on to an isotropic melt at higher temperatures.

CONCLUSION

It may, therefore, be concluded that intermolecular interaction energy calculations are helpful in analysing the liquid crystalline be-

haviour of PAA in terms of molecular forces in accounting for the mesomorphism. In principle, the study may be extended to predict the effect of addition of methylene group on the mesomorphic behaviour of the higher homologues of para-azoxyanisole.

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