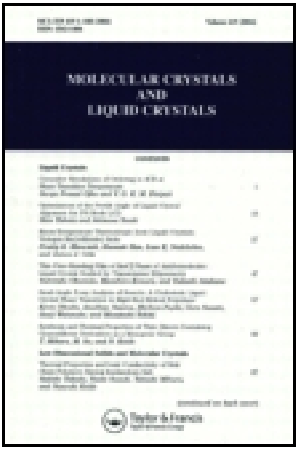

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Theoretical Study of Molecular Ordering in Biphenyl-4-Carboxylic Acid

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Theoretical Study of Molecular Ordering in Biphenyl-4-Carboxylic Acid

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Biphenyl compounds are very well known for their liquid crystalline behaviour. In this paper, molecular ordering, transition temperature and related parameters of biphenyl-4-carboxylic acid have been explained on the basis of inter-molecular interaction energy studies. Second order perturbation theory with multicentred-multipole approximation has been employed to evaluate interaction energies with the help of quantum-mechanical charge distribution. Stacking, in-plane and terminal interaction energy values between a pair of molecules have been reported. Results have been discussed in view of experimental evidences.

INTRODUCTION

Liquid crystalline materials have been the subject of extensive study due to the peculiar co-existence of the properties of anisotropic solid and that of isotropic liquid in a single thermodynamically stable state. Efforts have also been made to understand the relationship between the liquid crystallinity and chemical constitution of materials using various techniques resulting into a number of models.[1-8] Inter-molecular interactions, considered to be an important factor by many workers, have largely been dealt qualitatively. It was, therefore, decided to take up quantitative study of interaction energy between a homomolecular pair of liquid crystalline or similar systems. The successful application of interaction energy calculations in explaining the liquid crystalline behaviour of anisaldehydeazine[9] has led us to extend similar investigations to other systems showing mesophase during phase transition. Biphenyl-4-carboxylic acid (BCA), chosen for the present investigation, is not strictly a liquid crystal as it gives a clear melt at 225°C but seems to be quite interesting since it can be converted into a liquid crystal by choice of suitable substituents. Thus, p-methoxy biphenyl-4-carboxylic acid and 2-chlorobiphenyl-4-carboxylic acids are nematic liquid crystals while p-hydroxy-biphenyl-4-carboxylic acid does not show any mesophase. Formation of dimers is a common feature for almost all derivatives of biphenyl-4-carboxylic acid which accounts for their relatively high melting point.

METHOD

Second order perturbation theory as modified by Caillet and Claverie[10-13] for intermediate range interactions, has been employed to evaluate the intermolecular interaction energy between a pair of biphenyl-4-carboxylic acid molecules. The total energy (E_{TOT}) may be expressed as

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

where E_{EL}, E_{POL}, E_{DISP} and E_{REP} are electrostatic, polarization, dispersion and repulsion energies respectively. Electrostatic energy is again given by

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

where E_{QQ}, E_{QMI} and E_{MIMI} are monopole-monopole, monopole-dipole and dipole-dipole interaction energy values respectively. The details of the formalism may be found elsewhere.[9]

The net atomic charges at each atomic centre and corresponding atomic dipole components have been computed by CNDO/2 method[14] while the crystallographic data has been taken from literature.[15]

Energy minimization has been carried out by keeping one molecule fixed and varying the position of the other along the rectangular coordinate axes with a simultaneous rotation. An accuracy upto 0.1 Å during translation and 1° in rotation has been achieved. Energy has been minimised separately for stacking, in-plane and end to end interactions. The various interaction energy configurations reported correspond to lowest energies. All the computations have been made on a CDC 'Cyber' computer at T.I.F.R., Bombay.

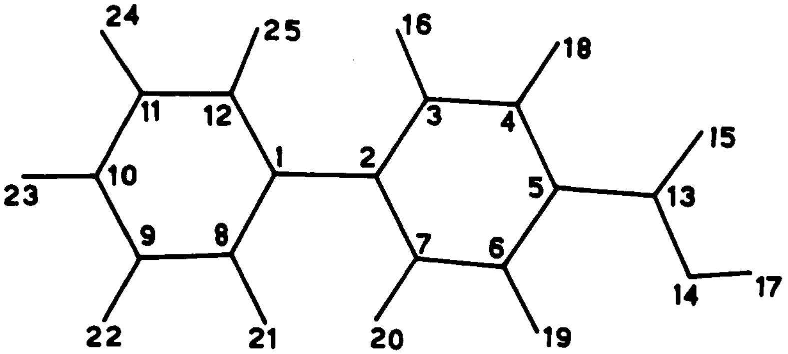

FIGURE 1 Molecular geometry of Biphenyl-4-carboxylic acid molecule with atomic index number.

RESULTS AND DISCUSSION

The molecular geometry of biphenyl-4-carboxylic acid has been shown in Figure 1 with the various atomic index numbers while the net atomic charges and dipoles are listed in table I. The binding energy, total dipole moment, and its components are listed in table II. The lowest energy configurations obtained for stacking, in-plane terminal and in-plane lateral interactions are shown in Figures 2(a), 2(b) and 2(c) respectively. The corresponding energy values with various contributing terms are given in table III.

It is clear from Figure 2(a) that a pair of biphenyl-4-carboxylic acid molecules are stacked one above the other, 3.50 Å apart; such that one molecule has been rotated by 180° about its long molecular axis. Also, a simultaneous sliding of one molecule with respect to other, along the long axis by approximately 1 Å and an axis normal to it by 0.30 Å, is observed. The energy corresponding to this configuration is -11.2752 KCal/mole. The end-to-end interaction energy configuration, resulting from terminal attractions of the BCA molecules, shown in Figure 2(b) bears the energy -7.2962 KCal/mole. The lowest energy configuration corresponding to in-plane lateral interactions with energy value -3.2561 KCal/mole is given in Figure 2(c).

These results clearly suggest a strong packing of the BCA molecules inside the crystal although the packing energy is asymmetrical. The minimum energy configurations obtained through these calculations agree with the crystallographic data. The relative stabilities of stacked and hydrogen bonded dimers can be understood with the help of Figure 3 as it shows the variation of the electrostatic and the total

TABLE I

Atomic charge distribution and corresponding atomic dipoles of Biphenyl-4-carboxylic Acid.

Atom no.	Atom	Charge	Atomic dipoles (Debye) X	Y	Z
1	C	0.023	-0.026	0.001	-0.008
2	C	0.042	0.067	-0.053	-0.011
3	C	-0.020	0.063	-0.131	0.009
4	C	0.035	-0.043	-0.156	-0.003
5	C	-0.037	-0.055	-0.024	-0.002
6	C	0.022	-0.038	0.134	0.007
7	C	-0.011	0.074	0.115	0.008
8	C	0.000	-0.067	0.112	0.007
9	C	0.008	0.071	0.133	0.003
10	C	0.012	0.119	0.001	0.002
11	C	0.008	0.054	-0.118	-0.004
12	C	-0.005	-0.082	-0.127	-0.003
13	C	0.391	0.238	-0.159	0.009
14	O	-0.275	0.616	1.183	0.055
15	O	-0.333	-0.767	-1.130	-0.061
16	H	-0.001	0.000	0.000	0.000
17	H	0.173	0.000	0.000	0.000
18	H	0.003	0.000	0.000	0.000
19	H	-0.002	0.000	0.000	0.000
20	H	-0.004	0.000	0.000	0.000
21	H	-0.006	0.000	0.000	0.000
22	H	-0.004	0.000	0.000	0.000
23	H	-0.011	0.000	0.000	0.000
24	H	-0.007	0.000	0.000	0.000
25	H	-0.001	0.000	0.000	0.000

energies with respect to the deviation from the optimum position in both the cases. The continuous increase in the total stacking energy is apparent as the separation between two molecules increases while the electrostatic part is effective over a long range but its contribution

TABLE II

Total dipole moment and components of Biphenyl-4-carboxylic acid. Total Dipole Moments = 0.8797 Debye. Total Binding Energy = −13.9644 A.U.

Components	Dipole moments X	Y	Z
Densities	-0.844	-0.407	-0.039
S.P.	0.225	-0.218	0.008
P.D.	0.000	0.000	0.000
Total	-0.619	-0.625	-0.031

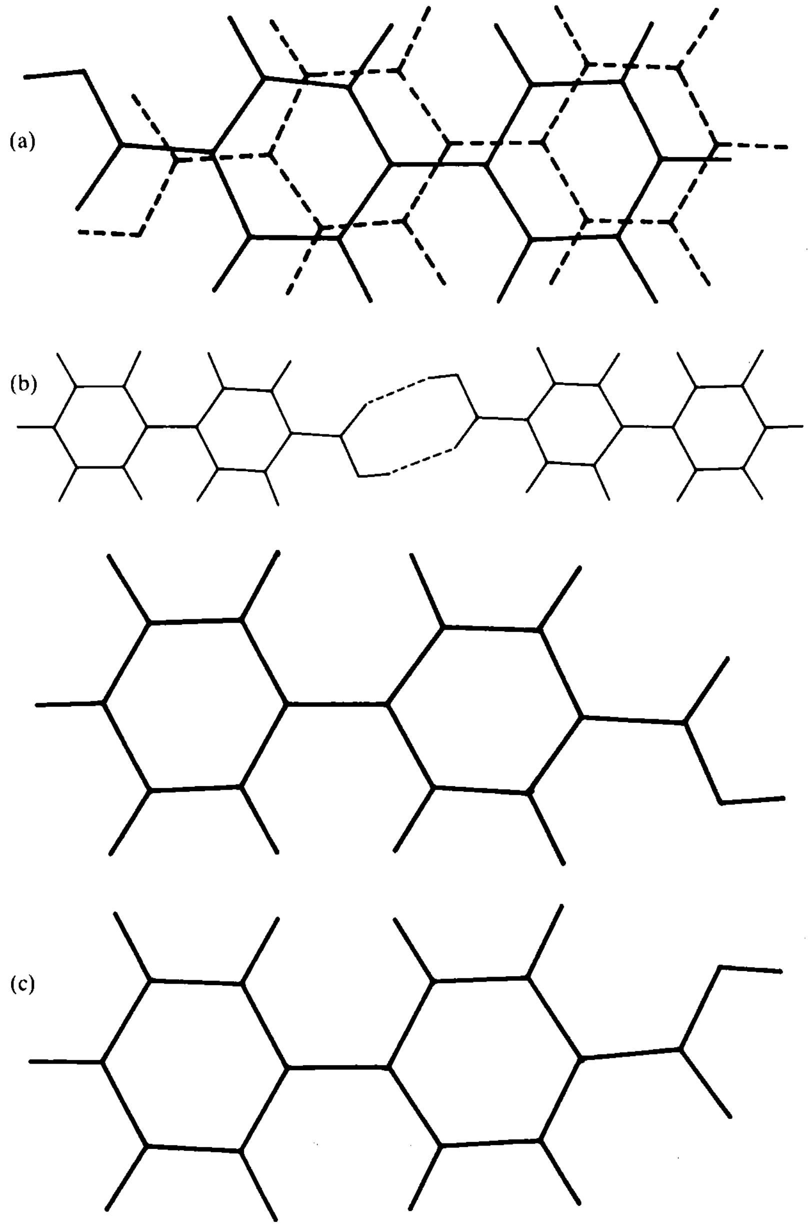

FIGURE 2 (a) Stacked configuration of Biphenyl-4-carboxylic acid dimer (E_{min} = −11.2752 KCal/mole of dimer). (b) Lowest energy configuration for terminal interactions between a pair of biphenyl-4-carboxylic acid molecules (E_{min} $\doteq$ −7.2962 KCal/mole of dimer). (c) Lowest energy configuration corresponding to in-plane lateral interactions (E_{min} = −3.2561 KCal/mole of dimer).

TABLE III

Dimer energies corresponding to stacking, terminal and in-plane interactions

Energy terms	Stacked	Terminal	Lateral
E_{QQ}	0.2012	-2.4023	0.0976
E_{QMI}	-0.3545	-2.7358	-0.0043
E_{MIMI}	-0.9927	-1.6041	-0.3531
$E_1(E_{QQ} + E_{QMI} + E_{MIMI})$	-1.1460	-6.7422	-0.2597
E_{POL}	-0.3107	-0.7977	-0.0607
E_{DISP}	-16.5228	-4.2938	-4.1269
$E_2(E_{POL} + E_{DISP})$	-16.8335	-5.0915	-4.1876
E_{REP}	6.7043	4.5374	1.1913
$E_{TOTAL} = (E_1 + E_2 + E_{REP})$	-11.2752	-7.2962	-3.2561

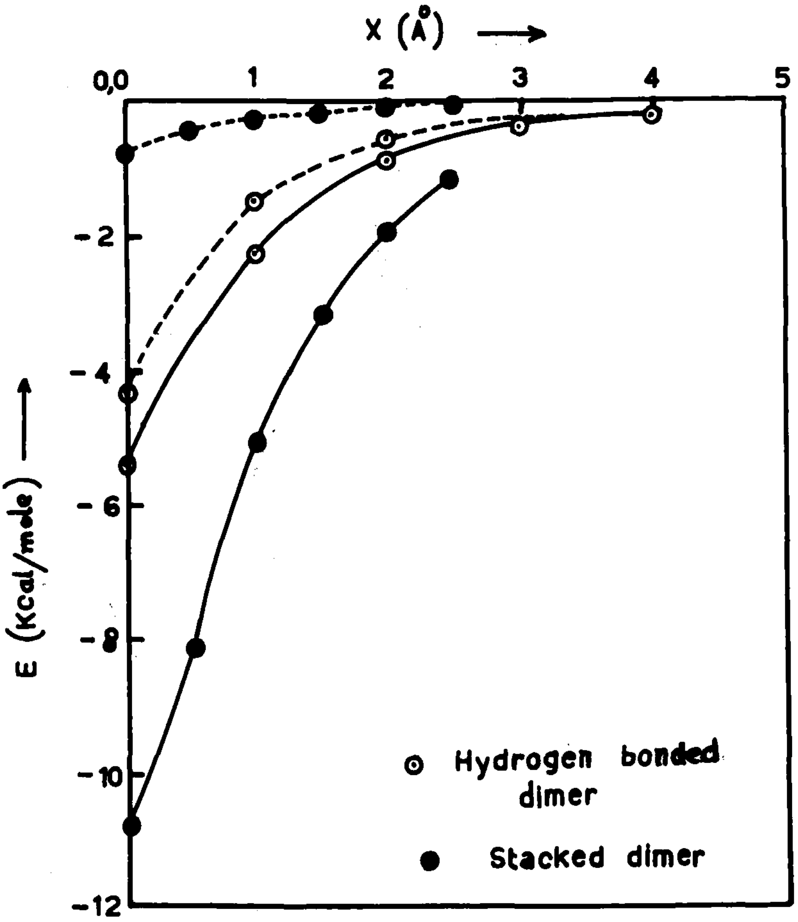

FIGURE 3 Energy variations with respect to deviation from minimum energy configurations corresponding to stacking and terminal interactions shown in Figure 2(a) and 2(b). Full line represents total while dotted line stands for only electrostatic energy.

is very small. It may, therefore, be inferred that long range forces are less significant as compared to the short range forces during stacking interactions. Both the curves obtained for the electrostatic and the total energy corresponding to hydrogen bonded dimers are similar in nature. It is evident that in the case of hydrogen bonded dimers the electrostatic energy plays a major role as compared to other contributions and is effective over a long range. Therefore, unlike stacking and in-plane lateral attractions, which have a larger contribution due to dispersion forces, terminal attractions require more thermal activation as it is mainly due to electrostatic energy and hence accounts for the high melting point of the system. At the melting point, thermal agitation will overcome the bindings of the BCA molecules in the crystal and the system will pass directly to isotropic melt. However, the inherent tendency of the molecule to retain order even after melting does not escape the notice. Hence, if suitable functional groups are attached to the molecule so that the length to breadth ratio is increased with dispersive energy, the molecules will show a change in the long range order, transition temperature and other related liquid crystalline properties.

CONCLUSION

It may be reasonable to conclude that inter-molecular interaction energy studies are helpful in explaining the molecular ordering, transition temperature and related parameters of liquid crystals. Also, the effect of substitution on the type of mesophase and its thermal stability in a homologous series may be predicted to a reasonable extent.

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