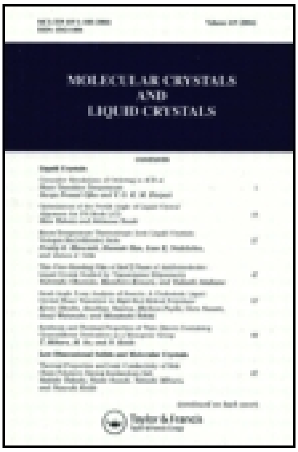

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Nematogenic Behaviour of Liquid Crystals—A Theoretical Study

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Nematogenic Behaviour of Liquid Crystals—A Theoretical Study

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Using the basic concepts of quantum mechanics and intermolecular forces, the molecular alignment of some nematic liquid crystals like MBA, CBA and PAA has been examined. Modified Rayleigh-Schrodinger perturbation theory along with multicentered-multipole expansion method, has been employed to evaluate long-range intermolecular interactions while a '6-exp' potential function has been assumed for short-range interactions. On the basis of stacking and in-plane interaction energy calculations, all possible geometrical arrangements between a molecular pair have been considered and the most favourable configuration of the pairing has been obtained. A comparative picture of molecular parameters like total energy, binding energy, total dipole moment etc. has been given. An attempt has been made to explain the nematogenic behaviour of these liquid crystals and thereby develop a molecular model for the liquid crystallinity.

Keywords: nematogen, liquid crystal, multicentered-multipole, intermolecular interactions

INTRODUCTION

In view of the wide-spread use of liquid crystals—from industrial/technological developments to biomedical applications, the subject of liquid crystal science has attracted increasing interest of the scientists from different disciplines.[1,2] The peculiar changes—characteristics of mesomorphic behaviour which occur at phase transitions, are primarily governed by the intermolecular interactions acting between sides, planes and ends of a pair of molecules.[3] Such type of interactions essentially comprise of (i) dipole—dipole attractions—the direct interactions between the permanent dipoles in the molecules, (ii) induced dipole attractions arising from the mutual polarization of the molecules by their permanent dipole moments, and (iii) dispersion forces.[3]

In view of the key role of molecular interactions in mesogenic compounds, semi-empirical calculations have been emphasized by several workers to explain liquid crystallinity.[4–6] Perrin and Berges have employed PCILO (Perturbational Configuration Interaction of Localised Orbitals), INDO (Intermediate Neglect of Diatomic Overlap), CNDO (Complete Neglect of Differential Overlap) etc. methods to analyse (i) the internal rotations, (ii) possibilities of motion in aromatic core as well as in the terminal chains, and (iii) the influence of the conjugation between the oxygen lone pairs and the benzene ring on the internal rotations in several mesomorphic compounds.[7-10] Further, it has been argued that detailed analysis of pair interactions between the molecules of crystal lattice is expected to offer a better understanding of the mesomorphism.[8] Tokita et al[11] used Lennard-Jones potential to evaluate intermolecular interactions between a couple of pure nematogens and attempted to correlate their results with those of the molecular field theory.[12-14] However, it has been observed that '6-exp' type of potential functions are found to be more effective in explaining the molecular packing instead of Lennard-Jones potential.[15] Sanyal and coworkers using second order perturbation theory, evaluated intermolecular interactions between pairs of some mesogens[16-20] and non-mesogens.[21,22] These authors have attempted to explain the properties of mesomorphic compounds to retain molecular order against increased thermal agitations.

In the present paper, intermolecular interactions between a pair of molecules of 4′-methoxybenzylidene-4-acetoxyaniline (MBA) have been examined. A possible explanation of liquid crystallinity in MBA has been furnished. Results have been discussed in the light of those obtained for other nematogens like PAA[19] and CBA.[23] The thermodynamic parameters[24] reveal that MBA shows crystal to nematic transition at 85.2°C and passes to an isotropic melt at 109°C.

METHOD OF CALCULATION

According to the second order perturbation theory as modified for intermediate range interactions,[25] the total interaction energy (E_{TOT}) between a pair of molecules is given by

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

where E_{EL}, E_{POL}, E_{DISP} and E_{REP} represent electrostatic, polarization, dispersion and repulsion components respectively. According to the multicentered-multipole expansion method,[26] the electrostatic energy may be expressed as the sum of interaction terms between atomic multipoles of successively higher orders.

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

where E_{QQ}, E_{QMI}, E_{MIMI} etc. are the monopole-monopole, monopole-dipole, dipole-dipole and other interaction terms caused by higher order multipoles. In general, for most of the molecular systems, the evaluation of the electrostatic energy up to dipole-dipole term has been found to be adequate.[27] Therefore, the computation was restricted up to dipole-dipole term only. The details of formalism may be found elsewhere.[20]

Net atomic charge and corresponding atomic dipole moment components at each of the atomic centres of the molecule have been computed by CNDO/2 method.[28]

The energy minimization has been carried out for both stacked and in-plane interactions separately. One of the interacting molecules is kept fixed throughout the process while both lateral and angular variations are introduced in the other in all respects relative to the fixed one. Accuracies up to 0.1 Å in sliding (translation) and 1° in rotation have been achieved. The details may be found in our other papers.[17,20]

All the computations have been carried out on CDC 'Cyber-170' computer at TIFR, Bomay.

RESULTS AND DISCUSSION

The molecular geometry of 4′-methoxybenzylidene-4-acetoxyaniline (MBA) is shown in Figure 1 along with various atomic index numbers. Net charge and dipole moment component corresponding to each of the atomic centres, have been listed in Table I while the total energy, binding energy and total dipole moment along with its components are given in Table II. Table III presents a comparative picture of the total energy, binding energy and dipole moments of MBA with other similar systems like PAA and CBA. As evident from Table III, the total energy and binding energy of these nematogens exhibit the following order (magnitude wise):

$$\text{MBA} > \text{PAA} > \text{CBA},$$

while the dipole moments are as under:

$$\text{CBA} > \text{MBA} > \text{PAA}.$$

The variation of the total interaction energy as a function of inter-planar separation between two MBA molecules, has been shown in Figure 2(a) corresponding to four distinct sets of rotation viz. X(0°)Y(0°), X(180°)Y(0°), X(0°)Y(180°) and X(180°)Y(180°). It is clear from this figure that optimum interplanar separation between a pair of MBA 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 curves corresponding to X(0°)Y(180°) and X(180°)Y(180°) exhibit similar nature and confer more stable complexes as compared to others. A deep and sharp minimum is observed for the rotational set,

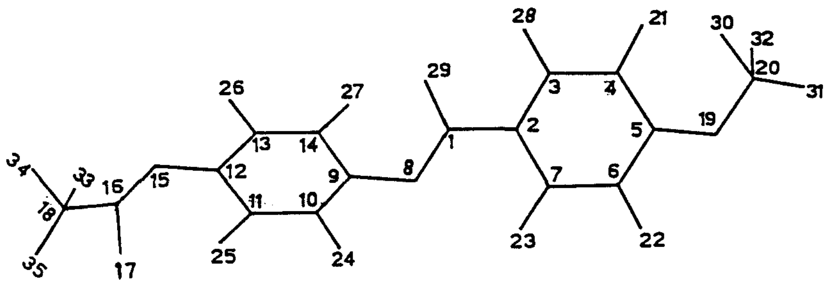

FIGURE 1 Molecular geometry of MBA along with various atomic index numbers.

TABLE I

Molecular charge distribution on MBA molecule

Sl No.	Atom	Charge	Atomic dipole components X	Y	Z
1	C	0.120	−0.075	−0.180	0.028
2	C	−0.015	0.074	0.025	0.001
3	C	0.032	0.086	−0.097	0.003
4	C	−0.056	−0.039	−0.115	0.006
5	C	0.191	0.166	−0.034	0.001
6	C	−0.048	−0.065	0.136	0.001
7	C	0.031	0.070	0.121	0.006
8	N	−0.160	−0.684	1.616	−0.103
9	C	0.095	0.036	−0.036	−0.003
10	C	−0.005	−0.008	0.099	−0.054
11	C	−0.039	0.052	0.090	−0.083
12	C	0.173	−0.220	0.015	−0.016
13	C	−0.033	0.055	−0.097	0.095
14	C	−0.011	−0.095	−0.088	0.068
15	O	−0.187	0.597	−0.775	0.798
16	C	0.127	−0.943	1.633	−1.695
17	O	−0.180	0.442	−0.873	0.905
18	C	0.133	0.219	0.179	−0.188
19	O	−0.206	−0.622	1.212	−0.099
20	C	−0.022	−0.340	−0.165	−0.718
21	H	−0.009	0.000	0.000	0.000
22	H	0.005	0.000	0.000	0.000
23	H	−0.004	0.000	0.000	0.000
24	H	−0.004	0.000	0.000	0.000
25	H	−0.003	0.000	0.000	0.000
26	H	0.004	0.000	0.000	0.000
27	H	−0.003	0.000	0.000	0.000
28	H	−0.010	0.000	0.000	0.000
29	H	−0.042	0.000	0.000	0.000
30	H	0.094	0.000	0.000	0.000
31	H	0.047	0.000	0.000	0.000
32	H	0.003	0.000	0.000	0.000
33	H	−0.009	0.000	0.000	0.000
34	H	0.002	0.000	0.000	0.000
35	H	−0.011	0.000	0.000	0.000

X(180°)Y(180°) where two molecules of MBA are stacked at an interplanar separation of 4.0 Å such that one of them is rotated by 180° both about X and Y-axes with respect to the other. The various components of interaction energy for this case has been depicted in Figure 2(b) as an illustrative example. As observed here, the electrostatic component has no contribution to the stacking interactions as it is always repulsive. Polarization component is very weak though it 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 i.e. the curve showing the sum of dispersion and repulsion energies. This indicates that only short-range forces such as dispersion and repulsion solely confer the stability to the interactions in a pair

TABLE II

Total energy,[a] binding energy,[b] total dipole moment and its components of MBA molecule. Total energy = −191.66 a.m.u., binding energy = −18.12 a.m.u., total dipole moment = 3.08 debyes

Components	X	Y	Z
Densities[+]	0.74	0.28	0.36
sp*	−1.37	2.67	−1.04
pd**	0.00	0.00	0.00
Total[++]	−0.63	2.94	−0.67

[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 the atomic energies of the constituent atoms.

[+] Contribution to dipole moment components due to electron densities.

* sp, Hybridization moment.

** pd, Hybridization moment.

[++] Sum of electron density and hybridization contributions to dipole moment components.

TABLE III

Total energy, binding energy, total dipole moment along with its components of MBA, PAA and CBA molecules

Molecule	Total energy (A.U.)	Binding energy (A.U.)	Dipole moment (μ) in Debyes μ_x	μ_y	μ_z	μ
MBA	−191.66	−18.12	−0.63	2.94	−0.67	3.08
CBA	−135.386	−14.99	−3.430	0.864	0.579	3.584
PAA	−188.796	−17.144	−1.012	0.623	0.782	1.422

of MBA molecules. Further, it is obvious that dispersion forces are the only major attractions which act between the planes of MBA molecules and account for a specific stacked geometry. The repulsion component has not been plotted explicitly as it can be easily obtained with the help of dispersion and kitaigorodskii curves.

The variation of various components of interaction energy with respect to sliding (translation) along the long molecular axis (X-axis) has been shown in Figure 3(a) corresponding to a particular rotation of 360° about the Z-axis. In fact, four fixed rotations about the Z-axis, namely Z(0°), Z(90°), Z(180°) and Z(270°) are introduced in one of the stacked molecules and interaction energy is calculated by giving translations in the range of ± 12 Å at an interval of 2 Å. Since most stable configuration corresponds to Z(0°) or Z(360°) curve, it has been analysed here in detail. It is evident from Figure 3(a) that electrostatic and polarization components are weak and have negligible contribution. Dispersion component is mainly responsible for the attractions between the pairs of MBA molecules though the exact optimum point is always located by kitaigorodskii energy curve which has a gross similarity with the total energy curve. The humps appear because of the violation of van der Waal's contact for C(H)—C(H) distance. A slight increase in the interplanar separation will obviously remove such regions. It is interesting to note here that for translations in the range of ±2 Å, minor variations in the energy (~0.5 kcal/mole) are observed which implies that in the stacked pair of MBA,

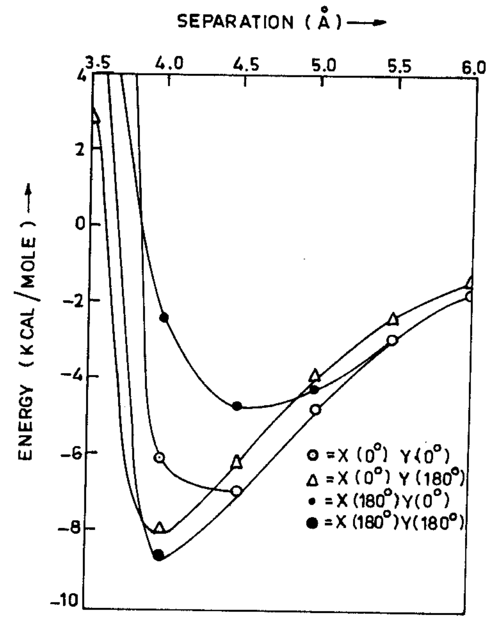

FIGURE 2(a) Variation of stacking energy with respect to interplanar separation corresponding to four distinct stacking patterns.

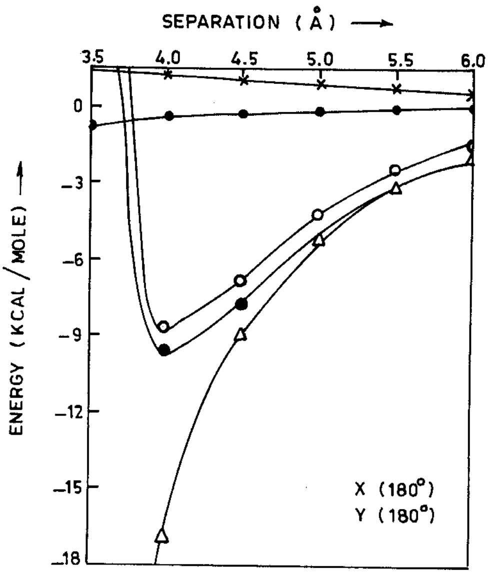

FIGURE 2(b) Variation of interaction energy components with respect to interplanar separation for stacking pattern: X(180°)Y(180°) x → E_{EL}; • → E_{POL}, △ → E_{DISP}, ● → E_{DISP} + E_{REP}, ○ → E_{TOT}.

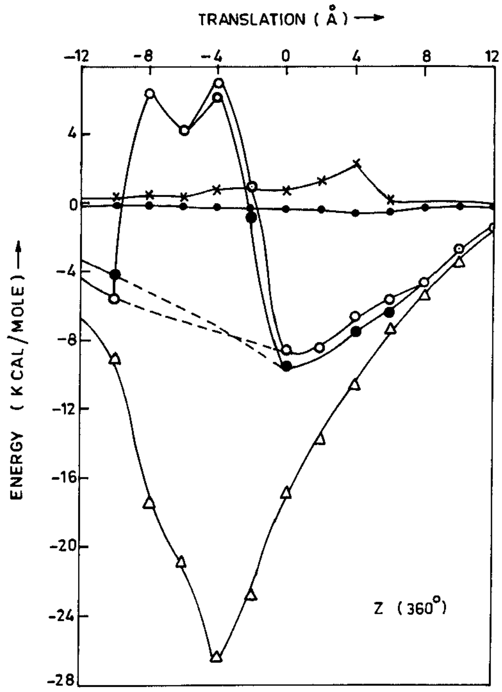

FIGURE 3(a) Variation of interaction energy components with respect to translation along the long molecular axis. Notations are the same as mentioned in Figure 2(b).

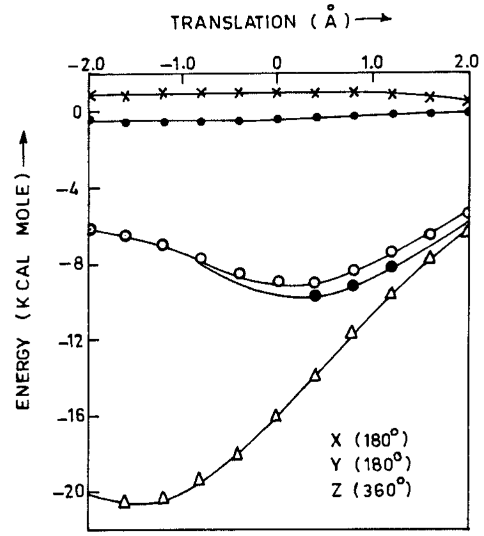

FIGURE 3(b) Variation of interaction energy components with respect to translation along an axis perpendicular to long molecular axis. Notations are the same as mentioned in Figure 2(b).

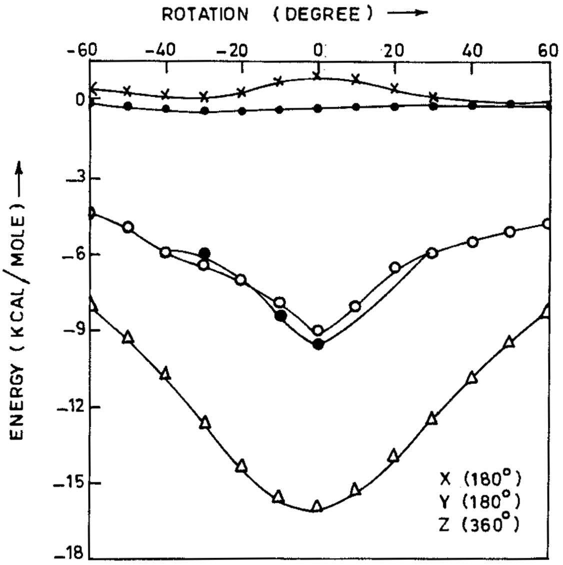

FIGURE 4 Angular dependence of stacking energy. Notations are same as mentioned in Figure 2(b).

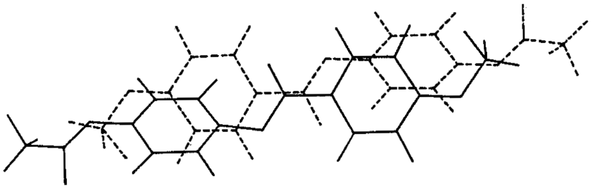

FIGURE 5(a) Stacked pair of MBA molecules with minimum energy −9.07 kcal/mole and interplanar separation 4.0 Å.

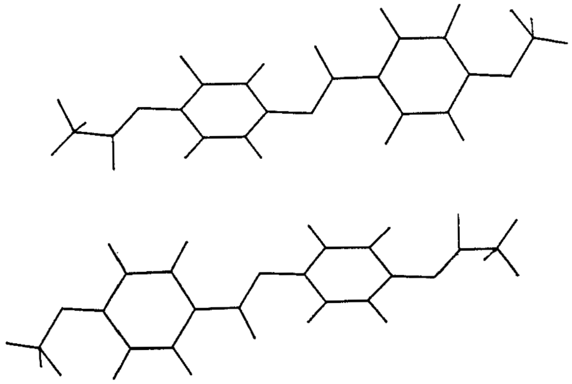

FIGURE 5(b) In-plane configuration of a pair of MBA molecules with minimum energy of −4.65 kcal/mole and intermolecular separation of 7.0 Å.

TABLE IV

Minimum energy values for stacked and in-plane configurations

Terms	Energy values in kcal/mole Stacking	In-plane
E_{QQ}	0.18	−0.02
E_{QMI}	−0.00	0.00
E_{MIMI}	0.74	0.18
E_{EL}	0.92	0.16
E_{POL}	−0.39	−0.17
E_{DISP}	−15.31	−7.77
E_{REP}	5.71	3.13
E_{TOT}	−9.07	−4.65

molecules can slide one above the other in the range of ± 2 Å without any significant change in the energy and, hence, is capable of retaining molecular order up to 4 Å against increased thermal agitations. It must also be pointed here that rotations, Z(90°) and Z(270°) give energetically less probable stacked geometry. This appears to be true also since the possibility of stacking between a pair of molecules capable of mesophase formation at right angles to one another is highly restricted.

The variation of interaction energy components with respect to translation along Y-axis has been graphically represented in Figure 3(b). Similar to the cases discussed in foregoing paragraphs (Figure 2b and 3a), 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 3 kcal/mole is noticed for translations within the range of ± 2.0 Å. This implies that the possibility of one of the molecules of the stacked pair to slide along Y-axis, is very much restricted.

It may be observed from Figure 4, representing the angular dependence of the energy during stacking, that both electrostatic and polarization components have negligible contribution to the total energy. The dominating role of dispersion energy is obviously marked here although the optimum angle is always governed by kitaigorodskii term. There is a gross similarity between the curves representing total and kitaigorodskii energies. For rotations in the range of ± 10°, an energy difference of only 1 kcal/mole is observed implying that at increased thermal agitations, the stacked molecules in a MBA pair may get oriented with respect to each other. The maximum angle of relative orientation will normally be 20° 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 Å in translation. The final lowest energy stacked geometry, thus obtained, has been shown in Figure 5(a) having an energy −9.07 kcal/mole. The in-plane minimum energy configuration has been presented in Figure 5(b) which bears an energy −4.65 kcal/mole. The details of the stacking as well as in-plane energy, are listed in Table IV. It seems important to note that the largest attractive contribution in stabilizing the stacked and in-plane interacting pair of MBA molecules, comes from dispersion forces. This supports earlier observations[29,30] and also the basic assumption of molecular field theory.[12–14]

The intermolecular interaction energy calculations may be reasonably correlated with the mesomorphic behaviour of the system. When the solid crystals of MBA molecules are heated, thermal vibrations disturb the molecular ordering of the strongly packed geometrical arrangement of MBA molecules. Consequently, the attractions between the pair of molecules which largely comprise of dispersion forces, tend to get weaker at higher temperatures and hence, the possibility of movement in a molecular pair along the long molecular axis is considerably enhanced (Figure 3a). As indicated in Figure 3(b), the freedom of the molecules in a stacked pair to slide along an axis perpendicular to long molecular axis (Y-axis) is energetically restricted while terminal attractions are quite insignificant due to the presence of methyl groups at both the ends (Figure 1).

These results favour the nematic behaviour of the system at higher temperatures because the molecules of MBA are capable of only sliding along the long molecular axis with a simultaneous relative orientation of 20°, similar results have been obtained in case of other nematogens like PAA[19] and CBA.[23] At very high temperatures, an all round breaking of the dispersion forces results and all possible stacking geometries (even perpendicular stacking) are equally favoured which ultimately cause the system to pass on to an isotropic melt state.

CONCLUSION

It may, therefore, be concluded that intermolecular interaction energy calculations are helpful in analysing the liquid crystallinity in terms of molecular forces. Based on energetic considerations, it is also found that nematogens like MBA, PAA and CBA exhibit the tendency to retain translational order in a small range (~4 Å) along with a simultaneous orientational freedom of 20° to 40°.

Acknowledgments

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