

Theoretical study of intermolecular interactions in nematogens : TBMA

Sugriva N Tiwari*, Madhurendra Mishra and Nitish K Sanyal[†]

Department of Physics, D D U Gorakhpur University, Gorakhpur-273 009, Uttar Pradesh, India

[†]U P Rajarshi Tandon Open University, Allahabad-221 001, Uttar Pradesh, India

E-mail : snt@gkpu.ernet.in

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Abstract In view of the key role of molecular interactions in governing the nature and characteristics of mesomorphism, intermolecular interactions between a pair of TBMA molecules have been evaluated using modified second order perturbation treatment along with multicentered-multipole expansion method. An all valence electron method, CNDO/2, has been employed to compute the net atomic charge and corresponding dipole components located at each atomic centre of the molecule. On the basis of stacking and in-plane interaction energy studies, an attempt has been made to elucidate the nematogenic behaviour of the system.

Keywords Intermolecular interactions, mesogens, CNDO

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1. Introduction

There are certain substances which do not directly pass from a crystalline solid to an isotropic liquid state and *vice versa*, rather adopt an intermediate structure which flows like liquids but still possesses the anisotropic physical properties similar to crystalline solids. In view of the wide-spread use of liquid crystals from industrial/technological developments to biomedical applications and display devices, the subject of liquid crystal science has attracted increasing interest of the scientists from different disciplines [1–4]. The peculiar changes-characteristics of mesomorphic behaviour which occur at phase transition, are primarily governed by the intermolecular interactions acting between sides, planes and ends of a pair of molecules [5]. To study the role of molecular interactions in mesogenic compounds, semi-empirical calculations have been emphasized by several workers with an aim to explain liquid crystallinity [6]. Perrin and Berges have employed PCILO, INDO, CNDO *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 conjunction between oxygen lone pairs and benzene ring on the internal rotations in

several mesomorphic compounds [7–9]. 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 [9]. Tokita *et al* [10] 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 [11]. 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 potentials [12].

In the light of above facts, intermolecular interaction energy studies in case of some mesogens have been carried out in our laboratory and efforts have been made to explain liquid crystallinity [13–18]. In continuation of our earlier studies on thermotropic liquid crystals, the present paper embodies the results of both stacking and in-plane intermolecular interactions in case of Terephthal-bis-4-n-methylaniline (TBMA) which is a lower homologue of TBBA (Terephthal-bis-4-n-butylaniline) [19]. Further, translational freedom and orientational selectivity *etc* between a molecular pair of TBMA molecules have been examined.

*Corresponding Author

The thermodynamic parameters reveal that TBMA shows crystal to nematic transition at 186.7°C and passes to an isotropic melt state at 252.6°C.

2. Method of calculation

According to the energy decomposition obtained by perturbation treatment, the total interaction energy (E_{TOT}) between two molecules is expressed as [20] :

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

where E_{EL} , E_{POL} , E_{DISP} and E_{REP} represent electrostatic, polarization, dispersion and repulsion energy components respectively. The formulae for various energy terms are given as under.

2.1 Electrostatic energy :

According to the multicentred-multipole expansion method [21], the electrostatic energy term is expressed as :

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

where E_{QQ} , E_{QMI} and E_{MIMI} etc represent monopole-monopole, monopole-dipole, dipole-dipole and interaction energy terms consisting of multipoles of higher orders respectively. However, consideration upto the first three terms has been found to be sufficient for most of the molecular interaction problems [21,22]. The monopole-monopole energy is given as :

$$E_{QQ} = C \sum_i \sum_j q_i q_j / r_{ij}$$

where q_i , q_j are the monopoles at each of the atomic centres of the interacting molecules i and j ; r_{ij} is the inter-atomic distance. The constant, C is a conversion factor, approximately equal to 332 which expresses the energy in kcal/mole of the dimer.

The monopole-dipole energy term is expressed as

$$E_{QMI} = C \sum_{i,j} q_i \mu_j \cdot r / r^3$$

and the dipole-dipole interaction term is given by

$$E_{MIMI} = C \sum_{i,j} 1/r^3 \left[\mu_i \cdot \mu_j - 3(\mu_i \cdot r/r)(\mu_j \cdot r/r) \right]$$

where μ_i , μ_j represent the atomic dipoles, the subscript of r has been removed without any change in its meaning.

2.2. Polarization energy :

The polarization energy of some molecule (say, s) is obtained as a sum of the polarization energies for the various bonds :

$$E_{POL}^{(s)} = C(-1/2) \sum_u^{(s)} \epsilon_u^{[s]} \cdot \bar{A}_u^{(s)} \cdot \epsilon_u^{[s]},$$

$$\text{where } \epsilon_u^{[s]} = \sum_{t \neq s} \sum_{\lambda}^{(t)} q_{\lambda}^{(t)} R_{\lambda u} / (R_{\lambda u})^3$$

is the electric field created at the bond u by all surrounding molecules and \bar{A}_u is the polarizability tensor of this bond. $R_{\lambda u}$ is the vector joining the atom λ in molecule (t) to the 'centre of polarizable charge' on bond u of molecule (s).

2.3. Dispersion and repulsion energy :

Dispersion and repulsion terms are calculated together using Kitaigorodskii type of formula as given below [23,24] :

$$E_{DISP} + E_{REP} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} E(\lambda, \nu),$$

$$\text{where } E(\lambda, \nu) = K_{\lambda} K_{\nu} \left(\frac{-A}{z^6} + B e^{-\gamma z} \right)$$

$$\text{and } \frac{1}{R_{\lambda\nu}^0} \cdot R_{\lambda\nu}^0 = \sqrt{(2R_{\lambda}^w)(2R_{\nu}^w)}$$

where R_{λ}^w and R_{ν}^w are the van der Waals radii of atoms λ and ν respectively. The parameters A , B and γ do not depend on the atomic species : this necessary dependence is brought about by $R_{\lambda\nu}^0$ and the factors K_{λ} and K_{ν} which allow the energy minimum to have different values according to the atomic species involved [25]. The values of these various parameters and of the van der Waals radii have been given by Caillet and Claverie [26,27]. The details of the mathematical formalism may be found in literature [20,28,29].

Molecular geometry of TBMA has been constructed using crystallographic data from literature [19]. Net charge and corresponding dipole moment components at each of the atomic centres of the molecule have been computed by CNDO/2 method [30]. The energy minimization has been carried out for both stacking 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. The first molecule has been assumed to be in the X-Y plane with X-axis lying along the long molecular axis while the origin is chosen approximately at the centre of mass of the molecule. The second molecule has been translated initially along the Z-axis (perpendicular to the molecular plane) and subsequently along X- and Y-axes. Variation of interaction energy with respect to rotation about Z-axis has been examined in the range of $\pm 60^\circ$. Accuracies up to 0.1 Å in sliding (translation) and 1° in rotation have been achieved.

3. Results and discussion

The molecular geometry of TBMA is shown in Figure 1 along with various atomic index numbers. Net charge and dipole moment components corresponding to each of the atomic centres have been listed in Table 1. The total energy, binding energy and total dipole moment along with its components are given in Table 2.

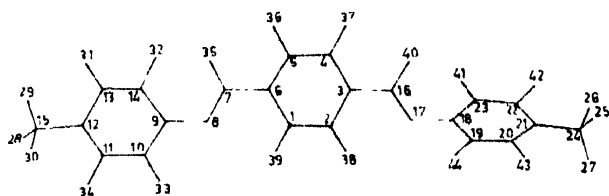


Figure 1. Molecular geometry of TBMA molecule along with various atomic index numbers

Table 1. Net charge and dipole components corresponding to each atomic centre of the TBMA molecule.

Sl. No.	Atom symbol	Charge (e u)*	Atomic dipole components (debye)		
			X	Y	Z
1	C	0.006	0.063	0.131	0.005
2	C	0.008	-0.061	0.129	0.004
3	C	0.015	-0.057	0.011	0.005
4	C	0.008	-0.050	-0.112	-0.009
5	C	0.005	0.060	-0.124	0.065
6	C	0.017	0.051	0.015	0.002
7	C	0.112	0.055	-0.183	-0.022
8	N	0.158	-0.721	1.581	0.171
9	C	0.103	0.050	-0.041	0.002
10	C	-0.016	0.077	0.111	-0.010
11	C	0.002	0.044	0.103	-0.016
12	C	0.027	0.067	0.007	0.008
13	C	0.007	0.060	0.100	0.037
14	C	-0.024	0.058	-0.120	0.032
15	C	-0.021	0.131	-0.005	0.023
16	C	0.118	0.060	-0.172	-0.086
17	N	-0.155	0.712	1.503	0.453
18	C	0.114	0.070	-0.029	-0.010
19	C	0.025	0.063	0.096	0.076
20	C	0.002	0.047	0.064	0.078
21	C	0.024	-0.090	0.041	0.025
22	C	0.012	-0.050	0.046	-0.083
23	C	-0.032	0.059	-0.094	-0.085
24	C	-0.023	-0.125	0.008	0.009
25	H	0.009	0.000	0.000	0.000
26	H	0.002	0.000	0.000	0.000
27	H	0.010	0.000	0.000	0.000
28	H	0.009	0.000	0.000	0.000
29	H	0.001	0.000	0.000	0.000
30	H	0.009	0.000	0.000	0.000
31	H	-0.014	0.000	0.000	0.000
32	H	-0.004	0.000	0.000	0.000
33	H	-0.003	0.000	0.000	0.000
34	H	-0.015	0.000	0.000	0.000
35	H	-0.035	0.000	0.000	0.000
36	H	-0.006	0.000	0.000	0.000
37	H	-0.010	0.000	0.000	0.000
38	H	-0.003	0.000	0.000	0.000
39	H	-0.002	0.000	0.000	0.000
40	H	-0.041	0.000	0.000	0.000
41	H	-0.002	0.000	0.000	0.000
42	H	-0.016	0.000	0.000	0.000
43	H	-0.012	0.000	0.000	0.000
44	H	-0.002	0.000	0.000	0.000

* e.u. = electron unit

Table 2. Total energy^a, binding energy^b and total dipole moment distribution of TBMA molecule

Total energy	= -194.76 atomic unit
Binding energy	= -24.20 atomic unit
Total dipole moment	= 2.96 debye

Components	X	Y	Z
Densities	0.058	0.221	0.069
sp [*]	0.039	2.691	0.447
pd ^{**}	0.000	0.000	0.000
Total	-0.097	2.912	0.516

* hybridization moment due to s and p orbitals.

** hybridization moment due to p and d orbitals

^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.

The variation of total interaction energy with respect to inter-planar separation between two stacked TBMA molecules 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°) has been shown in Figure 2. It is clear from this figure that optimum inter-planar separation between a pair of TBMA molecules,

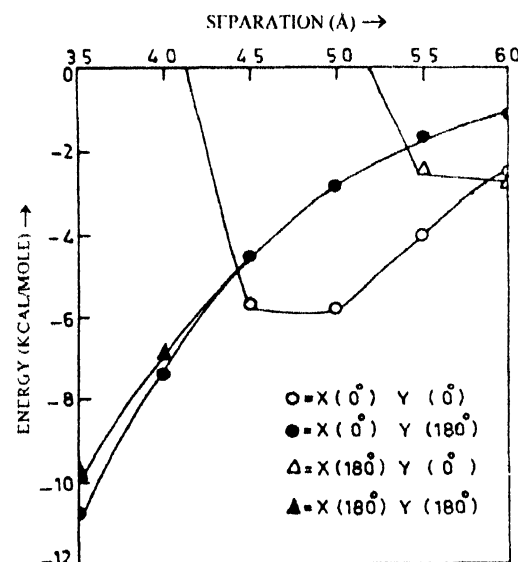


Figure 2. Variation of stacking energy with respect to inter-planar separation corresponding to four distinct stacking patterns.

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. The minimum energy stacked configuration is observed for the rotational set, X(0°)Y(180°) where two molecules of TBMA are stacked at an inter-planar separation of 3.5 Å with energy -10.75 kcal/mole such that one of them

is rotated by 180° about Y-axis. The various components of interaction energy for this case has been depicted in Figure 3. As evident from Figure 3, electrostatic component has no contribution to the stacking interactions as it is always

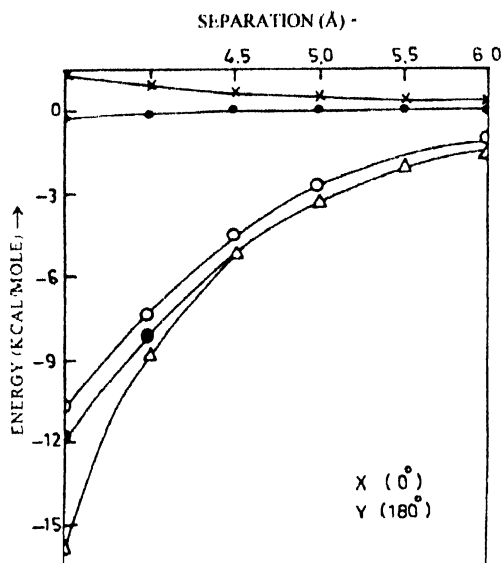


Figure 3. Variation of interaction energy components with respect to inter-planar separation for the stacking pattern $X(0^\circ)Y(180^\circ)$ [\times — E_{FI} , \bullet — E_{POL} , Δ — E_{DISP} , \bullet — $E_{DISP} + E_{REP}$, \circ — E_{TOT}]

repulsive; polarization component is very weak though it persists over a long range while dispersion energy, which has a major contribution to the total energy plays a decisive role. At shorter distances below 4.0 \AA , the dispersion energy rapidly decreases and goes to -15.94 kcal/mole 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 due to interactions in a pair of TBMA molecules. Further, dispersion forces are the only major attractions which act between the planes of TBMA 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 interaction energy with respect to sliding (translation) along the long molecular axis (X-axis) corresponding to four fixed rotations about the Z-axis, namely $Z(0^\circ)$, $Z(90^\circ)$, $Z(180^\circ)$ and $Z(270^\circ)$ has been shown in Figure 4. Interaction energy has been calculated by giving translations in the range of $\pm 12.0 \text{ \AA}$ at an interval of 2.0 \AA . Here most stable configuration corresponds to $Z(180^\circ)$. For this case, various interaction energy components are plotted in Figure 5. It is evident from Figure 5 that electrostatic and

polarization components are weak and have negligible contribution. Dispersion component is mainly responsible for the attractions between the pairs of TBMA molecules though the exact optimum point is always located by

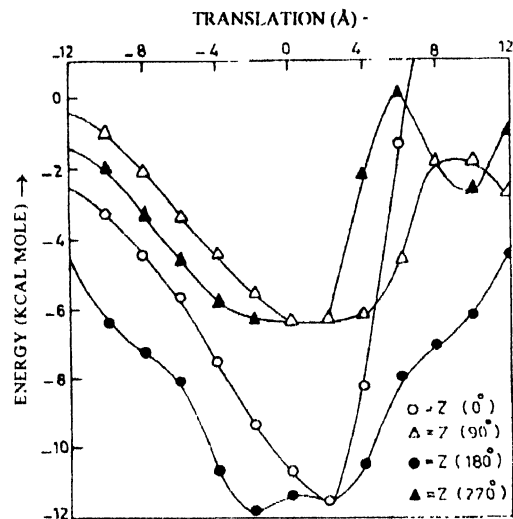


Figure 4. Variation of interaction energy with respect to sliding along the long molecular axis (X-axis) corresponding to four fixed rotations about the Z-axis

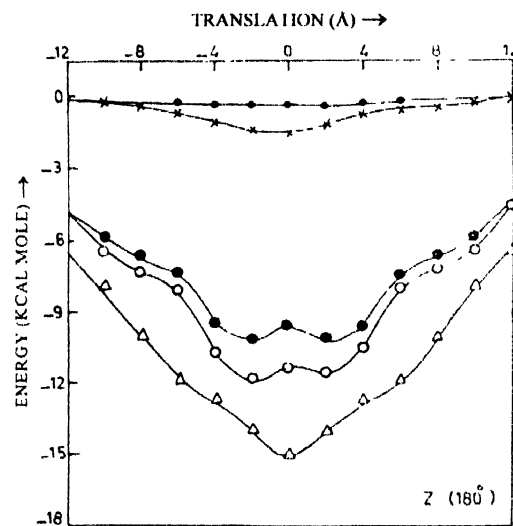


Figure 5. Variation of interaction energy components with respect to sliding along the long molecular axis corresponding to a particular rotation of 180° about the Z-axis. Notations are the same as mentioned in Figure 3.

Kitaigorodskii energy curve which has a gross similarity with the total energy curve. It is interesting to note here that for translation in the range of $\pm 2.0 \text{ \AA}$, minor variation in the energy ($\sim 1.0 \text{ kcal/mole}$) is observed which implies that in the stacked pair of TBMA, molecules can slide one above the other in a range of $\pm 2.0 \text{ \AA}$ without any significant change in the energy. It must also be pointed here that rotations, $Z(90^\circ)$ and $Z(270^\circ)$ give energetically less probable stacked geometry. This appears to be true also since the possibility

of stacking at right angles to one another between a pair of molecules capable of mesomorphic phase formation is highly restricted.

The variation of interaction energy components with respect to translation along an axis perpendicular to the long molecular axis (Y-axis) has been graphically represented in Figure 6 which implies that the possibility of one of the molecules of the stacked pair to slide along Y-axis, is very much restricted. The angular dependence of stacking energy components (Figure 7) reveals that both electrostatic and polarization terms have negligible contribution to the total energy. The role of dispersion energy is obviously dominant here although the optimum angle is always governed by

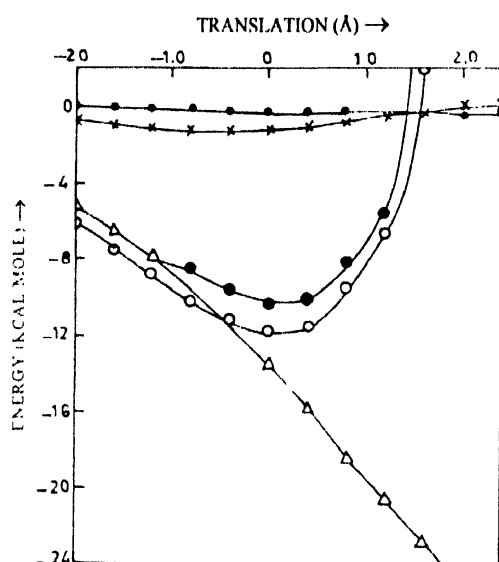


Figure 6. Variation of interaction energy components with respect to sliding along an axis perpendicular to the long molecular axis. Notations are the same as mentioned in Figure 3

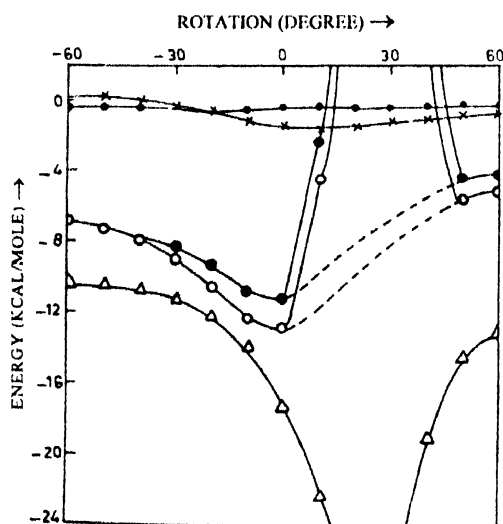


Figure 7. Angular dependence of interaction energy components for the stacking pattern X(0°)Y(180°)Z(180°). Notations are the same as mentioned in Figure 3.

Kitaigorodskii term. There is a gross similarity between the curves representing total and Kitaigorodskii energies. Further, dotted line in the range of +20° to +40° shows that energy is much more positive (repulsive) in this region. This region is noticed because of the violation of van der Waal's contact for C(H)-...C(H) distance. The maximum angle of relative orientation will normally be 30°, which however, at very high temperatures, may go up.

The energy corresponding to the optimum angle located at 0° 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 8 having an energy -13.67 kcal/mole and inter-planar separation

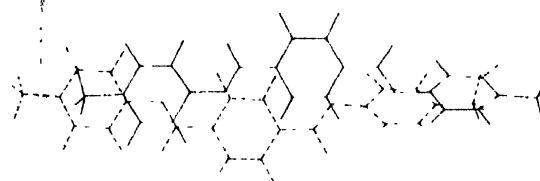


Figure 8. Stacked pair of TBMA with minimum energy -13.67 kcal/mole and inter-planar distance of 3.1 Å

3.1 Å. The in-plane minimum energy configuration which bears an energy -4.80 kcal/mole and inter-planar separation 6.4 Å has been shown in Figure 9. The details of the stacking as well as in-plane energy are listed in Table 3. It seems important to note that the largest attractive contribution in

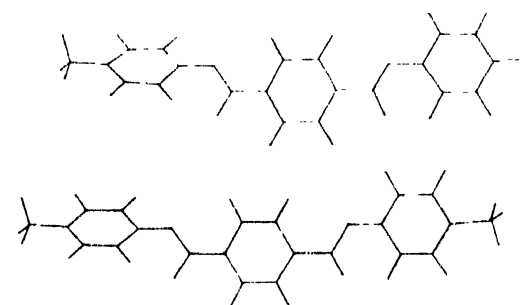


Figure 9. In-plane configuration of a pair of TBMA molecules with minimum energy of -4.80 kcal/mole and inter-molecular separation of 6.4 Å.

Table 3. Interaction energy components for stacking and in-plane minimum energy configurations of TBMA molecules. Energy is expressed in kcal/mole.

Energy terms	Stacking	In-plane
E_{QQ}	-0.06	-0.01
E_{QM}	-0.55	-0.17
E_{MIM}	-0.96	-0.26
E_{EL}	-1.57	-0.43
E_{POL}	-0.54	0.16
E_{DISP}	-20.53	-6.32
E_{REP}	8.97	2.12
E_{TOT}	-13.67	-4.80

stabilizing the stacked and in-plane interacting pair of TBMA molecules, comes from dispersion forces. This supports earlier observations [31,32] and also the basic assumption of molecular field theory [11]. The intermolecular interaction energy calculations may be reasonably correlated with the mesomorphic behaviour of the system. When the solid crystal of TBMA molecules are heated, thermal vibrations disturb the molecular ordering of the strongly packed geometrical arrangement of TBMA molecules. Consequently, the attractions between the pair of molecules which largely comprise of dispersion forces, tend to get weaker at higher temperature and hence translational freedom along the long molecular axis (Figure 5) and orientational flexibility in a molecular pair (Figure 7) are considerably enhanced. The freedom of the molecules in a stacked pair to slide along an axis perpendicular to the long molecular axis is energetically restricted while terminal attractions are inherently insignificant.

4. Conclusion

It may therefore, be concluded that intermolecular interaction energy calculations are helpful in analyzing the liquid crystallinity in terms of molecular forces. Results favour the nematic behaviour of the system at higher temperatures because the molecules of TBMA are capable of sliding along the long molecular axis with a simultaneous relative orientation of 30°. 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.

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