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Study of Intermolecular Interactions in Liquid Crystals: Para-butyl-p'-cyano-biphenyl

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ABSTRACT

Various characteristics of mesomorphism can be explained using intermolecular interactions between a pair of liquid crystalline molecules. The intermolecular interactions have been calculated considering multipole-multicentere expansion method and modified by second order perturbation treatments. For calculation of multipole *i.e*. charge, dipole, etc. at each atomic center of molecules, para-butyl-p'-cyano-biphenyl, GAMESS, an *ab initio* program, with 6-31G[*] basis set has been used. The stacking, in-plane and terminal interaction energies explain the liquid crystalline behaviour of the system.

KEYWORDS

Liquid Crystals; Phase Transition; Intermolecular Interactions; GAMESS; Multicentred-Multipole Expansion

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 and technological developments to biomedical applications and display devices, the subject of liquid crystal science has attracted increasing interest of the researchers from different disciplines [1-4]. The peculiar changes—characteristics of mesomorphic behaviour which occur at phase transition, are primarily governed by the nature and strength of intermolecular interactions acting between sides of planes and ends of a pair of molecules [5]. To study the role of molecular interactions in mesogenic compounds, semiempirical calculations have been emphasized with an aim to explain liquid crystallinity [6]. Perrin and Berges have employed PCILO, INDO, CNDO etc. methods to analyse—1) the internal rotations, 2) possibilities of motion in aromatic core as well as in the terminal chains and 3) the influence of the conjugation 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 mesomorphism [9]. Tokita *et al*. used Lennard-Jones potential to evaluate intermolecular interactions between a couple of pure nematogens [10]. However, it has been observed that "6-exp" types of potential functions are found to be more effective in explaining the molecular packing instead of Lennard-Jones potentials [11].

In the light of the 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 mesomorphism [12-17]. 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 p-butyl-p'-cyano-biphenyl (4CB) which is a lower homologue of p-alkyl-p'-cyano-biphenyl series. Thermodynamic parameters reveal that 4CB shows crystal to nematic transition at 48˚C and passes to an isotropic melt state at 16.5˚C [18].

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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 [19]:

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

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 multicentered-multipole expansion method [20], the electrostatic energy term is expressed as:

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

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 are found to be sufficient for most of the molecular interaction problems [21]. The monopole-monopole energy is given as:

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

where q_i and q_j are the monopoles at each of the atomic centre 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

$$E_{QMI} = C \sum_{ij} q_i \mu_j \cdot \boldsymbol{r} / r^3$$

and the dipole-dipole interaction term is given by

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

where μ_i and μ_j represent 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:

$$E^{(s)}{}_{POL} = C\left(-1/2\right) \sum_u^{(s)} \varepsilon_u^{[s]} \cdot \overline{\overline{\boldsymbol{A}}}_{\boldsymbol{u}}^{(s)} \cdot \varepsilon_u^{[s]},$$

where $\varepsilon_u^{[s]} = \sum_{t \neq s} \sum_\lambda^{(t)} q_\lambda^{(t)} \boldsymbol{R}_{\boldsymbol{\lambda u}} / \left(R_{\lambda u}\right)^3$ is the electric field created at the bond u by all surrounding molecules and

$\overline{\overline{\boldsymbol{A}}}_{\boldsymbol{u}}$ is the polarizability tensor of this bond. $\boldsymbol{R}_{\lambda,\mu}$ 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 [22-24]:

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

where $E(\lambda, \nu) = K_\lambda K_\nu \left(-\dfrac{A}{z^6} + Be^{-\gamma z} \right)$

and $z = \dfrac{R_{\lambda \nu}}{R_{\lambda \nu}^0}, R_{\lambda \nu}^0 = \sqrt{\left(2R_\lambda^w\right)\left(2R_\nu^w\right)}$

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 [24]. The values of these parameters and van der Waals radii have been given by Caillet and Claverie [25,26]. The details of the mathematical formalism may be found in literature [13,19,27,28].

Molecular geometry of 4CB has been constructed using crystallographic data from literature [18]. Net charge and corresponding dipole moment components at each of the atomic centres of the molecule have been computed by GAMESS, an *ab initio* method, with 6-31G* basis set. 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 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 ±60°. Accuracies up to 0.1 Å in sliding (translation) and 1° in rotation have been achieved [12,13, 28].

3. Results and Discussion

The schemes of three modes of interactions of a molecular pair are shown in **Figure 1**. In this figure the consideration of sides, faces and terminals of a molecule has been shown in **Figure 1(a)**. Whereas the three mode of
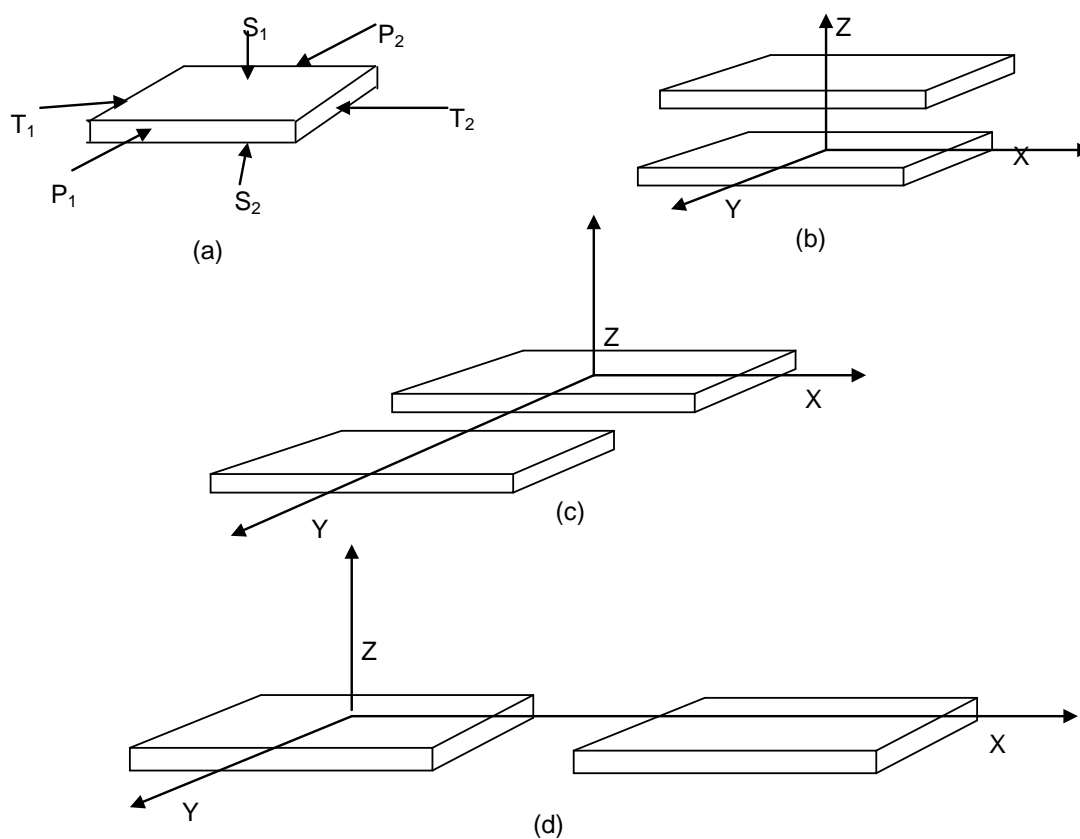
Figure 1. The three modes of interactions of a molecular pair: (a) Sides, faces and terminals of a molecule; (b) Stacking interaction; (c) In-plane interaction and (d) Terminal interaction.

interaction namely stacking, in-plane and terminal interactions have been shown in **Figures 1(b)-(d)** respectively. The molecular geometry of 4CB as optimized by GAMESS with 6-31G* basis set is shown in **Figure 2** 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 variation of total interaction energy with respect to inter-planar separation between two stacked 4CB molecules corresponding to four distinct sets of rotations viz. $X\left(0^\circ\right)Y\left(0^\circ\right)$, $X\left(180^\circ\right)Y\left(0^\circ\right)$, $X\left(0^\circ\right)Y\left(180^\circ\right)$ and $X\left(180^\circ\right)Y\left(180^\circ\right)$ has been shown in **Figure 3**. It is clear from this figure that optimum inter-planar separation between a pair of 4CB molecules corresponds to 3.0 Å for all the rotational sets. Further, all the interaction energy curves exhibit similar nature. However, the minimum energy stacked configuration is observed for the rotation set, $X\left(180^\circ\right)Y\left(180^\circ\right)$ where two molecules of 4CB are stacked at an inter-planar separation of 3.0 Å with energy −11.61 kcal/mole. The various components of interaction energy for this case have been depicted in **Figure 4**. As evident from **Figure 4**, 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 while dispersion energy, which has a major contribution to the total energy plays a decisive role. At shorter distance 3.5 Å, the dispersion energy rapidly decreases and goes to −22.59 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 energy terms together. Further, dispersion forces are the only major attractions which act between the planes of 4CB molecules and account for a specific stacked geometry. The repulsion component has not been plotted explicitly as it can easily be estimated with the help of dispersion and Kitaigorodskii energy curves.

The variation of interaction energy with respect to sliding (translation) of one of the stacked molecules along the long molecular axis (X-axis) corresponding to four fixed rotations about the Z-axis, namely $Z\left(0^\circ\right)$, $Z\left(90^\circ\right)$, $Z\left(180^\circ\right)$ and $Z\left(270^\circ\right)$ has been shown in **Figure 5**. Interaction energy has been calculated by giving translations in the range of ±12.0 Å at an interval of 2.0 Å. Here most stable configuration corresponds to $Z\left(0^\circ\right)$. For this case, various interaction energy components are plotted in **Figure 6**. It is evident from **Figure 6** that monopole-monopole interaction plays a significant role
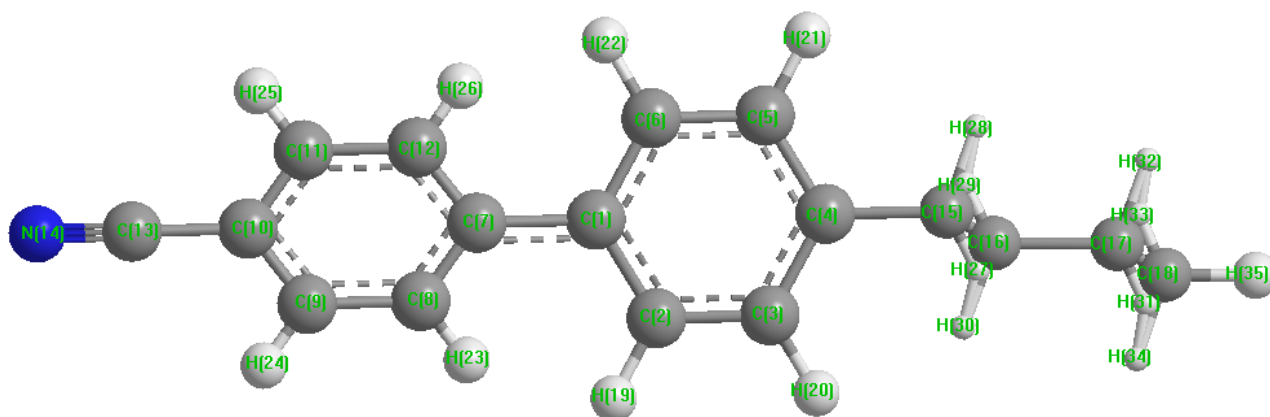
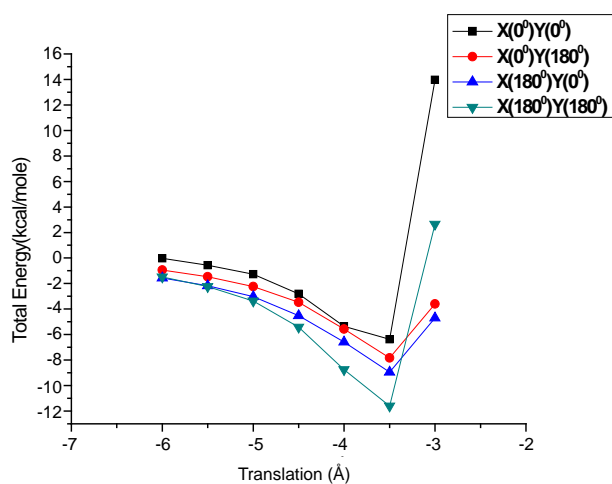**Figure 2.** Optimized geometry of 4CB molecule.

Figure 3. Variation of stacking energy with respect to inter-planar separation corresponding to four distinct cases of stacking patterns.
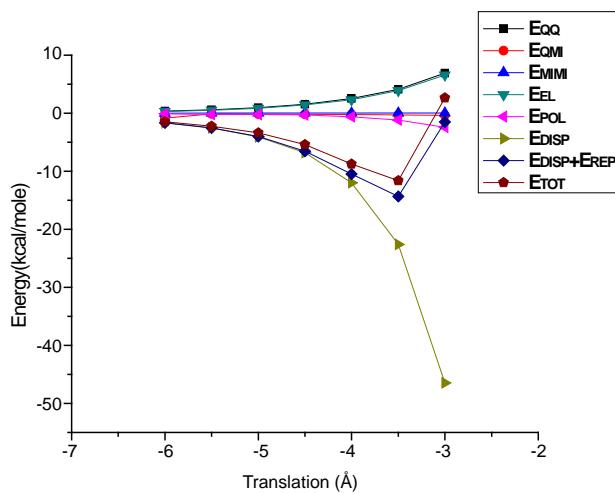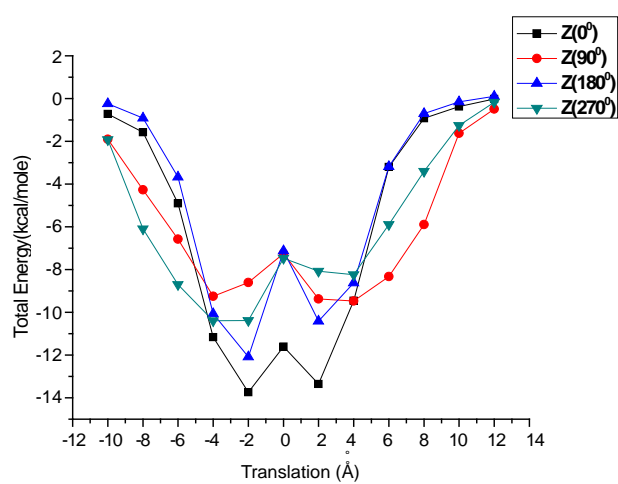

Figure 5. Variation of interaction energy with respect to sliding of one of the stacked molecules along the long molecular axis (X-axis) corresponding to four fixed rotations about the Z-axis.
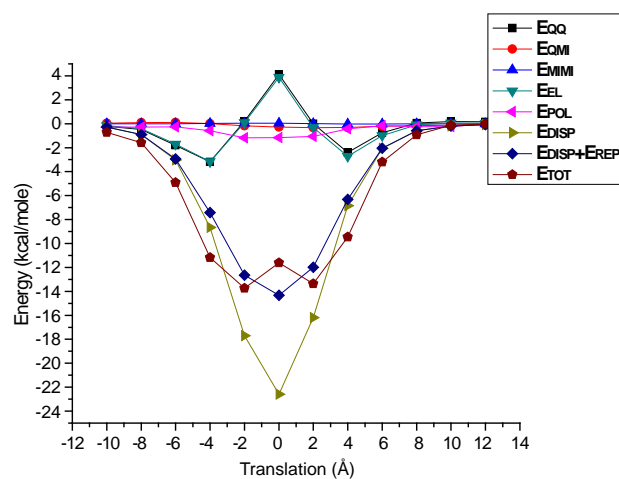

Figure 4. Variation of interaction energy components with respect to inter-planar separation for the stacking pattern: $X\left(180^{\circ}\right) Y\left(180^{\circ}\right)$.

Figure 6. Variation of interaction energy components with respect to sliding of one of the stacked molecules along the long molecular axis (X-axis) corresponding to $Z\left(0^{\circ}\right)$.

Table 1. Net charge and dipole components corresponding to each atomic centre of the 4CB molecule as computed by an *ab initio* method, GAMESS with 6-31G* basis set.

Sl. No.	Atomic No.	Charge (e.u.)	Atomic Dipole Components (debye)		
			μ_x	μ_y	μ_z
1	6	−0.006	−0.003	0.002	0.001
2	6	−0.208	−0.080	−0.101	−0.040
3	6	−0.220	−0.097	−0.085	−0.040
4	6	0.060	−0.087	0.008	−0.015
5	6	−0.230	−0.077	0.093	0.047
6	6	−0.207	0.080	0.103	0.022
7	6	0.036	−0.010	0.000	0.000
8	6	−0.228	−0.081	−0.103	0.046
9	6	−0.170	0.054	−0.118	0.026
10	6	−0.007	−0.025	0.000	0.003
11	6	−0.170	0.042	0.119	−0.039
12	6	−0.228	−0.093	0.101	−0.023
13	6	0.266	−0.556	−0.007	0.073
14	7	−0.470	0.426	0.005	−0.056
15	6	−0.356	−0.100	−0.009	0.040
16	6	−0.294	−0.002	0.003	−0.048
17	6	−0.295	0.011	−0.010	0.058
18	6	−0.469	0.008	0.003	−0.020
19	1	0.214	−0.017	0.033	0.018
20	1	0.205	0.017	0.036	0.014
21	1	0.206	0.014	−0.035	−0.017
22	1	0.214	−0.020	−0.034	−0.013
23	1	0.225	0.019	0.036	−0.014
24	1	0.241	−0.022	0.037	−0.008
25	1	0.241	−0.019	−0.037	0.014
26	1	0.225	0.023	−0.035	0.009
27	1	0.170	0.012	0.040	−0.030
28	1	0.170	0.019	−0.031	−0.036
29	1	0.161	−0.017	−0.039	0.020
30	1	0.156	−0.018	0.031	0.033
31	1	0.151	0.017	0.040	−0.019
32	1	0.151	0.019	−0.032	−0.030
33	1	0.154	−0.003	−0.040	0.022
34	1	0.154	−0.006	0.031	0.033
35	1	0.159	0.045	0.002	−0.006

within electrostatic terms in comparison to monopole-dipole and dipole-dipole interactions. Polarization term is found to be insignificant in stabilizing the molecules in the crystals. Again dispersion components are mainly responsible for the attractions between the pairs of 4CB molecules though the exact optimum point is always located by 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 ±2.0 Å, minor variation in the energy (less than 1.0 kcal/mole) is observed which implies that in the stacked pair of 4CB, molecules can slide one above the other in a range of ±2.0 Å without any significant change in the energy (**Figure 5**). It must be pointed here that rotations, $Z(90°)$ and $Z(270°)$ give energetically less probable stacked geometry. This is because the possibility of stacking at right angles to one another between a pair of molecules capable of mesomorphic phase formation is 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 Kitaigorodskii term. There is a gross similarity between the curves representing total and Kitaigorodskii energies. Further, for relative orientation of about ±20°, there occurs a very small change in the stacking energy (less than 1.0 kcal/mole) of the molecular pair.

The energy corresponding to the optimum angle located at 0° has been 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(a)** having an energy −18.52 kcal/mole and inter planar separation 3.0 Å. The in-plane minimum energy configuration which bears energy −5.70 kcal/mole and intermolecular separation 9.1 Å has been shown in **Figure 8(b)**. The details of stacking as well as in-plane energy are listed in **Table 2**. It seems important to note that the largest attractive contribution in stabilizing the stacked and in-plane interacting pair of 4CB molecules comes from dispersion forces. This supports earlier observations [29,30] and also the basic assumptions of molecular field theory.

The intermolecular interaction energy calculations may reasonably be correlated with the mesomorphic behaviour of the system. When the solid crystals of 4CB molecules are heated, thermal vibrations disturb the molecular ordering of the strongly packed geometrical arrangement of 4CB molecules. Consequently, attractions between the pair of molecules which largely comprise of dispersion forces tend to get weaker at higher temperatures and hence translational freedom along the long molecular axis (**Figure 5**) and orientational flexibility in a
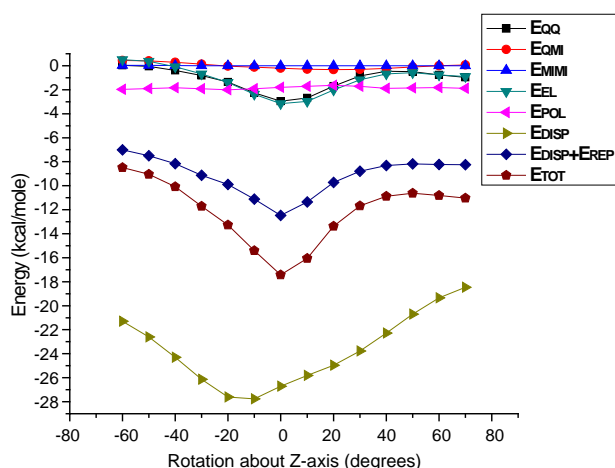
Figure 7. Angular dependence of interaction energy components for the stacking pattern: $X(180°)\,Y(180°)\,Z(0°)$.

Table 2. Interaction energy (in kcal/mole) components corresponding to minimum energy configurations of 4CB molecules during stacking, in-plane and terminal interactions.

Configurations 1, 3 and 5

Interaction	E_{QQ}	E_{QMI}	E_{MIMI}	E_{EL}	E_{POL}	E_{DISP}	E_{REP}	E_{TOT}
Stacking	−4.69	−0.15	0.00	−4.84	−1.74	−25.08	13.15	−18.52
In-plane	−1.34	−0.89	0.03	−2.19	−0.75	−5.43	2.68	−5.70
Terminal	0.17	0.00	−2.13	−0.35	−1.75	−2.10	1.63	−2.59

Configurations 2, 4 and 6

Interaction	E_{QQ}	E_{QMI}	E_{MIMI}	E_{EL}	E_{POL}	E_{DISP}	E_{REP}	E_{TOT}
Stacking	−4.13	−0.10	−0.03	−4.26	−1.73	−25.04	12.79	−18.23
In-plane	−1.32	−1.01	0.00	0.32	−0.55	−6.37	2.74	−3.86
Terminal	−2.33	−0.06	0.00	−2.40	−0.39	−1.83	1.80	−2.81

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. All these parameters favour the nematic behaviour of the system.

The length of molecule is approximately 15 Å, to investigate the terminal interactions away from the van der Waals contacts, the interacting molecule has been shifted along the axis by ±20 Å with respect to fixed one and allowed to rotate along the X- and Y-axis. The energies at such point having examined and found terminal interaction of a pair of 4CB molecule with minimum energy of −2.81 kcal/mole with interplaner separation 4.55 Å.

The minimum energy configuration in case of terminal interaction has been shown in **Figure 8(c)**. Terminal interactions are much weaker than the stacking or in-plane interactions. Rotations about the X-axis show absolutely no preference for any angle, *i.e.* the molecules are free to rotate about their long molecular axis.

The interaction energy calculation can be correlated with the mesomorphic behavior of the system. When solid crystals of 4CB are heated, thermal vibrations disturb the molecular order of the strongly packed 4CB molecules. Consequently, the attraction within a pair of molecules, largely comprising the dispersion forces, tend to get weaker at higher temperatures, and hence the possibility of relative movement within a molecular pair along the long molecular axis is considerable enhanced. The freedom of molecule in a pair to slide along an axis perpendicular to long molecular axis (Y-axis) is energetically restricted. While terminal interactions, are quite insignificant. The results favour the nematic behaviour of the system. At very high temperature breaking of all dispersion forces results and possible stacking geometry even perpendicular stacking become equally probable which ultimately causes the system to become an isotropic melt.

The most prominent energy minima of above mentioned interactions are refined, and values thus obtained are listed in **Table 2** with all contributing terms to enable comparison. These results indicate that the refinement corresponding to the stacking energy at face F_1 is maximum and ultimate magnitude of stacking is larger than in-plane and terminal interactions. Further, all possible geometrical arrangements between a molecular pair during stacking, in-plane and terminal interactions have been considered.

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 4CB are capable of sliding along the long molecular axis with a simultaneous relative orientation of 40°. At very high temperatures, an all-round breaking of dispersion forces results and all possible stacking geometries (even perpendicular stacking) are almost equally favoured, which ultimately cause the system to pass on to an isotropic melt state.

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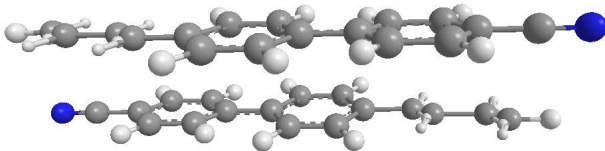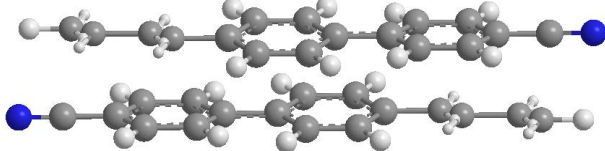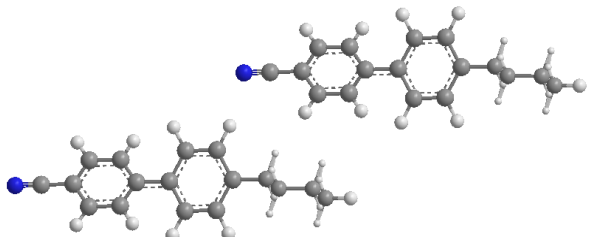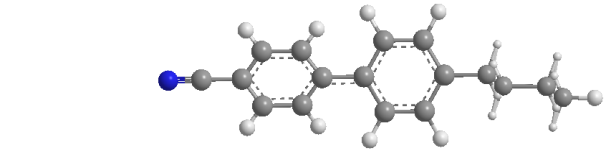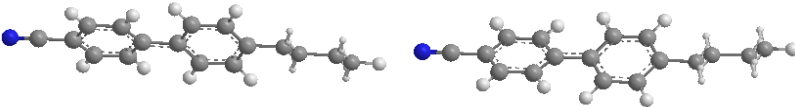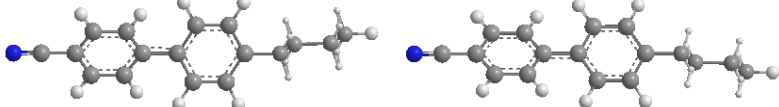
Interaction Type	Configuration	Interaction energy
Stacking (a)	(configuration-1)	−18.52 kcal/mol
	(configuration-2)	−18.23 kcal/mol
In-plane (b)	(configuration-3)	−5.70 kcal/mol
	(configuration-4)	−3.86 kcal/mol
Terminal (c)	(configuration-5)	−2.59 kcal/mol
	(configuration-6)	−2.81 kcal/mol

Figure 8. (a) Stacked pair of 4CB molecules with minimum energy −18.52 kcal/mole with inter-planer separation of 3.0 Å; (b) In-plane configuration of a pair of 4CB molecules with minimum energy of −5.70 kcal/mole with inter-molecular separation of 9.1 Å and (c) Terminal interaction of a pair of 4CB molecule with minimum energy of −2.81 kcal/mole with inter-planer separation 4.55 Å.

Gordon for providing an *ab initio* program GAMESS.

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