



Molecular Structure, Intermolecular Interaction Energy Studies and Correlation of Mesogenic Properties with Intermolecular Interaction Energy of HO-(CH₂)₃-O-C₆H₄-C₆H₄-CN Molecule

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ABSTRACT

Molecular structure of 4, 4'-disubstituted biphenyl derivative HO-(CH₂)₃-O-C₆H₄-C₆H₄-CN (H3CBP) were fully optimized using hybrid density functional B3LYP combined with a 6-31G(d,p) basis set without any constraint taking crystallographic geometry as input. Using the optimized geometry, electronic structure of the H3CBP molecule has been evaluated on the basis of DFT calculation. Intermolecular interaction between a pair of H3CBP molecules have been analyzed in detail using optimized geometry and charge distributions obtained with the help of Gaussian 09 program. Intermolecular interaction energy between a pair of H3CBP molecules have been evaluated by using Rayleigh- Schrodinger perturbation theory modified with multi-centered multi-pole expansion method for the electrostatic part and Kitaigorodskii formula for dispersion and repulsion terms (RS+K method). The results have been reported for separate stacking, in-plane and terminal interactions. The stacking interaction energy of H3CBP molecules were computed with different methods i.e. DFT, DFT-D and M06 methods. A comparative analysis of the results has been carried out with a view to examine suitability of different methods to study molecular aggregations in moderately large organic systems. Results have been also used to elucidate the liquid crystalline behavior of the system.

Key words: Disubstituted biphenyl derivative, Intermolecular interaction, Nematic, DFT calculations, Dispersion corrections

INTRODUCTION

For many years matter was thought to exist in three phases: solid, liquid, and gas. However, this picture is not entirely correct. Certain materials, mostly organic, do not have a direct solid to liquid transition. Instead they show one or more intermediate phases. These phases are called liquid crystalline phases, or meso-morphic phases (mesophases). In a crystal the molecules are located at regular points in space; there is translational order. In a liquid this translational ordering of molecules does not exist. Mesophases may be obtained in two different ways. First the translational order can be confined to one or two dimensions rather than three dimensions, resulting in a smectic phase. Alternatively, for non-spherical molecules molecular orientations may be considered. Translational order

may be retained but the molecular orientations become disordered, resulting in a plastic crystal or the translational order may be lost and the orientational order retained, resulting in nematic phase [1-4].

Biphenyl and its derivative have been always generated interest among scientists on account of their peculiar conformational features and molecular order [5-7]. Several derivatives of biphenyl exhibit mesogenic character. The majority of mesogenic molecules are composed of an aromatic core, to which one or two alkyl chain are attached. The primary role of alkyl chain is to widen the liquid crystal range. The liquid crystal properties, such as the nematic, isotropic transition temperature and the entropy of transition are also influenced by the presence of alkyl chain [8]. Theoretical studies on intermolecular interaction have opened a new direction for quantitative estimation of mesogenic

character on molecular basis. The short range interaction involved in the molecular packing should be analyzed in order to understand the mesogenic behavior. These interactions can be classified as (a) stacking interaction between the planes, (b) in-plane interactions in layer and (c) end to end or terminal interactions as shown in figure1. The contribution of various intermolecular forces to the interaction energy was analyzed in [9-14].

The intermolecular interactions involved are similar in nature in all systems, but in specific problems, a particular type of interaction may dominate. In substrate – protein binding, electrostatic

interaction such as hydrogen bonding and dispersive interaction, particularly those responsible for π -stacking, are important [15]. In non-polar liquid crystals, the mesogenic behavior is generally governed by dispersive interaction only. The difficulty in evaluation of these interactions using quantum mechanical method is well known. High level ab initio methods with large basis sets are required but they are computationally expensive [16]. Density functional theory methods, although reducing the computational expense, often fail to adequately describe dispersive interactions [17].

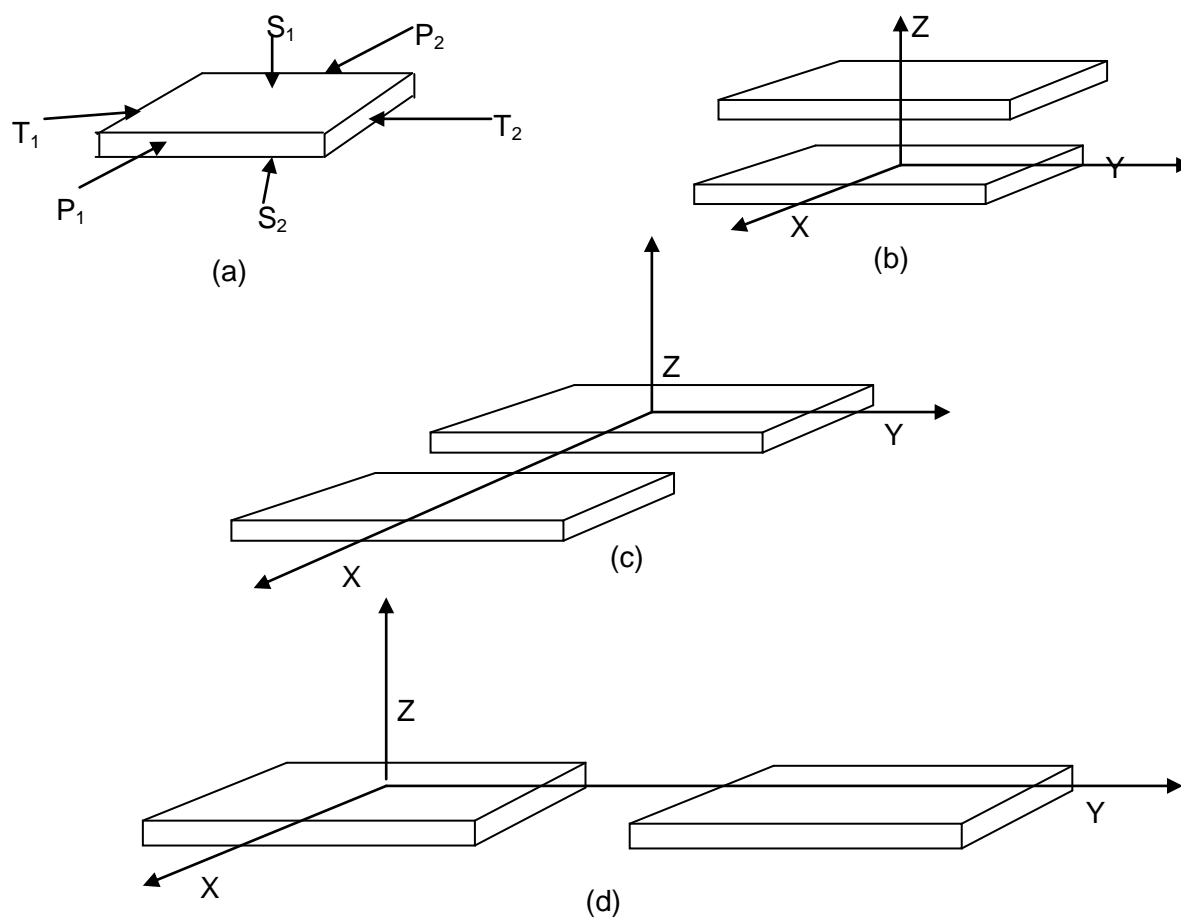


Figure 1: The three modes of interactions of a molecular pair (a) Sides, Faces and Terminals of a Molecule (b) Stacking Interaction (c) In-plane Interaction (d) Terminal interaction,

A popular approach is therefore to evaluate the electrostatic and induction parts of the interaction using the electronic charge and atomic dipole moment distribution obtained by employing DFT method and supplemented by the calculation of dispersion and repulsion terms using semi-empirical

method [18]. Grimme[17] has taken a step forward to include the R^{-6} term in DFT calculations and proposed DFT-D computations. Such an approach promise a way forward to model large biological systems, particularly when used within a hybrid QM/MM [19] or ONIOM [20] framework. The DFT-

D method, developed by Grimme has been tested on a large number of systems [21] and found to give good results. More recently developed functionals of Truhlar[22] are also promising and have been equally claimed to be suitable for estimating non-covalent interaction. A comparative study of both the newly developed methods along with unmodified DFT method to predict the global minimum among the various possible conformers of some selected biomolecules [23], favours M06-2X method developed by Truhlar with respect to estimating intramolecular interactions.

In order to compare some of the available methods to evaluate intermolecular interaction energy and discuss their relative merits, HO-(CH₂)₃-O-C₆H₄-C₆H₄-CN (H3CBP) a bipolar mesogenic molecule, has been chosen for the detailed investigation as it represents the class of Biphenyl derivatives, well known on account of their peculiar conformational features and molecular order [24-26]. Crystallographic studies on the series HnCBP was reported by Zugenmaier and Hieskee [27]. Among the members of this series, H3CBP seems to be interesting since the crystal and molecular structures of H3CBP differ significantly from all the others of the series. The molecule exhibits a conformational disorder in the alkyl chain. The molecule shows an imbricated structure in the crystal which is believed to be a solid state precursor of nematic phase. Earlier, we reported the results of our calculations on a member of this series H4CBP, by employing semi-empirical and DFT methods [28] and observed that under a separated molecular approach, calculation with charges and atomic dipoles computed using DFT method seems to overestimate the electrostatic interaction. In the present paper, we report the results of our investigations on H3CBP molecule using DFT calculations to determine the electronic structure and hence the intermolecular interaction energy between a pair of H3CBP molecule or directly optimizing the molecular pair treating it as a super molecule and calculating interaction energy there from. An attempt has been made to understand mesogenic property on the basis of theoretical results and the results obtained have been compared with the interaction energy value calculated by single point calculation with DFT, DFT-D M06 and RS+K methods.

METHOD OF CALCULATION

The molecular geometry of H3CBP compound was generated from crystallographic coordinates [27] and missing hydrogen atoms were added using Gauss view. Molecular structure of

H3CBP compound was fully optimized without any constraints using Gaussian09 program [29] with hybrid density functional B3LYP and 6-31G(d,p) basis set and frequency calculations were also performed. The calculated atomic net charges and atomic point dipole components were used for the evaluation of intermolecular interaction energy between a pair of molecules on the basis of multi-centered multi-pole expansion method under Rayleigh-Schrodinger perturbation approach for the electrostatic and induction terms along with Kitaigorodskii formula for the dispersion and repulsion terms. Details of this computational scheme have been discussed in our earlier communications [28] with the necessary formulae. Minimum energy configurations for each pair of molecules have been identified under different interacting conditions-stacking, in-plane and terminal interactions. As the stacking interaction dominates in the entire series, minimum energy stacked pairs have been further optimized using DFT-D [D97] and M06-2X/6-31++g** technique and interaction energy has been evaluated for both the cases. Thus a separated molecular approach for RS+K and a super molecular approach for DFT-D and M06 method have been followed.

RESULTS AND DISCUSSION

The optimized molecular geometry of the molecule H3CBP is shown in the figure 2 with atomic numbering scheme. The bond lengths, bond angles and dihedral angles are given in the table 1 while optimized coordinates, distribution of charges and atomic dipole components as obtained from electrostatic analysis are tabulated in table 2. The total dipole moment of the molecule is 7.03 debye (X=3.79, Y=5.84, Z=-0.95). The electronic energy is -823.920 hartree and zero-point energy is -823.645 hartree. The thermal energy, enthalpy and thermal free energy are -823.628, -823.627 and -823.692 hartree respectively.

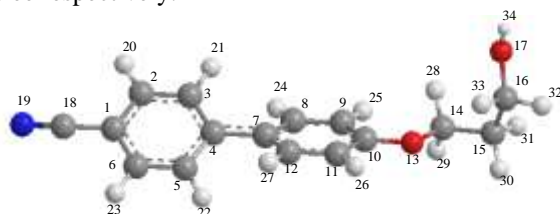


Figure 2: Optimized geometry of H3CBP molecule with atomic numbering Scheme.

Table 1: Comparison of bond length (Å), bond angle (°) and dihedral angle (°) of H3CBP molecule calculated using Gaussian B3LYP /6-31G(d,p) with crystallographic value

Bond length	Theoretical	Experimental	Bond angle	Theoretical	Experimental	Dihedral angle	Theoretical	Experimental
C₁-C₁₈	1.433	1.425	C ₂ -C ₁ -C ₁₈	120.3	119.5	C ₆ -C ₁ -C ₂ -C ₃	-0.15	358.66
C ₁ -C ₂	1.405	1.383	C₂-C₁-C₆	119.3	119.8	C ₁₈ -C ₁ -C ₂ -C ₃	179.82	177.07
C ₁ -C ₆	1.405	1.387	C ₁ -C ₂ -C ₃	120.1	119.8	C ₂ -C ₁ -C ₆ -C ₅	-0.12	1.25
C ₂ -C ₃	1.389	1.378	C ₂ -C ₃ -C ₄	121.3	121.5	C ₁₈ -C ₁ -C ₆ -C ₅	179.90	182.88
C ₃ -C ₄	1.408	1.396	C₃-C₄-C₅	117.9	117.9	N ₁₉ -C ₁₈ -C ₁ -C ₂	-79.46	348.07
C ₄ -C ₅	1.408	1.390	C ₄ -C ₅ -C ₆	121.4	121.0	N ₁₉ -C ₁₈ -C ₁ -C ₆	100.52	166.44
C ₅ -C ₆	1.389	1.385	C ₁ -C ₆ -C ₅	120.1	119.9	C ₁ -C ₂ -C ₃ -C ₄	0.29	359.97
C₄-C₇	1.481	1.477	C ₆ -C ₁ -C ₁₈	120.3	120.7	C ₂ -C ₃ -C ₄ -C ₅	-0.16	1.48
C ₇ -C ₈	1.402	1.393	C ₃ -C ₄ -C ₇	121.1	119.6	C ₂ -C ₃ -C ₄ -C ₇	179.89	184.03
C ₇ -C ₁₂	1.409	1.399	C ₅ -C ₄ -C ₇	121.1	122.4	C ₃ -C ₄ -C ₅ -C ₆	-0.12	358.42
C ₈ -C ₉	1.395	1.382	C ₄ -C ₇ -C ₈	121.3	121.3	C ₇ -C ₄ -C ₅ -C ₆	179.82	175.80
C ₉ -C ₁₀	1.401	1.374	C ₄ -C ₇ -C ₁₂	121.2	121.4	C₃-C₄-C₇-C₈	-35.64	324.44
C ₁₀ -C ₁₁	1.404	1.386	C₈-C₇-C₁₂	117.5	117.2	C ₃ -C ₄ -C ₇ -C ₁₂	144.35	140.90
C ₁₁ -C ₁₂	1.387	1.376	C ₇ -C ₈ -C ₉	121.9	122.2	C ₅ -C ₄ -C ₇ -C ₈	144.41	147.11
C ₁₀ -O ₁₃	1.360	1.366	C ₈ -C ₉ -C ₁₀	119.7	119.5	C ₅ -C ₄ -C ₇ -C ₁₂	-35.60	323.56
O ₁₃ -C ₁₄	1.432	1.420	C₉-C₁₀-C₁₁	119.3	119.6	C ₄ -C ₅ -C ₆ -C ₁	0.26	0.24
C ₁₄ -C ₁₅	1.523	1.499	C ₁₀ -C ₁₁ -C ₁₂	120.3	120.8	C ₄ -C ₇ -C ₈ -C ₉	-179.00	177.24
C ₁₅ -C ₁₆	1.525	1.203	C ₇ -C ₁₂ -C ₁₁	121.4	120.8	C ₁₂ -C ₇ -C ₈ -C ₉	0.03	0.64
C ₁₆ -O ₁₇	1.425	1.396	C ₉ -C ₁₀ -O ₁₃	124.8	124.3	C ₄ -C ₇ -C ₁₂ -C ₁₁	-179.00	183.90
C₁₈-N₁₉	1.164	1.152	C ₁₁ -C ₁₀ -O ₁₃	115.9	116.1	C ₈ -C ₇ -C ₁₂ -C ₁₁	0.16	0.49
			C ₁₀ -O ₁₃ -C ₁₄	119.0	117.9	C ₇ -C ₈ -C ₉ -C ₁₀	-0.22	357.55
			O ₁₃ -C ₁₄ -C ₁₅	107.6	108.2	C ₈ -C ₉ -C ₁₀ -C ₁₁	0.22	3.09

			C ₁₄ -C ₁₅ -C ₁₆	113.1	124.4	C ₈ -C ₉ -C ₁₀ -O ₁₃	-179.00	181.84
			C ₁₅ -C ₁₆ -O ₁₇	107.6	115.1	C ₉ -C ₁₀ -C ₁₁ -C ₁₂	-0.03	357.99
			C ₁ -C ₁₈ -N ₁₉	179.9	178.0	O ₁₃ -C ₁₀ -C ₁₁ -C ₁₂	-179.00	179.14
						C ₁₀ -C ₁₁ -C ₁₂ -C ₇	-0.16	0.19
						C₉-C₁₀-O₁₃-C₁₄	0.97	0.36
						C ₁₁ -C ₁₀ -O ₁₃ -C ₁₄	-179.20	179.15
						C ₁₀ -C ₁₁ -C ₁₂ -C ₇	-0.16	0.19
						C ₁₀ -O ₁₃ -O ₁₄ -C ₁₅	176.82	177.95
						O ₁₃ -C ₁₄ -C ₁₅ -C ₁₆	-66.71	287.38
						C₁₄-C₁₅-C₁₆-O₁₇	-63.09	291.54

From table 1 it is observed that the bond length C₁-C₁₈ is 1.433Å corresponds to a single bond (σ) while nitrogen containing bond C₁₈-N₁₉ (1.164Å) is close to triple bond (2σ and π). The inter ring bond C₄-C₇ (1.481Å) is showing the partial presence of π electrons. The oxygen containing bonds are also showing the presence of double bond (σ and π). From table1 it is clear that the bond angles inside the benzene ring C₂-C₁-C₆, C₃-C₄-C₅, C₈-C₇-C₁₂ and C₉-C₁₀-C₁₁ are slightly deviated from the average 120° which is in agreement with literature [27]. The dihedral angle (C₃-C₄-C₇-C₈) between the planes of the two rings is -35.6° which is also in agreement with literature [27]. Thus the two rings are out of plane to each other. The chain of compound has three carbon and two oxygen atoms. The dihedral angle (C₁₄-C₁₅-C₁₆-C₁₇) of alkoxy tail is -63.1°. The plane of chain and ring are almost in same plane (C₉-C₁₀-O₁₃-C₁₄). From figure2 and table1, it clear that the molecule exhibits a conformational disorder in the alkyl chain which is also reported in literature [27]. From table1 it is observed that calculated values of

bond lengths and bond angles are closer to that of experimental values. There are some differences in dihedral angles.

It may be observed from table 2 that the almost all the electronegative atoms have acquired negative charge except nitrogen at position 19. The benzene ring carbon atoms have mostly negative charges except inter ring carbon atoms at position 4 and 7. The alkyl carbon atoms have only positive charge. The benzene ring hydrogen atoms have acquired only positive charge and alkyl chain hydrogen atoms have mostly negative charges. From dipole moment component, it is clear that mostly all atoms oriented along X and Y axis. The dipole moment components along Z-axis are small and in total it has moderate value.

The electronic energy, dipole moment and their components of H3CBP molecule as obtained through optimization by DFT, DFT-D and M06 methods have been presented in table3. All the energy values and dipole moments show that molecule is stabilized in gaseous state.

Table 2: Computed optimized coordinate (Å), net atomic charges (e u) and point dipole moment components (debye) at various atomic positions of H3CBP molecule

Atom No	Atomic No	Optimized Coordinate			Atomic charges q	Point Dipole component		
		X	Y	Z		μ_x	μ_y	μ_z
1	6	-0.019	0.011	0.018	-0.634	0.642	1.058	-0.076

2	6	1.385	-0.036	-0.007	-0.355	-0.221	-0.128	0.023
3	6	2.119	1.140	-0.083	-0.316	-0.149	-0.453	0.038
4	6	1.487	2.397	-0.130	0.082	-0.241	-0.541	0.054
5	6	0.080	2.427	-0.100	-0.249	-0.282	-0.175	0.001
6	6	-0.666	1.257	-0.030	-0.322	-0.061	-0.130	0.024
7	6	2.276	3.647	-0.209	0.101	-0.765	-0.905	-0.039
8	6	3.504	3.777	0.455	0.042	-0.019	0.861	-0.420
9	6	4.257	4.949	0.389	-0.629	-0.119	0.228	-0.129
10	6	3.788	6.034	-0.362	0.540	-0.187	0.213	-0.223
11	6	2.560	5.923	-1.034	-0.731	-0.120	0.426	-0.264
12	6	1.821	4.752	-0.956	-0.003	0.979	0.587	0.357
13	8	4.435	7.222	-0.498	-1.010	-0.407	-0.041	-0.154
14	6	5.701	7.401	0.146	1.715	-0.811	-1.301	0.187
15	6	6.224	8.778	-0.238	0.454	0.440	-0.718	0.072
16	6	6.569	8.893	-1.719	0.646	0.243	-0.133	0.120
17	8	7.627	7.977	-1.989	-1.031	0.241	-0.181	-0.014
18	6	-0.782	-1.198	0.093	0.172	1.201	1.949	-0.106
19	7	-1.403	-2.181	0.153	0.456	0.417	0.644	-0.035
20	1	1.889	-0.996	0.020	0.197	-0.002	0.037	-0.002
21	1	3.202	1.085	-0.135	0.254	-0.088	0.043	0.006
22	1	-0.433	3.383	-0.107	0.177	0.036	-0.018	0.003
23	1	-1.750	1.299	-0.001	0.172	0.019	0.008	-0.001
24	1	3.872	2.957	1.064	0.382	-0.060	0.112	-0.085
25	1	5.194	5.009	0.929	0.265	-0.108	-0.092	-0.035
26	1	2.213	6.768	-1.621	0.080	-0.017	0.024	-0.02
27	1	0.888	4.680	-1.507	0.423	0.147	-0.029	0.106
28	1	6.404	6.628	-0.185	-0.538	0.286	-0.210	-0.122
29	1	5.576	7.323	1.234	-0.561	0.004	0.051	0.403

30	1	7.125	8.981	0.351	-0.231	0.141	0.081	0.128
31	1	5.479	9.538	0.021	0.090	-0.012	0.030	-0.017
32	1	6.871	9.928	-1.945	-0.097	0.028	0.073	-0.021
33	1	5.678	8.664	-2.320	-0.050	-0.060	-0.031	-0.019
34	1	7.747	7.925	-2.945	0.507	-0.031	0.016	0.061

Table 3: Comparison of electronic energy and dipole moment components of H3CBP molecule computed with different methods

Method	Electronic energy E(RB+HF-LYP) (Hartree)	Dipole moment components (Debye)		
		μ_x	μ_y	μ_z
DFT	-823.920413	1.492	2.299	-0.374
DFT-D	-824.175184	1.469	2.319	-0.334
M06	-823.793846	1.406	2.232	-0.332

Table 4: Interaction energy of H3CBP molecule calculated with RS+K method using Gaussian charges and dipoles

Interaction type	Configuration type	E_{el}	E_{pol}	E_{disp}	E_{rep}	E_{tot}
Stacking	Anti-parallel	-16.96	-9.69	-16.71	8.05	-35.31
	Parallel	-1.02	-3.27	-20.46	9.28	-15.47
In-plane	Anti-parallel	-11.83	-2.07	-10.72	3.15	-21.48
	Parallel	-4.18	-1.40	-10.55	5.55	-10.58
Terminal	OH-OH	-4.87	-0.46	-3.23	1.76	-6.80
	OH-N	-1.19	-0.38	-1.75	0.67	-2.65

The optimized coordinates, atomic charges and point dipole moment components as obtained from B3LYP/6-31G(d,p) method were used to calculate the interaction energy between the pair of H3CBP molecule using RS+K method. Calculations of interaction energy are carried out for stacking, planer and terminal interactions, keeping one molecule on either side of another fixed molecule. All possible configurations for interacting molecule i.e. flipping about the molecular axis and translating the molecule along all the three axes were computed. Various interaction energy components between a pair of H3CBP molecule at different interacting

configurations as obtained after refinement are shown in table 4. The computed result suggests that stacking interaction with antiparallel mode is the most preferred out of the three interacting mode. The next

preference goes with in-plane interaction while the terminal interaction is the least preferred one, unless there is a polar group at the end. From the table 4 it is clear that dispersion energy term has major contribution towards total interaction energy than electrostatic in the case of stacking and in-plane interaction whereas in terminal interaction electrostatic has larger contribution than dispersion. Thus, the interaction potential for this molecule is

highly asymmetrical in nature, which is also one of the requisites of the mesogenic character. The sum of planer energy (in-plane + terminal interaction energy) of H3CBP molecule is lower in magnitude in comparison to anti-parallel stacking, which suggests a pure nematic character. The major contribution to the total interaction energy in case of terminal interaction comes from the electrostatic energy, showing that the molecules have a strong tendency to form hydrogen bond, which results in formation of

long chain. Due to hydrogen bonding between polar groups, the melting and clearing temperature of H3CBP molecule is probably high.

The minimum energy configuration of a pair of H3CBP molecule under different interacting conditions as obtained through B3LYP/6-31G(d,p) method are shown in figure3. The interaction energy is found minimum for anti-parallel stacking interaction, which reflects that this molecule is packed in an anti-parallel fashion as reported in

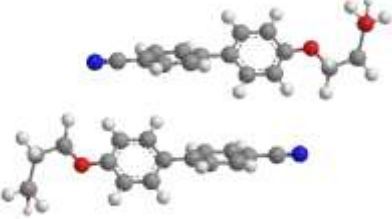
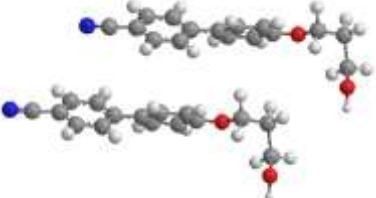




Configuration no. and type	Configurations	Interaction energy (kcal/mole)
1 Stacking anti-parallel		-35.31
2 Stacking parallel		-15.47
3 In-plane anti-parallel		-21.48
4 In-plane parallel		-10.58
5 Terminal OH-OH		-6.80
6 Terminal OH-N		-2.65

Figure 3: Minimum energy configurations for a pair of H3CBP molecules with charges and dipoles obtained with B3LYP/6-31G(d,p) basis sets.

Table 5: Stacking interaction energy between a pair of H3CBP molecule with M06, DFT-D, DFT and RS+K

Configuration type	Interaction energy with M06 (kcal/mol)	Interaction energy with DFT_D (kcal/mol)	Interaction energy with DFT (kcal/mol)	Interaction energy with RS+K (kcal/mol)
Anti-parallel	-7.55	-9.67	-2.15	-35.31
Parallel	-11.59	-13.82	-2.79	-15.47

literature [27]. Hydrogen bonds are generally formed between cyano and hydroxyl groups. The displaced anti-parallel stacked geometry is found in the case of this molecule, which indicates that layered structure may not be formed. Displaced geometry also indicates that a weak dipole-dipole interaction exists between cyano groups. In the case of planer interactions, parallel interaction is not favourable for this molecule while anti-parallel interaction exists because alkoxy oxygen faces interacting each other. Due to this interaction the molecule is shifted towards an imbricated structure as mentioned by Zugenmeir. In terminal interactions, this molecule shows hydrogen bonding between cyano & hydroxyl groups and hydroxyl-hydroxyl groups.

We also evaluate interaction energy between a pair of H3CBP molecule by optimizing the pair treating it as a supermolecule using M06 and DFT-D methods. For optimization, we take anti-parallel and parallel stacking configuration 1&2 shown in figure 3 as input. Table 5 shows comparison of interaction energy between a pair of H3CBP molecule with different methods. The magnitude of interaction energy, however, is considerably lower than that calculated using RS+K method. It should be mentioned here that attaining the minimum energy has brought some conformational changes in the molecule.

It may be mentioned here that attempt was also made to optimize the pair using PM3 and PM6 level of approximation, but in such cases the value of interaction energy came out to be positive (repulsive).

CONCLUSIONS

Geometrical parameters (bond lengths, bond angles) of this molecule as computed by B3LYP/6-31G(d,p) are found to be in good agreement with crystallographic data. In mesogenic molecules, the nature of intermolecular interaction is highly asymmetric. The magnitude of interaction energy of this molecule for the three modes of interactions is in the following order-

Stacking > in-plane > terminal

The sum of planer energy (in-plane + terminal interaction energy) of H3CBP molecule is lower in magnitude in comparison to anti-parallel stacking interaction energy, which suggests a pure nematic character. Higher magnitude of packing energy indicates in general a high melting point. From above calculation it is observed that this molecule packed in an antiparallel fashion.

Anti-parallel interaction energy calculated with M06 and DFT-D methods are lower in magnitude in comparison to RS+K method. The separated molecular approach seems to overestimate the electrostatic and polarization energy. Hence, crystal energy calculated on the basis of RS+K results is much larger in magnitude than the experimental values. Thus, direct estimation of interaction energy using DFT-D or M06 method appears to be the best method available so far.

ACKNOWLEDGEMENTS

Authors are thankful to the department of Science and Technology, New Delhi for providing

computational facility under FIST program (Ref.

No.SR/FST/PSI-087/204).

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