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Electronic structure and intermolecular interaction energy calculations of a bipolar mesogen HO-$(CH_2)_5$-O-C_6H_4-C_6H_4-CN

Physics

Rakesh Kumar Srivastav Department of physics, DDU Gorakhpur University, Gorakhpur U.P. – 273009, India

Mihir Roychoudhury Department of physics, DDU Gorakhpur University, Gorakhpur U.P. – 273009, India

ABSTRACT

Molecular geometry of a bipolar mesogen HO-$(CH_2)_5$-O-C_6H_4-C_6H_4-CN (H5CBP) was fully optimized without any constraint and checked for imaginary frequencies using hybrid density functional B3LYP combined with 6-31g** basis set taking crystallographic geometry as input. Using the optimized geometry, electronic structure of the H5CBP molecule has been evaluated on the basis of DFT calculation. Intermolecular interaction between a pair of H5CBP molecules have been analyzed in detail using optimized geometry and charge distributions obtained with the help of Gaussian03 program. Intermolecular interaction energy between a pair of H5CBP 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 H5CBP molecules was computed with different methods i.e. DFT, DFT-D and M06 methods. Analysis of the molecular geometry, molecular packing in crystal and mesogenic behavior has been carried out in the light of the obtained results.

KEYWORDS:

Nematic, RS+K, DFT, DFT-D, M06, H3CBP

Introduction

Biphenyl and its derivatives have been always generated interest among scientists on account of their peculiar conformational features and molecular order [1-3]. Several derivatives of biphenyl exhibit mesogenic character. As it is yet not possible to predict the existence of a definite phase on account of the molecular shape and interactions, attempts have been made to draw conclusion based on selected properties of molecules [4]. Theoretical studies on intermolecular interaction have opened a new direction for quantitative estimation of mesogenic character on molecular basis. Earlier attempts used approximate methods to carry on such calculations due to limitations imposed by computers [5-6]. However, with the advent of faster and more efficient computer at reasonable cost, it seems proper to use more sophisticated computational method to evaluate molecular parameters. With this view, we have taken up a systematic study on the homologous series of HnCBP. Crystallographic study on this series was reported by Zugenmaier and Hieske [7]. Among the members of this series, H5CBP seems to be interesting, so we have taken this molecule for detailed investigations. The molecule shows an imbricated structure in the crystal which is believed to be a solid state precursor of nematic phase.

In the present paper, we report the results our investigations on this molecule using DFT calculation for determining electronic structure. The results have been compared with the observed crystal structure and an attempt has been made to understand mesogenic property on the basis of the theoretical results. Intermolecular interaction energy also calculated using super molecular approach with DFT, DFT-D and M06 methods.

Method of Calculation

Molecular structure of H5CBP compound was fully optimized without any constraint using Gaussian03 program [8] along with hybrid density functional B3LYP combined with a 6-31G** basis set taking crystallographic geometry as input and missing hydrogen were added using Gauss view. The optimized structure was further employed to calculate atomic net charges and point dipole components. The calculated coordinates, atomic net charges and atomic point dipole components were used for evaluation of intermolecular interaction energy between a pair of molecules was carried out 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 communication [9] 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 (figure1). As the stacking interaction dominates in the entire series, minimum energy stacked pairs have been further optimized using DFT-D and M06 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.

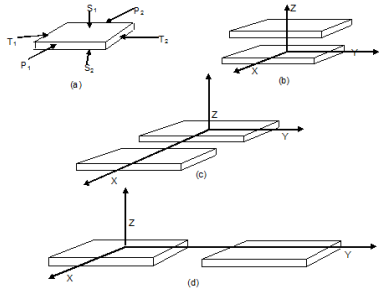

Figure 1: The three modes of interactions of a molecular pair
(a) Sides, Faces and Terminals of a Molecule
(b) Stacking Interaction
(c) In-plane Interaction
(d) Terminal interaction

Results and Discussion

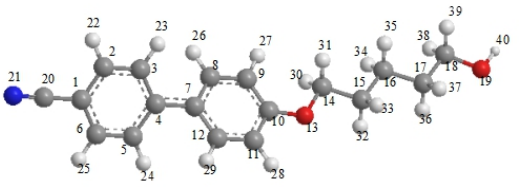

Figure 2: Optimized geometry of H5CBP molecule with atomic numbering scheme.

The optimized molecular geometry of the molecule H5CBP is shown in the figure2 with atomic numbering scheme. It may be observed that the molecule exhibits some conformational adjustment to reach optimum structure. The important bond lengths, bond angles and dihedral angles are given in the table1. The total dipole moment of the molecule is 7.08 Debye (X=5.17, Y=4.66, Z=1.29). The electronic energy is -902.550 hartree and zero-point energy is -902.218 hartree. The thermal energy, enthalpy and thermal free energy are -902.198, -902.197 and -902.270 hartree respectively.

Table 1: Computed bond length, bond angle and dihedral angle of H5CBP

Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
C_1-C_{20}	1.433	C_2-c_1-C_{20}	120.3	N_{21}-C_{20}-C_1-C_2	-44.1
C_{20}-N_{21}	1.164	C_2-C_1-C_6	119.3	C_3-C_4-C_7-C_8	-35.6
C_4-C_7	1.481	C_3-C_4-C_5	117.8	C_9-C_{10}-O_{13}-C_{14}	0.5
C_{10}-O_{13}	1.360	C_5-C_4-C_7	121.0	C_{11}-C_{10}-O_{13}-C_{14}	-179.5
O_{13}-C_{14}	1.428	C_4-C_7-C_8	121.3	C_{10}-O_{13}-C_{14}-C_{15}	179.6
C_{16}-C_{17}	1.533	C_8-C_7-C_{12}	117.5	O_{13}-C_{14}-C_{15}-C_{16}	-179.9
C_{18}-O_{19}	1.422	C_9-C_{10}-C_{11}	119.2	C_{16}-C_{17}-C_{18}-O_{19}	-180.0
		C_9-C_{10}-O_{13}	124.8		
		C_{10}-O_{13}-C_{14}	118.9		
		O_{13}-C_{14}-C_{15}	107.7		
		C_{16}-C_{17}-C_{18}	112.9		
		C_{17}-C_{18}-O_{19}	107.8		

The optimized coordinates as obtained from B3LYP method were used to calculate the interaction energy between the pair of molecules 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 molecules 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 H5CBP molecules at different interacting configurations as obtained after refinement are tabulated in table2. The computed result suggests that stacking interaction with antiparallel alignment is the most preferred out of the three interacting modes. 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 table2 it is clear that dispersion energy term has major contribution towards total interaction energy in comparison to 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 such molecules is highly anisotropic in nature, which is also one of the requisites of the mesogenic character. The sum of planer energy (in-plane + terminal interaction energy) of H5CBP molecules 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 such molecules are probably high.

Table 2: Interaction energy (kcal/mole) between a pair of H5CBP molecule with RS+K method

Interaction type	Configuration type	Eel	Epol	Edisp	Erep	Etot
Stacking	Anti-parallel	-13.75	-9.74	-33.11	23.58	-33.02
	Parallel	-1.71	-2.65	-23.65	9.96	-18.06
In-plane	Anti-parallel	-4.76	-4.73	-18.98	11.64	-16.83
	Parallel	-0.89	-1.70	-14.04	5.36	-11.26
Terminal	OH-OH	-11.72	-0.85	-5.05	6.51	-11.12
	OH-N	-11.56	-1.25	-3.61	7.01	-9.41

The minimum energy configuration of a pair of H5CBP molecules under different interacting conditions as obtained through RS+K method using B3LYP/6-31G** charges and dipole components are shown in figure3. The interaction energy is found minimum for anti-parallel stacking interactions, which reflect that the H5CBP molecule are packed in an anti-parallel fashion with more or less strong interactions between the polar end groups as reported in literature [7]. Hydrogen bonds are generally formed between cyno and hydroxyl groups. In the case of planer interactions parallel interaction is not favourable while anti-parallel interaction exists because alkoxy oxygen faces interact with each other. Due to this interaction the molecules are shifted towards an imbricated structure as mentioned by Zugenmeir. Also strong CN-CN (dipole-dipole) interactions involved in packing contacts generate a high thermal stability. In terminal interactions, hydrogen bonding forms between cyno & hydroxyl groups and hydroxyl-hydroxyl groups.

We also evaluate interaction energy between a pair of H5CBP 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 figure3 as input. Table3 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.

Table 3: Stacking interaction energy between a pair of H5CBP 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	-8.01	-10.77	0.07	-33.03
Parallel	-9.90	-12.18	-1.63	-18.06

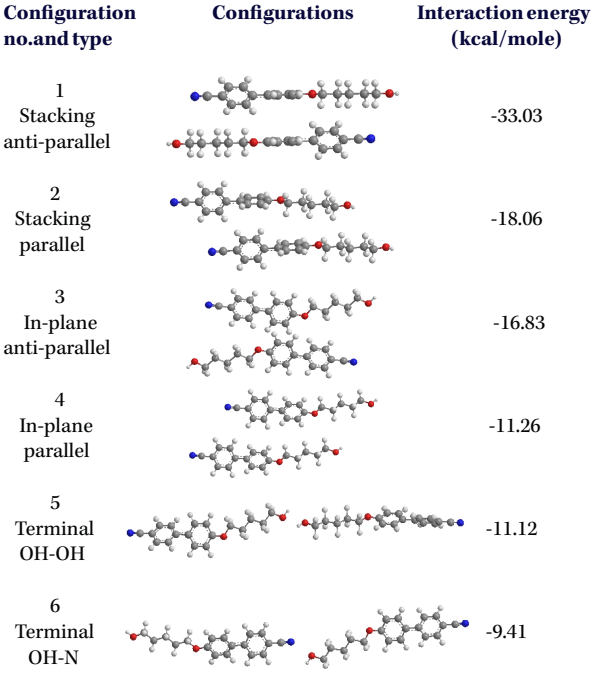

Figure 3: Minimum energy configurations for a pair of H5CBP molecules with charges and dipoles obtained with B3LYP/6-31G basis sets.**

Conclusion

Geometrical parameters (bond lengths, bond angles) of H5CBP molecule as computed by B3LYP/6-31 g** 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 H5CBP 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.

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