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DFT Computational Studies on *(E)*-4-bromo-5-fluora-2-((4-methoxyphenylimino)methyl)phenol

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Abstract **–** In this study, the molecular structure, molecular electrostatic potential, atomic charges, and molecular orbital energies have been investigated of *(E)*-4-bromo-5-fluoro-2-((4-methoxyphenylimino)methyl)phenol using the densitiy functional theory calculations. The Becke's three parameter hybrid functional and Lee-Yang-Parr correlation functionals (B3LYP) were utilized in the calculations with the 6-31G(d) basis set. The molecular electrostatic potential map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. Namely, the title compound can act as multidentate ligand to bind one or two metal centers, so resulting in interesting metal complexes with different coordination geometries. Both the highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are mostly the p-antibonding type orbitals. The value of the energy separation between the HOMO and LUMO is very large. This large HOMO–LUMO gap automatically means high excitation energies for many of excited states, a good stability and a high chemical hardness for the title compound.

Keywords *– Atomic charges, DFT, MEP, Schiff Base,HOMO-LUMO.*

I. Introduction

Schiff bases (known as imine or azomethine) exhibit interest as materials for wide spectrum applications, particularly as corrosion inhibitors, a metal ion complexing agents, in biological systems and thermo-stable materials [1]. Schiff bases are an important class of compounds in the medicinal and pharmaceutical fields and have been found to play an important role in development of coordination chemistry. These compounds show biological activities including antifungal, antibacterial, anticancer and herbicidal activities [2]. They are also becoming increasingly important in the dye and plastic industries as well as for liquid-crystal technology. The Schiff bases have been also under investigation during last years because of their potential applicability in optical communications and many of them have NLO behaviour [3].

The aim of this study is to investigate the energetic and structural properties of the Schiff base compound, *(E)*-4-bromo-5-fluoro-2-((4-methoxyphenylimino)methyl)phenol, using density functional theory calculations. Molecular geometry, molecular electrostatic potential (MEP), frontier molecular orbitals, Mulliken charges were investigated at B3LYP/6-31G(d) level of theory.

II. Materials and Method

Density functional theory calculations of the compound have been performed using the B3LYP method at the 6-31G(d) basis set. Molecular geometry, molecular electrostatic potential (MEP), frontier molecular orbitals, Mulliken charges were investigated at B3LYP/6-31G(d) level of theory.

III. Results and Discussion

A. Optimized geometries

The atomic numbering scheme for the title compound is shown in Fig 1. The optimized parameters (bond lengths, bond angles, and torsion angles) of the compound have been obtained using the B3LYP/6-31G(d) method. These results are listed in Table 1

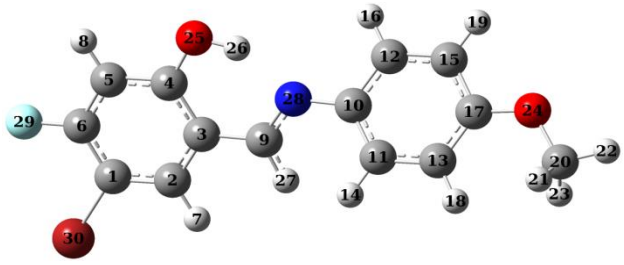

Fig. 1. The theoretical structure of the compound

The molecular structure is not planar. The dihedral angle between the aromatic ring systems is 32.42°. In the molecular structure of the title compound, the bond lengths and angles are within normal ranges and they are comparable with those

related structures [2-4]. The azomethine bond length of the C9=N28 double bond is 1.291 A, which is slightly longer than standard 1.28 A value.

According to this result, it may be concluded that the B3LYP calculation well reproduce the geometry of the compound.

Table 1 Selected molecular structure parameter

Parameters	DFT
Bond Lengths (Å)	
C6-F29	1.33974
C1-Br30	1.90031
C4-O25	1.33764
C9-N28	1.29183
N28-C10	1.40742
C17-O24	1.36278
O24-C20	1.41939
Bond angles (º)	
C3-C4-O25	122.05297
C3-C9-N28	122.07423
C9-N28-C10	121.76515
C17-O24-C20	118.37396
Torsion angles (º)	
C3-C9-N28-C10	177.45794
O25-C4-C3-C9	0.05120
C9-N28-C10-C12	151.01473

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B. Atomic Charge

The Mulliken atomic charges of the compound calculated at DFT/B3LYP method in gas-phase are presented in Figure 2. It can be seen from the figure that the Mulliken atomic charges of the O24, O28, Br30 and F29 have negative atomic charges in gas phase.

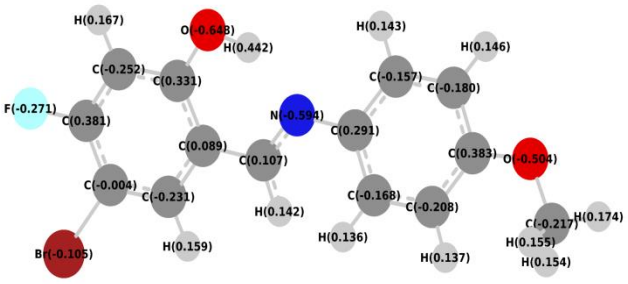

Figure 2. Mulliken atomic charges of the title compound.

C. MEP Surface

Molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions [5].

To predict reactive sites for electrophilic and nucleophilic attack for the molecule, MEP was calculated at the B3LYP/6-31G(d) optimized geometry. The negative (red color) regions of MEP were related to electrophilic reactivity and the positive (blue color) ones to nucleophilic reactivity shown in Fig. 3.

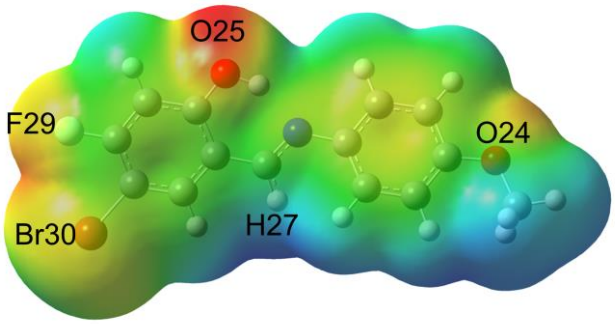

Fig 3 MEP surface of the compound

As easily can be seen in Fig. 3, this molecule has three possible sites for electrophilic attack. The negative V(r) values are -0.034 a.u. for the O1 atom which is the most negative region: about -0.022 a.u. for O24, -0.012 a.u. for Br30 and -0.019 a.u. for F29 atom. A maximum positive region is localized on the H27 atom with a value of +0.032 a.u. indicating a possible site for nucleophilic attack.

D. Frontier Orbitals

The frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV–vis spectra and chemical reactions [6]. Fig. 3 shows the distributions and energy levels of the HOMO and LUMO orbitals for the compound. Both the highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital (LUMO) are mostly the p-antibonding type orbitals. The value of the energy separation between the HOMO and LUMO is 3.864 eV. This large HOMO–LUMO gap automatically means high excitation energies for many of excited states, a good stability and a high chemical hardness for the title compound.

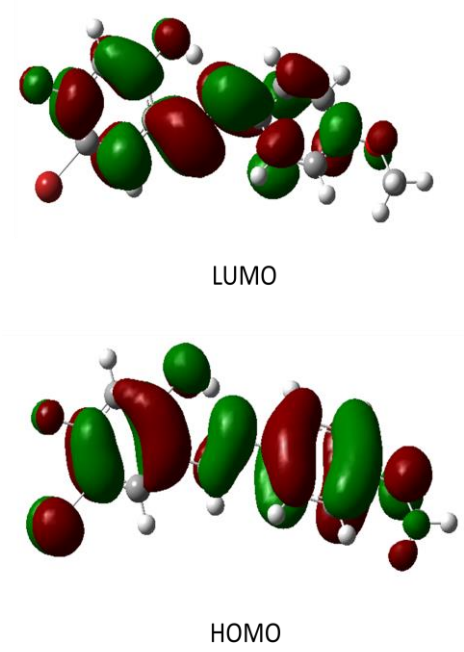

Fig. 3 Frontier molecular orbitals of the title compound

IV. Conclusions

Density functional calculations have been performed for the title compound and the calculated results show that B3LYP/6-31G(d) method can reproduce the structural parameters well. The MEP map shows that the negative potential sites are on electronegative O, F and Br atoms while the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have non-covalent interactions and metallic bonding. The value of the energy separation between the HOMOs and LUMOs is very large and this energy gap gives significant informations about the title compound.

Acknowledgment

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References

[1] H. Tanak, Molecular Physics, 112 (2014) 1553-1565.

[2] H. Tanak, A.A. Agar, O. Buyukgungor, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 (2014) 672–682

[3] H. Tanak, A.A. Agar, O. Buyukgungor, Journal of Molecular Structure 1048 (2013) 41–50

[4] H. Tanak, Molecular Physics, 112 (2014) 1553-1565

[5] N. Okulik and A.H. Jubert, J. Mol. Des. 4 (2005) 17

[6] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, London, 1976.