

Quantum chemical computational studies on 4-Fluoro-N-(4-hydroxybenzylidene)-aniline

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Abstract – Density functional theory calculations of the molecular structure have been performed at B3LYP/6-31G(d) level of theory for the title compound. To investigate the nonlinear optical properties of the title compound, the electric dipole moment, the polarizability and the first hyperpolarizability were calculated using the DFT/B3LYP method with the 6-31G(d) basis set. According to results, the title compound exhibits nonzero hyperpolarizability value revealing second order nonlinear optical behavior. In order to investigate reactive sites for electrophilic or nucleophilic sites for the investigated molecule, the molecular electrostatic potential at the B3LYP/6-31G(d) basis optimized geometry was also calculated. Besides, atomic charges, and molecular orbital energies have been investigated of the title compound using the density functional theory calculations. The highest occupied molecular orbital and the lowest-lying unoccupied molecular orbital are mostly the p-antibonding type orbitals. The value of the energy separation between the HOMO and LUMO is quite large.

Keywords – Atomic charges, DFT, MEP, Schiff Base, NLO.

I. INTRODUCTION

Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics, antiphlogistic, antiallergic and antitumor substances [1]. On the industrial scale, Schiff bases have a wide range of applications, such as dyes and pigments [2]. They are also important for the progress of coordination chemistry including enzymatic and catalysis reactions, molecular architectures and magnetism [3]. They have been also under investigation during last years because of their potential applicability in optical communications and many of them have NLO behaviour [4].

The aim of this study is to investigate the physicochemical properties of the Schiff base compound, 4-Fluoro-N-(4-hydroxybenzylidene)-aniline, using density functional theory calculations. In this study, molecular structure, molecular electrostatic potential (MEP), Mulliken atomic charges, frontier molecular orbitals, NLO properties were investigated at B3LYP/6-31G(d) level of theory.

II. MATERIALS AND METHOD

Quantum chemical studies of the title compound have been performed using the DFT/B3LYP method with the 6-31G(d) basis set. Molecular structure, molecular electrostatic potential (MEP), frontier molecular orbitals, Mulliken charges and NLO properties of the title compound were investigated at B3LYP/6-31G(d) level of theory.

III. RESULTS AND DISCUSSION

A. Optimized geometries

The experimental atomic numbering scheme [5] and theoretical structure of the title compound is shown in Fig 1. The optimized parameters (bond lengths, bond angles, and

torsion angles) of the title compound have been obtained using the B3LYP/6-31G(d) method. These results are listed in Table 1

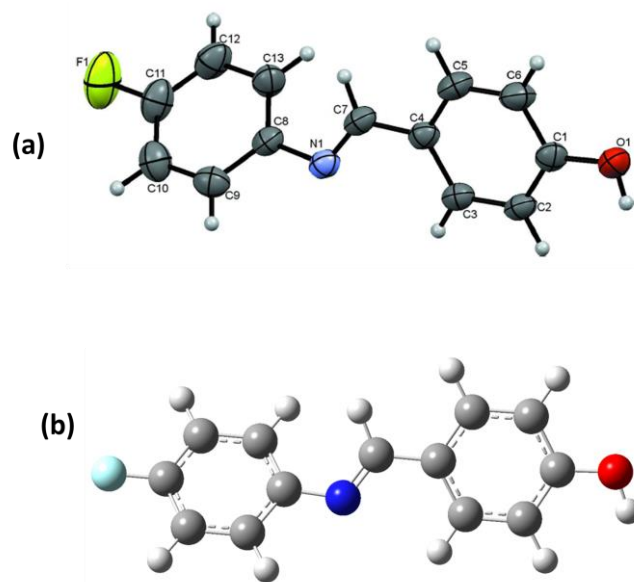


Fig. 1. (a) Ortep-3 diagram of the compound.
(b) The theoretical structure of the compound.

Table 1 Selected molecular structure parameter

	Exp [5]	DFT
Bond Lengths (Å)		
C1-O1	1.355 (3)	1.363
C7-N1	1.270 (3)	1.282
C8-N1	1.430 (3)	1.405
C11-F1	1.350 (3)	1.351
Bond angles (°)		
O1-C1-C2	123.07	122.52
C9-C8-N1	118.62	117.53
F1-C11-C10	119.0 (3)	119.10
C7-N1-C8	118.89	120.26
N1-C7-C4	124.80	122.85
Torsion angles (°)		
O1-C1-C2-C3	-176.2	-179.91
C5-C4-C7-N1	-172.8	-178.86
N1-C8-C9-C10	179.1 (2)	-179.8
C9-C10-C11-F1	-179.8	179.17
C9-C8-N1-C7	-145.9	-146.05

As can be seen from Table 1, calculated bond parameters are slightly different from the experimental ones. It can be noted that the experimental results belong to the solid phase and theoretical calculations belong to the gas phase. In the solid state the experimental results are related to molecular packing but in gas phase the isolated molecules are considered in the theoretical calculations.

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

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 N1, O1 and F1 have negative atomic charges in gas phase.

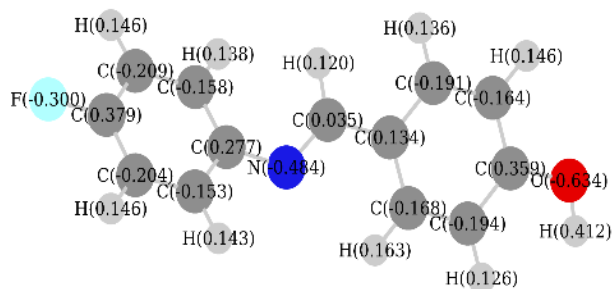


Fig 2. Mulliken atomic charges of the title compound.

C. MEP Surface

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.

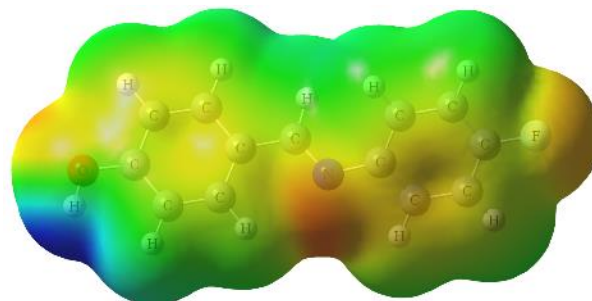


Fig 3 MEP surface of the compound

As easily can be seen in Fig. 6, this molecule has three possible sites for electrophilic attack. The negative $V(r)$ values are -0.035 a.u. for the N1 atom which is the most negative region: about -0.027 a.u. for O1 and -0.022 a.u. for F1 atom. A maximum positive region is localized on the H1 atom with a value of +0.072 a.u. indicating a possible site for nucleophilic attack.

D. Frontier Orbitals

Fig. 4 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 4.226 eV.

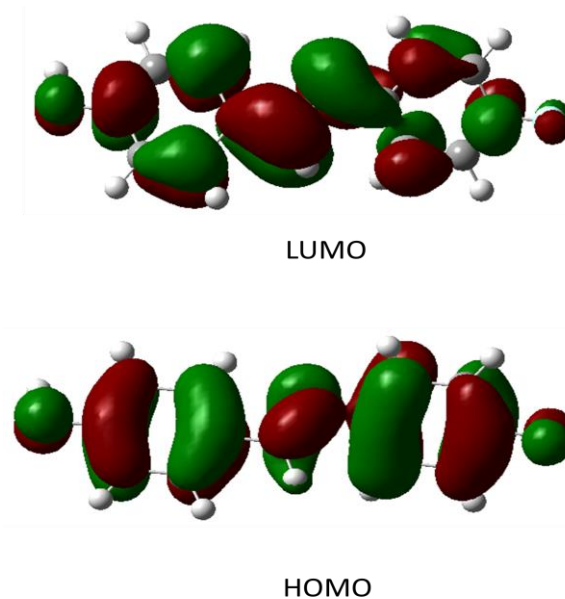


Fig. 4 Frontier molecular orbitals of the title compound

IV. CONCLUSIONS

E. NLO properties

NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [7].

The electronic dipole moment (μ), polarizability (α), and the first hyperpolarizability (β) of the title compound were calculated at the B3LYP/6-31G(d) level using Gaussian 09W program package and listed in Table 2.

Table 2 The calculated dipole moments (Debye), static polarizability components (a.u.) and first hyperpolarizability components (a.u.) for the title compound.

Dipole moments	
μ_x	-1.077
μ_y	0.139
μ_z	-0.062
μ_{tot}	2.765 Debye
Polarizabilities	
α_{xx}	299.10
α_{xy}	2.36
α_{yy}	136.82
α_{xz}	1.83
α_{yz}	-0.69
α_{zz}	59.98
α_{tot}	24.497 Å ³
First hyperpolarizabilities	
β_{xxx}	460.18
β_{xxy}	-138.59
β_{xyy}	-43.56
β_{yyy}	-3.73
β_{xxz}	128.52
β_{xyz}	66.01
β_{yyz}	8.38
β_{xzz}	-6.27
β_{yzz}	-7.39
β_{zzz}	0.27
β_{tot}	3.955×10 ⁻³⁰ cm ⁵ /esu

Quantum chemical calculations have been performed for the title compound and the calculated results show that B3LYP/6-31G(d) method can well reproduce the structural parameters. The MEP map shows that the negative potential sites are on electronegative O, F and N atoms while the positive potential sites are around the hydrogen atoms. The electric dipole moment, the polarizability and the first hyperpolarizability were calculated using the DFT/B3LYP method with the 6-31G(d) basis set. According to results, the title compound exhibits nonzero hyperpolarizability value revealing second order nonlinear optical behavior. 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.

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