

## Spectroscopic and DFT Studies on 2-[[2-chlorophenyl)-imino]methyl}phenol

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**Abstract** – In this study, molecular geometry, vibrational frequencies and gauge including atomic orbital (GIAO) <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values of 2-[[2-chlorophenyl)-imino]methyl}phenol in the ground state were calculated using the density functional method (B3LYP) with 6-31G(d) basis set. The calculated results show that the optimized geometry can well reproduce the crystal structure, and the theoretical vibrational frequencies and chemical shift values show good agreement with experimental values. The UV-vis spectra of the title compound has been predicted using TD-DFT method with the 6-31G(d) basis set in gas phase.

**Keywords** – DFT, FT-IR, NMR, Schiff Base.

### I. INTRODUCTION

Schiff bases are an important class of organic compounds. Schiff bases have biological activities such as antimicrobial, antifungal, antitumor activities and herbicidal properties [1]. On the industrial scale, they have a wide range of applications, such as in dyes and pigments [2]. Schiff base compounds display interesting photochromic and thermochromic features in the solid state and can be classified in terms of these properties. Schiff bases display two possible tautomeric forms, the enol-imine and the keto-amine forms [3]. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O–H···N in enol-imine and N–H···O in keto-amine tautomers [4].

In previous publication, the X-ray, IR, <sup>1</sup>H and <sup>13</sup>C NMR of 2-[[2-chlorophenyl)-imino]methyl}phenol were reported [5]. In despite of its importance, mentioned above, there is no theoretical calculations. The aim of this work is to investigate the spectral and structural properties of the Schiff base compound, 2-[[2-chlorophenyl)-imino]methyl}phenol, using density functional theory calculations. In this study, the molecular structure, vibrational spectra and assignments, <sup>1</sup>H and <sup>13</sup>C NMR spectra, UV-Vis spectra and frontier molecular orbitals have been investigated on 2-[[2-chlorophenyl)-imino]methyl}phenol.

### II. MATERIALS AND METHOD

The DFT calculations of the title compound have been performed using the Gaussian 09W program [6]. 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 harmonic vibrational frequencies were calculated at the same level of theory for the optimized structure and the obtained

frequencies were scaled by 0.96. Vibrational band assignments were made using the Gauss-View molecular visualisation program [7]. The theoretical <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values were calculated using the Gauge-Independent Atomic Orbital (GIAO) approach [8]. The electronic absorption spectra of the molecule were computed with TD-DFT [9], using the 6-31G(d) basis set.

### III. RESULTS AND DISCUSSION

#### A. Optimized geometries

The experimental and theoretical geometric structures are shown in Fig 1. The optimized geometric parameters (bond lengths, bond angles, and torsion angles) of the title compound have been calculated using the B3LYP/6-31G(d) method. These results are listed in Table 1.

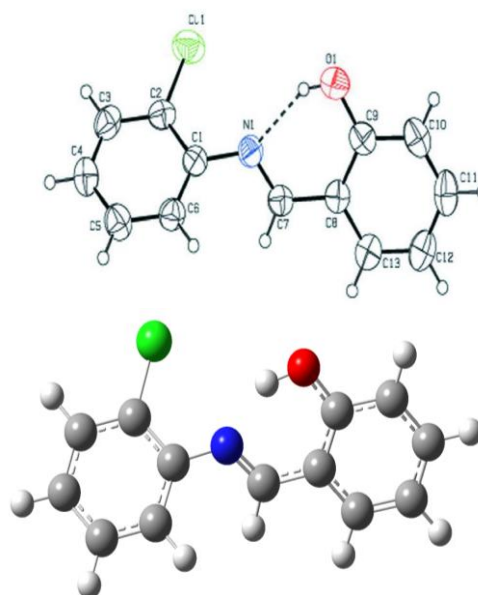


Fig 1. (top) Ortep-3 diagram of the compound [5]. (bottom) calculated geometrical structure

Table 1 Selected molecular structure parameter

	Exp [5]	DFT
Bond Lengths (Å)		
C11 C2	1.7333(15)	1.754
O1 C9	1.355(2)	1.340
N1 C7	1.275(2)	1.292
N1 C1	1.423(2)	1.400
Bond angles (°)		
C1 N1 C7	118.70(13)	121.09
N1 C1 C6	121.68(15)	122.78
C11 C2 C3	118.93(14)	118.86
N1 C7 C8	122.21(13)	122.47
O1 C9 C10	118.96(18)	118.28
Torsion angles (°)		
C7 N1 C1 C6	47.5(2)	38.68
N1 C1 C2 C11	2.9(2)	2.59
O1 C9 C10 C11	179.40(19)	-179.73

As seen from Table 1, calculated bond lengths and angles are slightly different from the experimental data. We noted that the experimental findings belong to the solid state and theoretical results belong to the gas phase. In the solid phase the experimental results are related to molecular packing but in gas phase the isolated molecules are considered in the theoretical calculations.

A logical method for globally comparing the structures obtained with the theoretical calculations is by superimposing the molecular skeleton with that obtained from X-ray diffraction, giving a Root Mean Square Error (RMSE) of 0.213 Å for B3LYP (Fig. 2).

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

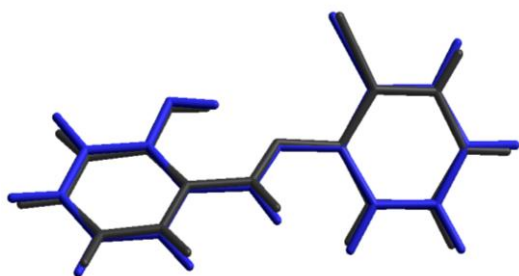


Fig 2 Superimposition of the X-ray structure of the compound (black) and its DFT (blue) optimized counterpart.

### B. Vibrational spectra

Harmonic vibrational frequencies were calculated using the DFT/B3LYP method with the 6-31G(d) basis set. The vibrational frequencies over the region 4000-500  $\text{cm}^{-1}$  were given in Table 2. The IR spectra contain some characteristic

bands of the stretching vibrations of the O-H, C-H, C-O, C=N, C-Cl and C-N groups. Simulated IR spectrum is given in Fig. 3.

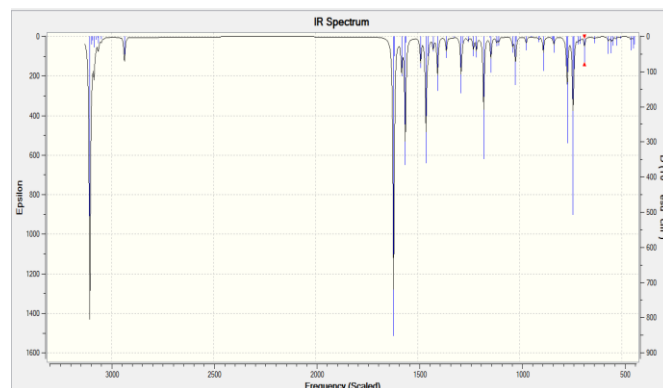


Fig 3. Simulated IR spectra of the title compound.

Table 2 Experimental and calculated frequencies ( $\text{cm}^{-1}$ )

Assignments <sup>a</sup>	Exp. [5]	DFT
$\nu$ (O-H)	3437	3106
$\nu$ (C-H) ring s	—	3085
$\nu$ (C-H) ring s	—	3064
$\nu$ (C-H) imine	—	2936
$\nu$ (C=N)	1614	1618
$\nu$ (C=C) + $\gamma$ (O-H)	—	1578
$\nu$ (C=C) + $\gamma$ (O-H)	—	1560
$\nu$ (C=C) + $\gamma$ (C-H)	—	1459
$\gamma$ (O-H) + $\gamma$ (C-H)	—	1402
$\nu$ (C-O)	—	1287
$\nu$ (C-N)	—	1176
$\nu$ (C-Cl)	—	1020
$\omega$ (C-H)	—	968
$\omega$ (O-H)	—	766
$\omega$ (C-H)	—	739
$\nu$ (C-Cl)	—	682

<sup>a</sup>  $\nu$ , stretching;  $\gamma$ , rocking;  $\omega$ , wagging;  $\alpha$ , scissoring; s, symmetric; as, asymmetric.

### C. NMR spectra

$^1\text{H}$  and  $^{13}\text{C}$  chemical shift values were calculated using the DFT/B3LYP method with 6-31G(d) basis set and generally compared with  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift values. The calculated results are given in Table 3.

$^1\text{H}$  chemical shift values are calculated to be 6.71–11.52 ppm at B3LYP/6-31G(d) level, while the experimental results are observed to be 6.93–13.17 ppm. The aromatic CAH signals were observed to be 6.93–7.5 ppm. These were calculated 6.71–7.25 ppm at B3LYP level. The OH proton of the

compound gave a singlet at 13.17 ppm [5] while calculated as 11.52 ppm.

As can be seen from Table 3, the theoretical  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift results for the title compound are generally closer to the experimental  $^1\text{H}$  and  $^{13}\text{C}$  shift data.

Table 3. Theoretical and experimental  $^1\text{H}$  and  $^{13}\text{C}$  isotropic chemical shifts (ppm)

Atom	Exp [5]	Calculated
H1	13.17	11.52
H7	8.63	8.12
H3	6.93-7.5	7.19
H4	6.93-7.5	7.02
H5	6.93-7.5	7.08
H6	6.93-7.5	6.81
H10	6.93-7.5	6.81
H11	6.93-7.5	7.25
H12	6.93-7.5	6.71
H13	6.93-7.5	7.06
C1	-	140.81
C2	-	132.75
C3	-	124.24
C4	-	119.82
C5	-	120.7
C6	-	113.21
C7	163.3	155.49
C8	-	113.27
C9	161.4	155.87
C10	-	111.93
C11	-	127.66
C12	-	111.51
C13	-	127.35

#### D. UV-Vis spectra

The electronic absorption spectra of the compound were recorded and observed at 275 and 340 nm [5]. Calculated values are predicted as 281 and 343 nm. From the Fig. 4, 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 4.077 eV.

#### IV. CONCLUSIONS

In this study, DFT calculations of molecular structure, FT-IR, NMR and UV-Vis spectra have been performed. The optimized geometrical parameters, vibrational frequencies and chemical shifts have been calculated using the DFT/B3LYP method with LanL2dz basis set. The theoretical results show that the optimized geometry can well reproduce the molecular structure and the calculated vibrational

frequencies and chemical shift values show good agreement with experimental values.

#### ACKNOWLEDGMENT

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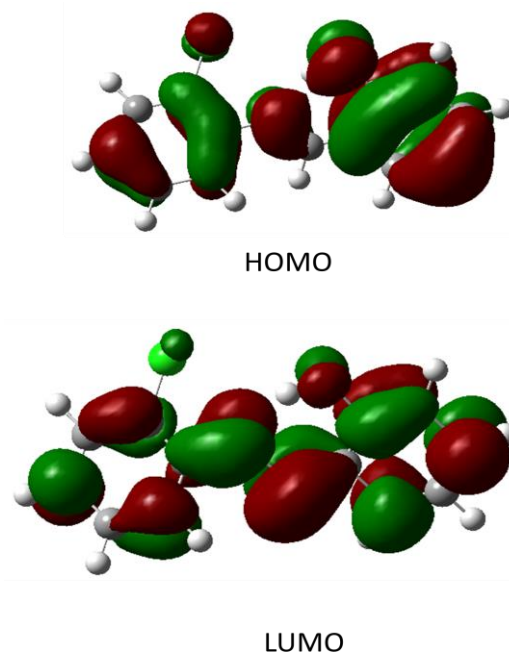


Fig. 4 Frontier molecular orbitals of the title compound

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