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Experimental and density functional theory studies on (*E*)-2-[(2-(hydroxymethyl) phenylimino)methyl]benzene-1,4-diol

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ABSTRACT

The Schiff base compound (*E*)-2-[(2-(hydroxymethyl)phenylimino)methyl]benzene-1,4-diol has been synthesized and characterized by ¹H NMR, ¹³C NMR, IR, UV–Vis and single-crystal X-ray diffraction. Molecular geometry of the title compound in the ground state have been calculated using the density functional method (DFT) with 6-31G(d) basis set and compared with the experimental data. The calculated results show that the optimized geometry can well reproduce the crystal structure. By using TD-DFT method, electronic absorption spectra of the compound have been predicted and a good agreement with the TD-DFT method and experimental one is determined. The energetic behavior of the compound in solvent media has been examined using B3LYP method with the 6-31G(d) basis set by applying the polarizable continuum model (PCM). The total energy of the title compound, molecular electrostatic potential (MEP), natural bond orbital analysis (NBO) and non-linear optical (NLO) properties were performed at B3LYP/ 6-31G(d) level of theory.

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1. Introduction

Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances [1–3]. They have been extensively used as ligands in the field of coordination chemistry [4,5]. Schiff base compounds display interesting photochromic and thermochromic features in the solid state and can be classified in terms of these properties [6]. Photo- and thermochromism arise via H-atom transfer from the hydroxy O atom to the imine N atom [7,8]. Such proton-exchanging materials can be utilized for the design of various molecular electronic devices [9,10].

In general, Schiff bases display two possible tautomeric forms, the phenol-imine (OH) and the keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: $O-H\cdots N$ in phenol-imine [11,12] and $N-H\cdots O$ in keto-amine [13,14] tautomers. Another form of the Schiff base compounds is also known as zwitterion having an ionic intramolecular hydrogen bond ($N^+-H\cdots O^-$) and this form is rarely seen in the solid state [15,16].

Non-linear optical materials (NLO) have been attractive in recent years with respect to their future potential applications in

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the field of optoelectronic such as optical communication, optical computing, optical switching, and dynamic image processing [17,18]. Due to their high molecular hyperpolarizabilities, organic materials display a number of significant non-linear optical properties. NLO materials were categorized as multilayered semiconductor structures, molecular based macroscopic assemblies, and traditional inorganic solids. A variety of inorganic, organic and organometallic molecular systems have been studied for NLO activity [17–19].

By means of increasing development of computational chemistry in the past decade, the research of theoretical modeling of drug design, functional material design, etc., has become much more mature than ever. Many important chemical and physical properties of biological and chemical systems can be predicted from the first principles by various computational techniques [20,21]. Currently, density functional theory (DFT) method has been accepted as a popular post-HF approach for the computation of structural characteristics, vibrational frequencies and energies of molecules by the *ab initio* community [22] and for the efficiency and accuracy with respect to the evaluation of a number of molecular properties [23,24].

In this study, we report the synthesis, characterization and crystal structure of a new Schiff base, (E)-2-[(2-(hydroxy-methyl)phenylimino)methyl]benzene-1,4-diol (Scheme 1). The properties of the structure geometry, molecular electrostatic potential (MEP), natural bond orbitals (NBO), and non-linear





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Scheme 1. (*E*)-2-[(2-(hydroxymethyl)phenylimino)methyl]benzene-1,4-diol (C_{14} H₁₃NO₃).

optical (NLO) properties for the title compound at the DFT/B3LYP/ 6-31G(d) level were studied. These studies are valuable for providing insight into molecular properties of Schiff base compounds.

2. Experimental and computational method

2.1. Synthesis

The compound (*E*)-2-[(2-(hydroxymethyl)phenylimino)methyl] benzene-1,4-diol was prepared by reflux a mixture of a solution containing 2,5-dihydroxybenzaldehyde (0.05 g 0.36 mmol) in 20 ml ethanol and a solution containing 2-aminobenzylalcohol (0.045 g 0.36 mmol) in 20 ml ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-[(2-(hydroxymethyl)phenylimino)methyl]benzene-1,4-diol, suitable for X-ray analysis were obtained from ethyl alcohol by slow evaporation (yield% 76; m.p. 167–169 °C). ¹³C NMR (δ in ppm, CDCl₃): 160.5 (C=N), 153.9, 151.6, 150.3, 135.5, 132.9, 129.1, 122.7, 121.5, 120.9, 120.1, 118.9, 116.9 (Ar—C), 60.5 (—CH₂ —). ¹H NMR (δ in ppm, CDCl₃): 11.65–9.49 [s, 2H, Ar—OH], 8.92 [s, 1H, CH=N], 7.45–6.92 [m, 7H, Ar—(CH)], 5.30 [s, 1H, CH₂—OH], 4.71 [s, 2H, CH₂].

2.2. Instrumentation

The FT-IR spectrum of the title compound was recorded in the 4000–400 cm⁻¹ region by a Shimadzu FTIR-8900 spectrophotometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded with a Bruker AC 200 MHz spectrometer (TMS as internal standard). Electronic absorption spectra were measured on a Unicam UV–VIS spectrophotometer in EtOH solvent.

2.3. X-ray crystallography

A red crystal of the compound with dimensions of $0.75 \times 0.45 \times 0.06$ mm was mounted on goniometer and data collection was performed on a STOE IPDS II diffractometer by the *w* scan technique using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 296 K. The systematic absences and intensity symmetries indicated the orthorhombic $P2_12_12_1$ space group. A total of 17318 reflection (1422 unique) with $[1.8^{\circ} < \theta < 26^{\circ}]$ were collected in the *w* scan mode and cell parameters were determined by using X-AREA software [25]. Absorption correction ($\mu = 0.1 \text{ mm}^{-1}$) was obtained by the integration method via X-RED32 software [25]. The crystal structure was solved by direct methods using SHELXS-97 [26]. The maximum peaks and deepest hole observed in the final $\Delta \rho$ map were 0.13 and $-0.14 \text{ e} \text{Å}^{-3}$, respectively. The

scattering factors were taken from SHELXL-97 [26]. The molecular graphics were done using *Ortep-3* for Windows [27]. The data collection conditions and parameters of refinement process are listed in Table 1.

2.4. Computational procedures

The molecular geometry is directly taken from the X-ray diffraction experimental results without any constraints. In the next step, the DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at 6-31G(d) basis set by the Berny method [28,29] were performed with the Gaussian 03W software package [30] and Gaussview visualization program [31]. The electronic absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) method [32-35]. Also, it is calculated in ethanol solution using the Polarizable Continuum Model (PCM) [36–39]. In order to investigation the energetic and dipole moments behavior of the title compound in solvent media, we also carried out optimization calculations in three kinds of solvents (chloroform, ethanol and water) by using PCM method. To investigate the reactive sites of the title compound the molecular electrostatic potential was evaluated using the B3LYP/6-31G(d) method. The molecular electrostatic potential, V(r), at a given point r(x, y, z) in the vicinity of a molecule, is defined in terms of the interaction energy between the electrical charge generated by the molecule's electrons and nuclei and a positive test charge located at r. For the system studied the V(r) values were calculated as described previously using the equation [40],

$$V(r) = \sum_{A} \frac{Z_{A}}{R_{A} - r} - \int \frac{\rho(r')}{r' - r} dr'$$
(1)

Table 1

Crystallographic data for the title compound.

Crystal data	
Chemical formula	$C_{14}H_{13}NO_3$
Crystal shape/color	Plate/red
Formula weight	243.25
Crystal system	Orthorhombic
Space group	$P2_{1}2_{1}2_{1}$
Unit cell parameters	a = 4.6356(17) Å
	<i>b</i> = 13.9188(7) Å
	c = 18.700(7) Å
Volume	1206.6(4) Å ³
Z	4
D_x (Mg cm ⁻³)	1.339
$\mu (\mathrm{mm}^{-1})$	0.10
F ₀₀₀	512
Crystal size (mm ³)	$0.75 \times 0.45 \times 0.06$
Data collection	
Diffractometer/meas. meth	STOE IPDS II/w-scan
Absorption correction	Integration
T _{min}	0.950
T _{max}	0.989
No. of measured, independent and observed	17,318, 1422, 1200
Criterion for observed reflections	$l > 2\sigma(l)$
R ₁₁	0.040
America and Ameri America and America and Ameri America and America and Americ	26
Refinement	r?
Refinement on $p(r^2 > 2 - (r^2))$ with r^2	r- 0.020.0.87.1.05
R[r > 20 (r)], WR, S	0.039, 0.87, 1.03
No. of parameters	1422
No. 01 parameters	107
weighting Schenie	vv = 1/ $[-2(r^2) + (0.09.42 P)^2]$
	$[0^{-}(F_{0}^{-})^{+}(0.0843P)^{2}]$
	$P = F_0^2 + 2F_c^2)/3$
Δho_{max} , Δho_{min} (e A ⁻³)	0.13, -0.14

where Z_A is the charge of nucleus A, located at R_A , $\rho(r')$ is the electronic density function of the molecule, and r' is the dummy integration variable. The linear polarizability and first hyperpolarizability properties of the title compound were obtained from molecular polarizabilities based on theoretical calculations. In addition, NBO analysis was performed at B3LYP/6-31G (d) level by means of the NBO 3.1 program within the Gaussian 03W package [41].

3. Results and discussion

3.1. Description of the crystal structure

The title compound, an Ortep-3 view of which is shown in Fig. 1, crystallizes in the orthorhombic space group $P2_12_12_1$ with Z = 4 in the unit cell. The asymmetric unit in the crystal structure contains only one molecule. The C7-N1 and C6-O1 bonds of the title compound are the most important indicators of the tautomeric type. X-ray structure determinations reveal that the enol tautomer is favoured over the keto tautomer. This is evident from the observed C6–O1 bond distance of 1.351(3) Å, which is consistent with the C-O single bond; similarly the C7-N1 distance of 1.271(3) Å is also consistent with the C=N double bonding. These bond distances are comparable with those of compounds previously reported as enol-imine [11,42]. The molecular structure of the title compound is approximately planar. The dihedral angle between the C1-C6 and C8-C13 rings is 2.55(7)°. The molecular structure is stabilized by a O1-H1...N1 intramolecular hydrogen bond which generates an S(6) ring motif (Fig. 1) [43]. The sum of the Van der Waals radius of the N and O atoms [3.07 Å] is significantly longer than the intramolecular N1...O1 [2.612 Å] hydrogen bond length [44]. In the crystal structure, molecules are linked by intermolecular O-H···O hydrogen bonds (Fig. 2), namely O2-H21...O3 (symmetry code: -x + 2, y + 1/2) and O3-H3...O2 (symmetry code: -x + 3/2, -y + 1, z - 1/2). The details of the hydrogen bonds are summarized in Table 2.

3.2. Theoretical structure

The optimized parameters (bond length, angles, and dihedral angles) of the title compound have been obtained by using the B3LYP/ 6-31G(d) method. The obtained results are listed in Table 3. When the X-ray structure of the title compound is compared with its optimized counterpart (see Fig. 3), conformational discrepancies are observed between them.

The most remarkable discrepancy exists in the orientation of the phenylmethanol ring in the title compound. The orientation of the phenylmethanol ring is defined by torsion angles C13—C8—N1—C7 [180.0(2)°] and C9—C8—N1—C7 [$-0.3(4)^{\circ}$]. These torsion angles have been calculated at -145.3° and 32.3° for B3LYP/6-31G(d) level. According to X-ray studies, the dihedral angle between the C1/C6 and C8/C13 rings is 2.55(7)°, whereas the dihedral angle has been calculated at 37.91° for B3LYP.

As seen from Table 3, the optimized bond lengths and the bond angles are slightly different than the experimental values. We 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 the gas phase the isolated molecules are considered in the theoretical calculations. The maximum difference between the experimental values and those obtained from the theoretical calculations is 0.027 Å for bond distances and 2.4° for bond angles. According to these results, the biggest differences of bond lengths and bond angles mainly occurs in the groups involved in the hydrogen bond [i.e., C2–O1, C7–N1–C8, C13–C8–N1] which can be also easily understood taking into account the intra- and intermolecular hydrogen bond interactions present in the crystal.

A logical method for globally comparing the structure obtained with the theoretical calculation is by superimposing the molecular skeleton with that obtained from X-ray diffraction, giving a RMSE of 0.029 Å for B3LYP/6-31G(d) (Fig. 3). According to these results, it may be concluded that the B3LYP calculation well reproduce the geometry of the title compound.

3.3. IR spectroscopy

The IR spectrum of the title compound have some characteristic bands of the stretching vibrations of the OH, CN and CO groups. The experimental O—H stretching modes were observed at range of $3478-3347 \text{ cm}^{-1}$. In addition, the stretching frequency observed at 3019 cm^{-1} in the compound shows the presence of O—H…N intramolecular hydrogen bond [45]. The characteristic region of $1500-1700 \text{ cm}^{-1}$ can be used to identify the proton transfer of Schiff bases. The title compound shows a strong band at 1624 cm^{-1} which is assigned to C=N stretching vibration. Another characteristic region of the Schiff bases derivative spectrum is $1100-1400 \text{ cm}^{-1}$, which is attributed to C—O stretching vibrations. The title compound with strong band at 1216 cm^{-1} possesses highest percentage of enol-imine tautomer due to the stabilization of



Fig. 1. Ortep-3 diagram of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.



Fig. 2. Packing diagram of the title compound.

Table 2	
Hydrogen-bond geometry (Å, °).

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	D—H···A	D—H	H···A	$D{\cdots}A$	D—H···A
	$01-H1\cdots N1$	0.82	1.89	2.612(3)	146
	$02-H21\cdots 03^{i}$	0.82	1.84	2.619(2)	157
	$03-H3\cdots 02^{ii}$	0.82	1.99	2.724(2)	148

Symmetry codes: (i) -x + 2, y + 1/2, -z + 3/2; (ii) -x + 3/2, -y + 1, z - 1/2.

phenolic C–O bond [46]. The presence of O–H, C=N, and C–O stretching vibrations strongly suggest that the title compound has the enol-imine form in the solid state.

3.4. Electronic absorption spectra

The UV–visible spectrum of *o*-hydroxylated Schiff bases that exist mainly as the phenol-imine structure indicate the presence of a band at <400 nm, whereas compounds existing in the keto-amine form show a new band, especially in polar and non-polar solvents at >400 nm [47–49]. Electronic absorption spectra of the title compound in the ethanol solvent show a band at 368 nm (log ε = 4.037), which corresponds to the enol-imine form. This value for related compounds is similar to in the literature [50]. However, the compound showed no absorption above 400 nm. This indicates that the title compound is in the enol-imine form in ethanol solvent.

Electronic absorption spectra were calculated by using TD-DFT method based on the B3LYP/6-31G(d) level optimized structure in gas phase. The predicted absorption wavelength is at 372 nm with the oscillator strength being 0.224 for TD-DFT calculation. In addition to the results gas phase, TD-DFT calculations of the title compound in ethanol solvent were performed by using PCM model. The PCM calculations reveal that the calculated absorption

Table 3	
Selected molecular structure parameters.	

Parameters	Experimental	B3LYP/6-31G(d)
Bond lengths (Å)		
C1–C2	1.391(3)	1.413
C2-C3	1.371(3)	1.385
C3–C4	1.383(3)	1.406
C1–C7	1.453(3)	1.448
C6-01	1.351(3)	1.345
C7—N1	1.270(3)	1.293
C8–C13	1.393(3)	1.412
C8—N1	1.418(3)	1.410
C14-03	1.423(3)	1.421
Bond angles (°)		
C2-C1-C6	118.8(2)	119.2
C2-C1-C7	120.0(2)	119.3
02–C3–C4	117.4(2)	117.0
01-C6-C5	118.9(2)	118.5
01–C6–C1	122.2(2)	122.4
N1-C7-C1	121.8(2)	122.6
C9-C8-N1	124.6(2)	122.2
C13-C8-N1	115.9(2)	118.0
C10–C9–C8	120.5(2)	120.6
C7—N1—C8	123.3(2)	120.9
Torsion angles (°)		
C7-C1-C6-01	1.9 (3)	-0.1
C2-C1-C7-N1	-178.9(2)	-179.5
N1-C8-C13-C14	-0.7 (3)	1.2
C1-C7-N1-C8	178.7 (2)	177.0
C9-C8-N1-C7	-0.3 (4)	32.3
C13-C8-N1-C7	180.0(2)	-145.3

band has a red shift with a value of 380 nm with an oscillator strength of 0.270. The reason for the red shift is a solvent effect,



Fig. 3. Atom-by-atom superimposition of the calculated structure (red) over the X-ray structure (black) for the title compound.

which can affect the geometry and electronic structure as well as the properties of the molecule by inducing a lower energy [50,51]. Comparing these values with the corresponding experimental values, TD-DFT method for both in gas phase and solvent media is useful to predict UV–Vis spectrum (Fig. 4).

According to the TD-DFT calculational electronic absorption spectra, the maximum absorption wavelength corresponding to the electronic transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

As seen from Fig. 5, while the HOMO is localized on hydroquinone fragment and benzene ring, the LUMO is localized on the imine group and two benzene rings. Molecular orbital coefficients analyses based on optimized geometry indicate that, for the title compound, the frontier molecular orbitals are mainly composed of π -atomic orbitals, so the electronic transitions are mainly derived from the contribution of bands $\pi \to \pi^*$.

3.5. Total energies in solvent media

In order to evaluate the energetic behavior of the title compound in solvent media, we carried out calculations in gas phase and three kinds of solvent (water, ethanol, chloroform). The calculated total, HOMO and LUMO energies, dipole moment and chemical hardness (η) using the PCM by B3LYP/6-31G(d) are listed in Table 4. The chemical hardness is quite useful to rationalize the relative stability and reactivity of chemical species. Hard species having large HOMO–LUMO gap will be more stable and less reactive than soft species having small HOMO–LUMO gap [52]. From



Fig. 4. UV-Vis spectra of title compound in ethanol solvent and the comparison of calculated transitions in gas phase (vertical solid line) and ethanol solvent (vertical dashed line) with the experimental spectra.

Table 4, we can conclude that the total molecular energies obtained by PCM method decrease with the increasing polarity of the solvent, while the dipole moments and hardness will increase with the increase of the polarity of the solvent. According to these results, the stability of the title compound increases in going from the gas phase to the solution phase.

3.6. Molecular electrostatic potential

The molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [53–55]. The electrostatic potential V(r) is also well suited for analysing processes based on the 'recognition' of one molecule by another, as in drug–receptor and enzyme–substrate interactions, because it is through their potentials that the two species first 'see' each other [56,57]. Being a real physical property, V(r) can be determined experimentally by diffraction or by computational methods [58].

To predict reactive sites of electrophilic and nucleophilic attack for the investigated molecule, the MEP at the B3LYP/6-31G(d) optimized geometry was calculated. The negative (red¹) region of MEP was related to electrophilic reactivity and the positive (blue) region to nucleophilic reactivity as shown in Fig. 6. As can be seen from the figure, this molecule has several possible sites for electrophilic attack. Negative electrostatic potential regions (red color) are mainly localized over the O1 atom, the O2 and O3 atoms. The negative V(r) values are -0.049 a.u. for O3 atom which is the most negative region, -0.036 a.u. for O1 atom and -0.026 a.u. for O2 atom. However, a maximum positive region (blue color) is localized on the O2—H21 bond with a value of 0.069 a.u., indicating a possible site for nucleophilic attack.

According to these calculated results, the MEP map shows that the negative potential sites are on oxygen atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information concerning the region from where the compound can have metallic bondings and intermolecular interactions. So, Fig. 6 confirms the existence of the intermolecular O2—H21…O3 and O3—H3…O2 interactions.

3.7. NBO analysis

NBO analysis provides an efficient method for studying intraand intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [59]. The larger the $E^{(2)}$ value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. In order to investigate the intra and intermolecular interactions, the stabilization energies of the title compound were performed by using second-order perturbation theory. For each donor NBO(i) and acceptor NBO(j), the stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as [60,61]

$$E^{(2)} = -q_i \frac{\left(F_{ij}\right)^2}{\varepsilon_j - \varepsilon_i} \tag{2}$$

 $^{^{1}}$ For interpretation of color in Figs. 1–3, 5, and 6, the reader is referred to the web version of this article.



Fig. 5. HOMO and LUMO of the title compound.

Table 4 Calculated energies, dipole moments, frontier orbital energies and chemical hardness.

	Gas phase (ɛ = 1)	Chloroform $(\varepsilon = 4.9)$	Ethanol (ε = 24.55)	Water (ε = 78.39)
$ \begin{array}{l} E_{\rm total} ~({\rm Hartree}) \\ E_{\rm HOMO} ~({\rm eV}) \\ E_{\rm LUMO} ~({\rm eV}) \\ \eta ~({\rm eV}) \\ \eta ~({\rm eV}) \\ \mu ~({\rm D}) \end{array} $	-821.71678294	-821.73558671	-821.74327396	-821.74525316
	-5.513	-5.467	-5.465	-5.464
	-1.833	-1.749	-1.732	-1.725
	1.840	1.859	1.866	1.869
	4.2814	5.5114	6.0874	6.2327

where q_i is the donor orbital occupancy, ε_i , ε_j are diagonal elements (orbital energies), and F_{ij} is the off-diagonal NBO Fock matrix element. The results of second-order perturbation theory analysis of the Fock Matrix at B3LYP/6-31G(d) level of theory are presented in Table 5.

NBO analysis revealed that the $n(N1) \rightarrow \sigma(O1-H1)$ interactions give the strongest stabilization to the system of the title compound by 24.04 kcal mol⁻¹, and strengthen the intramolecular $O1-H1\cdots N1$ hydrogen bond. The NBO interactions of the $n(O3) \rightarrow \sigma$ (O2-H21) and $n(O2) \rightarrow \sigma$ (O3-H3) imply the existence of O-H···O hydrogen bonds which have the total stabilization energies 17.33 and 9.76 kcal mol⁻¹, respectively. Thus, it is apparent that $O-H\cdots N$ and $O-H\cdots O$ interactions significantly influence crystal packing with this molecule.

3.8. Non-linear optical effects

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [62]. Organic molecules with significant non-linear optical activity generally consist of a π -electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor



Fig. 6. Molecular electrostatic potential map calculated at B3LYP/6-31G(d) level.

Table 5

Second-order perturbation theory analysis of the Fock matrix in NBO basis, calculated at B3LYP/6-31G(d) level.

Donor orbital (i)	Acceptor orbital (j)	E ^{(2)c} (kcal/mol)	$\varepsilon_j - \varepsilon_i (a.u.)^a$	<i>F_{ij}</i> (a.u.) ^b
LP(1) N1	BD(1) O1-H1	27.27	0.78	0.133
LP(1) O3	BD(1) O2-H21	2.39	1.00	0.044
LP(2) O3	BD(1) O2-H21	14.94	0.86	0.102
LP(1) O2	BD(1) O3-H3	9.54	1.08	0.093
LP(1) O2	BD(1) O3-H3	0.22	0.80	0.012

^a Energy difference between donor and acceptor *i* and *j* NBO orbitals.

^b F_{ij} is the Fock matrix element between *i* and *j* NBO orbitals.

 $\vec{E}^{(2)}$ means energy of hyper conjugative interaction.

group on the other end, forming a 'push-pull' conjugated structure [63].

The total static dipole moment (μ), the linear polarizability (α) and the first hyperpolarizability (β) using the *x*, *y*, *z* components are defined as [24,64]:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}$$
(3)

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{4}$$

$$\beta = \sqrt{\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^2}$$
(5)

The dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) were calculated at the B3LYP/6-31G(d) level using Gaussian 03W program package. The calculated dipole moment (μ), polarizability (α) and first hyperpolarizability (β) for title compound are 4.28 D, 25.06 Å³ and 4.1 × 10⁻³⁰ cm⁵/esu respectively.

The calculated values of the title compound are greater than those of urea (the μ , α and β of urea are 1.3732 D, 3.8312 Å³ and 0.37289 × 10⁻³⁰ cm⁵/esu obtained by B3LYP/6-31G(d) method) [62]. Theoretically, the first-order hyperpolarizability of the title compound is of 10.1 times magnitude of urea. These results indicate that title compound is a good candidate of non-linear optical material.

4. Conclusion

(E)-2-[(2-(hydroxymethyl)phenylimino)methyl]benzene-1,4-diol has been synthesized and characterized by ¹H NMR, ¹³C NMR, IR, UV-Vis and single-crystal X-ray diffraction. The X-ray, IR, NMR and UV-Vis spectral data for the title compound show that the compound exists in the enol-imine tautomeric form, which is stabilized by the intramolecular O-H···N hydrogen bond. The comparisons between the calculated results and the X-ray experimental data indicate that B3LYP/6-31G(d) method shows a good agreement with the experimental results. The TD-DFT calculations lead to a very closer agreement with the experimental absorption spectra both gas phase and solvent media. Molecular orbital coefficient analyses suggest that the electronic spectrum corresponds to the $\pi \rightarrow \pi^*$ electronic transition. The total energy of the title compound decreases with increasing polarity of the solvent. The MEP map shows that the negative potential sites are on oxygen atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have intermolecular interactions and metallic bonding. The NBO analysis revealed that the $n(N1) \rightarrow \sigma$ (O1-H1) interaction gives the strongest stabilization to the system. The predicted non-linear optical (NLO) properties of the title compound are much greater than those of urea. This study

demonstrates that the title compound can be used as a good non-linear optical material.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 734185. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK (fax: +44 1223 336 033; e-mail: data_request@ccdc.cam.ac.uk).

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