

## Molecular and Computational Structure Characterizations of (*E*)-2-Ethoxy-6-[(4-fluorophenylimino)methyl]phenol

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The (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol compound was synthesized and characterized by X-ray Diffraction, IR and Electronic spectroscopy. X-Ray and IR results showed that the title compound preferred the enol form in solid state. UV-Vis absorption spectra of the title compound were recorded in different solvents. The results showed that the molecule existed only in enol form even in the solvent media. Electronic structure and spectroscopic properties of the title compound were investigated from calculative point of view. The gas phase geometry optimization was obtained based on X-ray geometry by DFT method with B3LYP applying 6-311G(d,p) basis set. Geometry optimizations in the solvent media were obtained with the same level of theory by the polarizable continuum model (PCM). TD-DFT calculations starting from the optimized geometry were made in both gas and solution phase to measure the excitation energies of enol and keto tautomers. Vibrational frequency and natural bond orbital analysis (NBO) were performed and the thermodynamic properties of the title compound were obtained at the optimized geometry with the same level of theory.

**Keywords:** Schiff base, X-Ray analysis, IR and UV-Vis spectroscopy, DFT, TD-DFT

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### INTRODUCTION

The *ortho*-hydroxy Schiff bases derived from the condensation of primary amines with carbonyl compounds are important compounds which show tautomerism *via* the intramolecular proton transfer from an oxygen atom to the neighboring nitrogen atom. These compounds can exist in three different structures, that is, enol, keto and zwitterionic forms in the solid state [1-3]. The *ortho*-hydroxy Schiff bases also show thermochromism and photochromism *via* the intramolecular proton transfer [4,5]. Photochromic compounds are used in optical switches and optical memories, variable

electrical currents, and ion transport through membranes [6]. In addition, they are widely used as ligands in the field of coordination chemistry [7] as well as in diverse fields of chemistry and biochemistry owing to their biological activities [8].

The aim of this work is to investigate the tautomeric forms, spectral properties and molecular structure of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol and report the results from both theoretical and experimental points of view.

### EXPERIMENTAL

#### Synthesis

The compound (*E*)-2-ethoxy-6-[(4-fluorophenylimino)

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methyl]phenol was prepared by refluxing a mixture of a solution containing 3-ethoxysalicylaldehyde (0.5 g, 3 mmol) in 20 ml ethanol and a solution containing aniline (0.33 g, 3 mmol) in 20 ml ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol, suitable for X-ray analysis, were obtained from the slow evaporation of ethyl alcohol (yield%, 86; m.p.: 356-358 K).

### Apparatus

The melting point was determined by StuartMP30 melting point apparatus. FT-IR spectrum of the title compound was recorded on a Bruker 2000 spectrometer in KBr disk. UV-Vis absorption spectra were recorded on a Thermo scientific BioGenesis UV-Vis spectrometer using a 1 cm path length of the cell.

### X-Ray Crystallography

A suitable sample of  $0.52 \times 0.41 \times 0.25 \text{ mm}^3$  size was selected for the crystallographic study. All diffraction measurements were made at room temperature (293 K) using graphite monochromated MoK $\alpha$  radiation and a STOE IPDS 2 diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using X-AREA software [9]. Absorption correction was made by the integration method *via* X-RED software [9]. The structure was solved by direct methods using SHELXS-97 [10]. The refinement was made by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 171 crystallographic parameters. All non-hydrogen atom parameters were refined anisotropically and all H atoms, except for H1, were located in their idealized positions and refined using a riding model with C-H distances in the range 0.93-0.96 Å,  $U_{\text{iso}}(\text{H})$  values in the range  $1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C})$  (for methyl group). The data collection conditions and the parameters of the refinement process are listed in Table 1.

### Supplementary Data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary

publication no. CCDC 768527. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

### Computational Procedures

All computations were done using Gaussian 03W program package running under Windows XP [11]. Full geometry optimization of the title molecule was obtained using DFT method with Becke's three-parameters hybrid exchange-correlation functional (B3LYP) [12] employing 6-311G(d,p) basis set [13-15] as implemented in Gaussian 03W. The crystallographically obtained geometrical data of the molecule were used for the optimization. The optimized geometry of the molecule, the total molecular energy, and the dipole moment were obtained from the optimization output. The ground state geometry optimization of the title compound for the gas phase was calculated using DFT method with B3LYP adding 6-311G(d,p).

The solution phase geometry optimizations were obtained with the same level of theory by the polarizable continuum model (PCM). TD-DFT calculations starting from the gas phase and solution phase optimized geometry, using the same level of theory, were made in both gas and solution phase to calculate excitation energies of enol and keto tautomers. The excitation energies of the title compound for enol and keto forms were obtained by TD-DFT calculation. In addition, gas-phase vibrational frequency and natural bond orbital analysis for enol form were performed by using the same level of theory. In addition, thermodynamic properties of the title compound were obtained by applying the same level of theory.

## RESULTS AND DISCUSSION

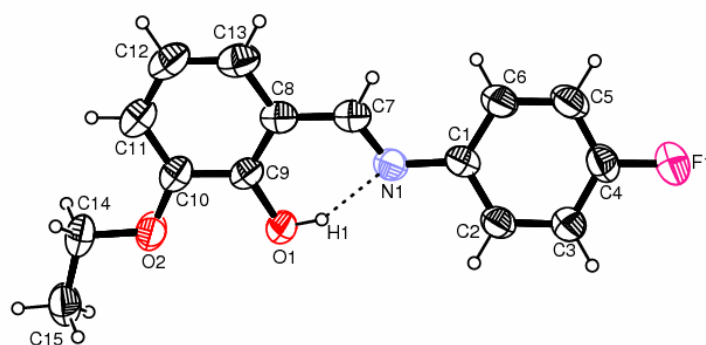
### Structure Determination

The crystal data and refinement details of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol compound are given in Table 1. The selected bond lengths and angles are given in Table 2. The molecular structure of this compound is shown in Fig. 1 with the atom numbering scheme. As can be seen in Fig. 1, the molecule adopts *E* configuration about the C=N double bond.

The C7-N1 bond length of 1.279(3) Å and C9-O1 bond

**Table 1.** Crystal Data, Data Collection and Refinement Details

Chemical formula	C <sub>15</sub> H <sub>14</sub> FNO <sub>2</sub>
Crystal system, Space group, Z	Monoclinic, P21/c, 4
a	11.5578(9) Å
b	12.5684(7) Å
c	9.7863(7) Å
β	113.023(6)°
V	1308.35(16) Å <sup>3</sup>
D <sub>x</sub>	1.32 mg m <sup>-3</sup>
Radiation, λ	MoKα, 0.71073 Å
μ	0.097 mm <sup>-1</sup>
T	293 K
T <sub>min</sub> , T <sub>max</sub>	0.9561, 0.9802
F(000)	544
Diffractometer	STOE IPDS II
Scanning mode	ω
Scan range	-14 < h < 14, -15 < k < 15, -12 < l < 12
θ <sub>min</sub> , θ <sub>max</sub>	1.62, 28.0°
Number of measured/independent reflections, R <sub>int</sub>	19354/2711, 0.077
Number of reflections with 2σ(I)	1824
Number of refined parameters	171
S	1.083
R[F <sup>2</sup> > 2σ(F <sup>2</sup> )]	0.054
wR (F <sup>2</sup> )	0.120
Δρ <sub>max</sub> , Δρ <sub>min</sub>	0.107, -0.167 e Å <sup>-3</sup>

**Fig. 1.** A view of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol, with the atom numbering scheme.

**Table 2.** The Selected Bond Lengths, Angles and Torsion Angles ( $\text{\AA}$ ,  $^\circ$ )

	X-Ray	DFT/B3LYP Enol form	DFT/B3LYP Keto form
C9-O1	1.349(2)	1.3363	1.2524
N1-C7	1.279(3)	1.2887	1.334
N1-C1	1.412(3)	1.4071	1.4042
C10-O2	1.361(3)	1.3584	1.3553
C14-O2	1.433(3)	1.4275	1.4257
C7-C8	1.438(3)	1.4488	1.3921
C8-C9	1.395(3)	1.4134	1.4644
C8-C13	1.406(3)	1.4123	1.4337
C9-C10	1.403(3)	1.4185	1.4658
C10-C11	1.376(3)	1.389	1.3696
C11-C12	1.379(4)	1.4051	1.4309
C12-C13	1.365(5)	1.3768	1.359
F1-C4	1.354(3)	1.3518	1.3508
C1-N1-C7	121.94(17)	121.3842	127.928
N1-C1-C2	117.62(18)	117.8607	117.8006
N1-C1-C6	124.16(18)	123.2288	122.9619
N1-C7-C8	122.85(19)	122.7873	123.1929
O1-C9-C8	121.7(2)	122.7218	122.7551
O1-C9-C10	117.80(18)	118.0842	121.3814
C2-C1-N1-C7	-159.94(18)	145.6804	165.0778
C6-C1-N1-C7	22.8(3)	-36.7235	-15.5089
N1-C1-C2-C3	-178.06(17)	179.7921	-179.979
N1-C1-C6-C5	177.6(2)	-179.1267	179.555
N1-C7-C8-C9	-2.5(3)	-0.7365	0.1263
C8-C7-N1-C1	-177.86(17)	177.2932	178.9236

length of 1.349(2) Å are consistent with the distances of the C-N double bond and the C-O single bond as presented for the related compounds previously studied [16-18]. The C7-N1 double bond and C9-O1 single bond distances in (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol show that the molecule exists in enol form in the solid state. A significant intramolecular interaction was noted involving phenolic atom O1 and nitrogen atom N1 which constituted a six-membered ring S(6) [19]. The O1-N1 distance of 2.611(2) Å is indicative of strong intramolecular hydrogen bonding. This length is

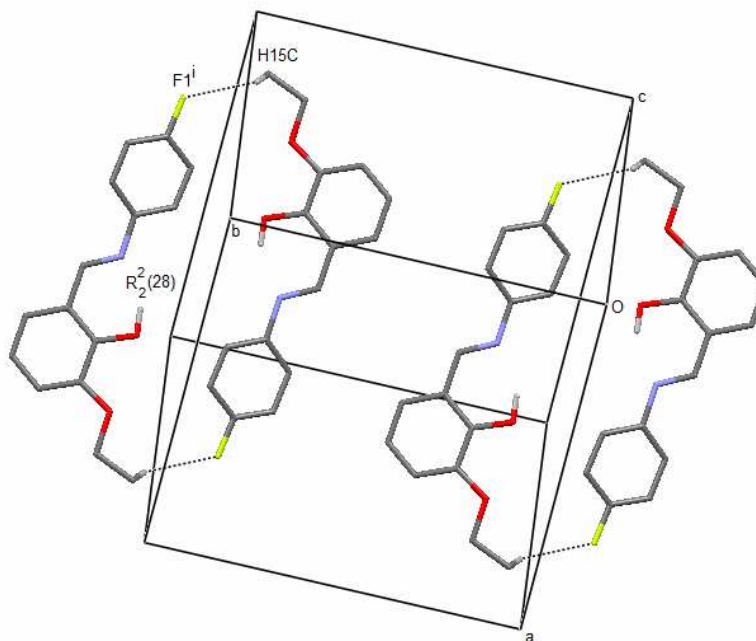
clearly shorter than the sum of the van der Waals' radii for N and O [20].

We used Parst [21] to analyze the intermolecular hydrogen bond interactions in the crystal structure. The intermolecular hydrogen-bonded geometry and the details of C-H...O interactions for the title compound are listed in Table 3. (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol molecules are linked to  $R_2^2(28)$  containing a total of 28 atoms, two donors and two acceptors [19] as shown in Fig. 2. Furthermore, C-H... $\pi$  interactions between  $\pi$  electrons of aromatic ring and

**Table 3.** Hydrogen Bonding Geometry (Å, °)

D-H...A	D-H	H...A	D...A	$\angle$ D-H...A
O1-H1...N1	0.84(2)	1.84(2)	2.611(2)	152(2)
C15-H(15C)...F1 <sup>i</sup>	0.960	2.627	3.383	135.89
C14-H(14A)...Cg <sup>ii</sup>	0.9706	2.817	3.615(3)	140.10
Calculated				
O1-H1...N1	0.992	1.737	2.630	147.80

Symmetry code: (i)  $-x+1, -y+2, -z+1$ ; (ii)  $x, 1/2-y, -1/2+z$ . Cg is the centroid of C8-C13 ring.



**Fig. 2.** A partial packing diagram for (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol, with C-H...F hydrogen bonds and shown as dashed lines. H atoms not included in intermolecular hydrogen bonding have been omitted for clarity. [Symmetry codes: (i)  $-x+1, -y+2, -z+1$ ].

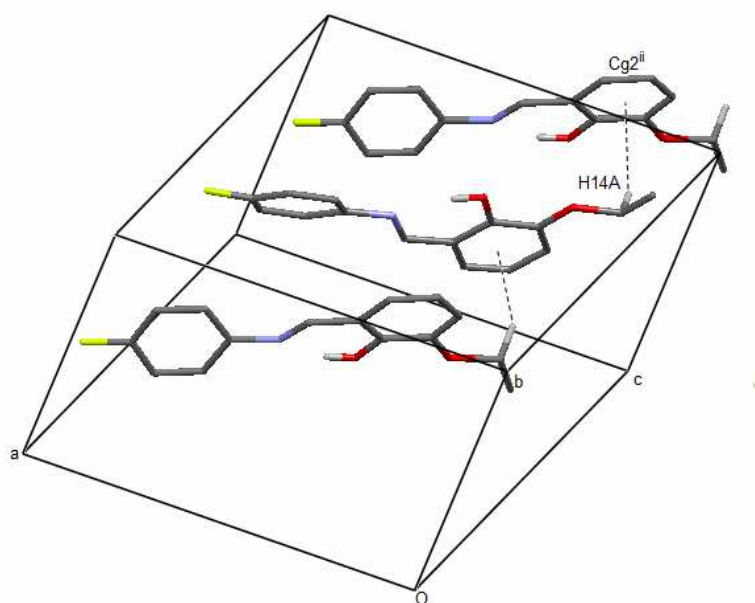
the methyl hydrogen exist in the crystal structure (Fig. 3).

The X-ray and optimized structures of the title compound were superimposed for visual comparison as shown in Fig. 4. The selected bond lengths and angles for the optimized structure and the X-ray geometry of the molecule are listed in Table 2. The corresponding C9-O1 and C7-N1 distances of the enol form at the optimized geometry are 1.3363 Å, and 1.2887 Å while these distances for the keto form are 1.2524 Å and 1.334 Å, respectively. From the X-ray geometry, the C-O

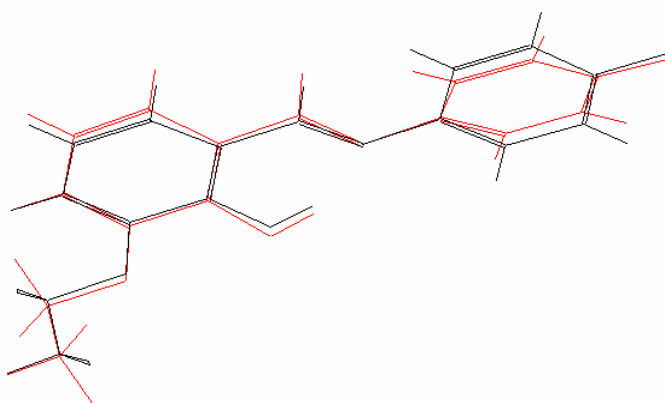
distance of 1.349(2) Å indicates single bond character and the C-N distance is 1.279(3) Å that shows double bond character. The results obtained from the optimization of the enol form are in reasonable agreement with the experimental as can be seen in Fig. 4.

### Natural Bond Orbital (NBO) Analysis

NBO analysis is important for the understanding of hydrogen bonding and delocalization effect from the lone pairs



**Fig. 3.** A partial packing diagram for (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol, with C-H... $\pi$  bonds shown as dashed lines. H atoms not included in intermolecular hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii)  $x, 1/2-y, -1/2+z$ ].



**Fig. 4.** Superimposition of gas phase optimized (red) and experimental geometry (black) of title compound.

(donor) to antibonding orbitals (acceptor). The interaction between the donor and acceptor orbitals can be used to measure delocalization. The stabilization energy derived from the interactions between the donor and acceptor orbitals was estimated by second order perturbation interaction energy ( $E^2$ ) in natural bond orbital (NBO) at optimized geometry. For each donor NBO ( $i$ ) and acceptor NBO ( $j$ ), the stabilization energy  $E^2$  associated with delocalization between donor and acceptor was estimated by Eq. 1 [22]:

$$E^2 = \Delta E_{ij} = -q_i \frac{F^2(i, j)}{\epsilon_j - \epsilon_i} \quad (1)$$

Where  $q_i$  is the donor orbital occupancy,  $\epsilon_i$ ,  $\epsilon_j$  are diagonal elements (orbital energies) and  $F(i, j)$  is the off-diagonal NBO Fock matrix element.

NBO analysis of the title compound was performed by applying same level of theory for the enol form in different solvents and gas phase. The interactions between donor N1 lone pair and acceptor H1-O1 bond for the title compound in various solvents and gas phase are shown in Table 4. NBO analysis for the title compound shows that there is a strong interaction  $n_{N1} \rightarrow \sigma^*_{O1-H1}$ . This interaction increases with the increase of polarity of the solvent and as a result O1-H1 bond weakens and lengthens. Table 4 shows the calculated delocalization energies of title compound in various solvents.

The delocalization energy of the title compound increases with the increase of polarity of the solvent. The increasing of delocalization energy of the title compound indicates that it is more stable in the polar solvent. In addition, N...O distance shortens with the increase of polarity of the solvent. The increase of  $n_{N1} \rightarrow \sigma^*_{O1-H1}$  delocalization with the increase of

polarity of the solvent strengthens intramolecular hydrogen bond, and weakens and elongates the O-H sigma bond.

### IR Absorption Spectrum

IR spectrum of the title compound is given in Fig. 5. It is noteworthy that there exist two absorption bands. One of these in 2000-3000  $\text{cm}^{-1}$  region is attributed to the  $\nu(\text{O-H})$  stretching frequencies which broaden owing to the formation of strong intramolecular hydrogen bonding O-H...N in the structure and the other, located at 1618  $\text{cm}^{-1}$ , is attributed to  $\nu(\text{C=N})$  stretching which shifted to the lower frequency of 1618  $\text{cm}^{-1}$  due to the formation of strong intramolecular hydrogen bonding O-H...N in the structure. The IR spectrum of the molecule shows also the presence of  $\nu(\text{C-O})$  stretching at 1255  $\text{cm}^{-1}$ . These values are in accordance with the literature [23].

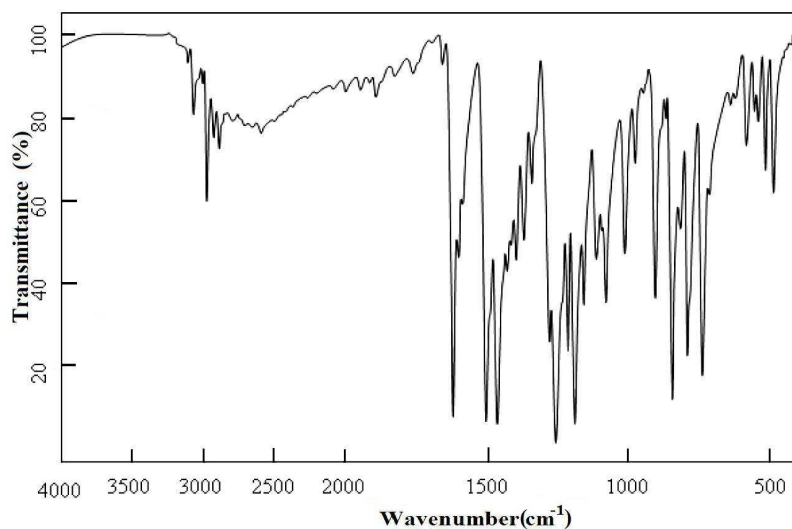
The vibrational frequencies of the title compound were calculated by using the same level of theory. The scale factor of 0.9682 was applied to vibrational frequencies [24]. Vibrational bands have been made by using Gaussview. The experimental and the calculated frequencies are given in Table 5. The calculated results from frequency analysis for C=N, O-H and C-O stretching show significant deviations from the experimental values due to intramolecular hydrogen bond between N and O.

### UV-Vis Absorption Spectra

For the evaluation of both the energies and dipole moments of enol and keto forms to be compared with each other, optimizations pertaining to each form of the title compound were performed. The geometric optimization in the solvent media was carried out using DFT/B3LYP method with 6-311G(d,p) basis set by adding the polarizable continuum

**Table 4.** Second Order Perturbation Theory Analysis of the Fock Matrix in NBO Basis and Intramolecular Hydrogen Bond Lengths in Different Solvents

Solvent	Donor	Acceptor	$E^2$ (Kcal mol <sup>-1</sup> )	O-H (Å)	N...H (Å)	N...O (Å)
Gas phase	LP(1)N1	BD*(1)O1-H1	23.44	0.9918	1.73692	2.62983
Benzene	LP(1)N1	BD*(1)O1-H1	24.88	0.9940	1.72410	2.62183
Chloroform	LP(1)N1	BD*(1)O1-H1	25.83	0.9954	1.71644	2.61732
EtOH	LP(1)N1	BD*(1)O1-H1	26.96	0.9970	1.70787	2.61213
DMSO	LP(1)N1	BD*(1)O1-H1	27.19	0.9973	1.70583	2.61091



**Fig. 5.** The IR spectrum of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol.

**Table 5.** The Experimental and the Calculated Frequencies of IR Spectra ( $\text{cm}^{-1}$ )

Assignments	Experimental	DFT/B3LYP
O-H str.	2000-3000	3228
C-H str. (aromatic)	3067	3186-3207
C-H ( $\text{CH}_3$ ) str.	3001	3109
N=C-H (imino) str.	2929	3034
C-H ( $\text{CH}_2$ ) str.	2976	2990
C=N str. + O-H bend. + C=C str.	1618	1668
C=C str. + C=N str.	1582	1639
C=C str. + C=N str. + O-H bend.	1503	1617-1537
C=C str. + C-O1 str. + O-H bend.	1461	1493
O-H bend. + C-H (aromatic) bend.	1367	1462
N=C-H bend. (imino)	1394	1398
C-O1 str. + C=C str. + N=C-H bend.	1341	1321
C-O2 str.	1255	1281
C-F str + C-H (aromatic) bend	1212	1251
C-N str. + C-H (aromatic) bend.	1187	1218
C-H bend. (aromatic)	1113-1077	1117-1099
C-H bend. (aromatic)	904-844	856-842
C-H bend. (aromatic)	789	819-772
C-H bend. (aromatic)	736	735

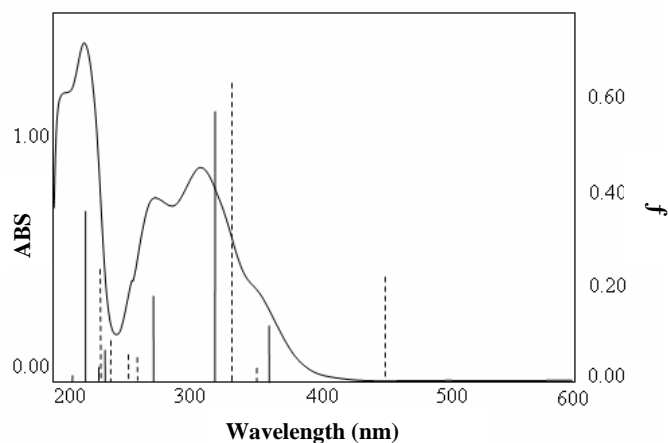
Str.: stretching, bend.: bending.

**Table 6.** The Energies and Dipole Moments of Enol and Keto Form in Gas Phase and Solution

	Enol form		Keto form	
	Energy (Hartree)	Dipole moment (D)	Energy (Hartree)	Dipole moment (D)
Gas phase	-885.28598146	2.8370	-885.27894254	2.0862
Benzene	-885.29190723	3.2754	-885.28670373	2.6172
CHCl <sub>3</sub>	-885.29628059	3.6586	-885.29249958	3.1463
EtOH	-885.30073532	4.0947	-885.29851305	3.7974
DMSO	-885.30122807	4.1573	-885.29899360	3.8735

model (PCM). The total energies and dipole moments of enol and keto forms in the solvent media are shown in Table 6. As shown in this table, the total energies of enol and keto forms decrease with the increase of polarity of the solvent, in other words, stability of the molecule increases. In addition, dipole moments for both enol and keto forms increase with the increase of polarity of the solvent. We calculated the first 10 spin-allowed singlet-singlet excitations for both enol and keto forms of the title compound by TD-DFT approach. TD-DFT calculations were started from gas phase and solution phase optimized geometry using the same level of theory and carried out in both gas and solution phase to obtain excitation energies. Among the methods to calculate excitation energies for organic compounds as well as inorganic ones, TD-DFT is of particular interest owing to the satisfactory results achieved with the experiment and low cost of computational demands [25-28].

In Fig. 6, the calculated transitions for both enol and keto forms are given for comparison with the experimental spectrum in EtOH. The percentage contributions of molecular orbitals to the formation of the bands were extracted from the output by using SWizard Program [29]. For both forms, wavelength ( $\lambda$ ), oscillator strength ( $f$ ) were selected to be larger than 0.1. The major contributions of the calculated transitions are given in Table 7. According to the results, the calculated excitation energies of enol form are at 224 nm [HOMO→LUMO+3(43%), HOMO-1→LUMO+2(18%)], at 276 nm [HOMO-2→LUMO(66%)], at 323 nm [HOMO-1→LUMO(82%)] and at 365 nm [HOMO→LUMO(89%)], and



**Fig. 6.** The comparison of calculated transitions for enol form (—) and keto form (---) of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol with the experimental spectrum in EtOH.

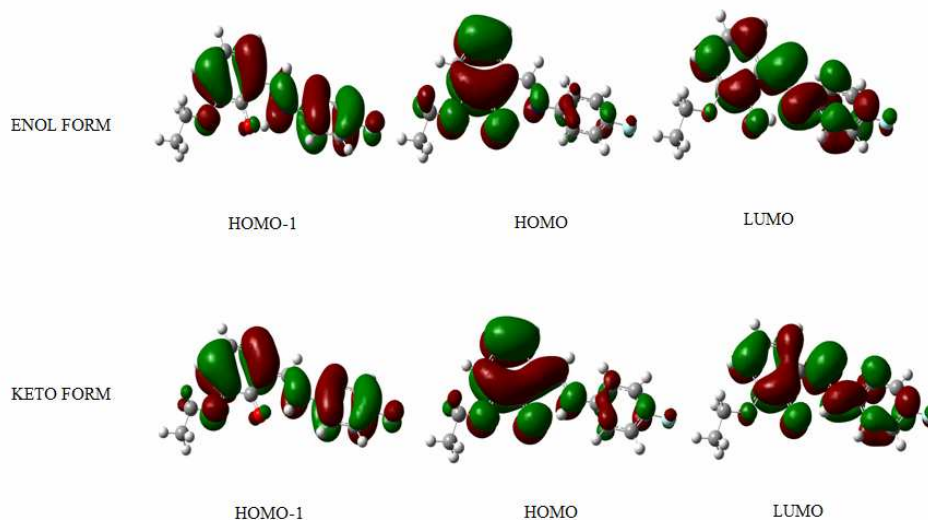
that of the keto form are at 234 nm [HOMO→LUMO+3(77%)], at 333 nm [HOMO-2→LUMO(6%), HOMO-1→LUMO(81%)] and at 449 nm [HOMO→LUMO(81%)] (Fig. 6). The frontier molecular orbitals of enol and keto form for the title molecule are shown in Fig. 7 in the EtOH.

The UV-Vis electronic spectra of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol in various organic solvents (EtOH, DMSO, Benzene and CHCl<sub>3</sub>) were recorded within 200-600 nm range. The characteristic UV-Vis absorption

**Table 7.** For Enol and Keto Forms Wavelength, Oscillator Strength, Major Contributions of Calculated Transitions

	Experimental		Calculated		
		Enol form	Major contribution	Keto form	Major contribution
	$\lambda$ (nm)	$\lambda$ (nm) (f)		$\lambda$ (nm) (f)	
Gas phase	-	223.48(0.3680)	H $\rightarrow$ L+3 (37%) H $\rightarrow$ L+2 (30%) H-1 $\rightarrow$ L+2 (18%)	232.72(0.2469)	H $\rightarrow$ L+3(77%) H-7 $\rightarrow$ L (6%)
	-	274.98(0.2132)	H-2 $\rightarrow$ L (67%) H-4 $\rightarrow$ L (15%) H-1 $\rightarrow$ L (5%)		
	-	322.91(0.5439)	H-1 $\rightarrow$ L (82%)	333.84(0.5515)	H-1 $\rightarrow$ L (73%)
	-	361.20(0.1265)	H $\rightarrow$ L (88%)	442.85(0.2354)	H $\rightarrow$ L (81%)
Benzene		225.63(0.3861)	H $\rightarrow$ L+3 (57%) H-1 $\rightarrow$ L+2(16%) H $\rightarrow$ L+2 (13%)	235.63(0.2249)	H $\rightarrow$ L+3(77%) H-7 $\rightarrow$ L (8%)
	278	276.67(0.1922)	H-2 $\rightarrow$ L(68%) H-4 $\rightarrow$ L(14%)		
	316	324.96(0.5871)	H-1 $\rightarrow$ L (83%)	335.82(0.6362)	H-1 $\rightarrow$ L (84%)
	360	370.65(0.1372)	H $\rightarrow$ L (89%)	459.18(0.2418)	H $\rightarrow$ L (81%)
CHCl <sub>3</sub>	242	224.82(0.3811)	H $\rightarrow$ L+3(52%) H $\rightarrow$ L+2(17%) H-1 $\rightarrow$ L+2(17%)	235.01(0.2313)	H $\rightarrow$ L+3 (77%) H-7 $\rightarrow$ L (8%)
	280	276.23(0.1939)	H-2 $\rightarrow$ L (68%) H-4 $\rightarrow$ L (15%)		
	316	324.23(0.5824)	H-1 $\rightarrow$ L (83%)	334.42(0.6317)	H-1 $\rightarrow$ L (82%)
	360	367.72(0.1292)	H $\rightarrow$ L (89%)	454.47(0.2324)	H $\rightarrow$ L (81%)
EtOH	224	223.90(0.3694)	H $\rightarrow$ L+3(43%) H $\rightarrow$ L+2(24%) H-1 $\rightarrow$ L+2(18%)	234.09(0.2350)	H $\rightarrow$ L+3 (77%) H-6 $\rightarrow$ L (8%)
	278	276.04(0.1875)	H-2 $\rightarrow$ L (66%) H-4 $\rightarrow$ L (16%)		
	314	323.19(0.5831)	H-1 $\rightarrow$ L (82%)	332.91(0.6229)	H-1 $\rightarrow$ L (81%) H-2 $\rightarrow$ L (6%)
	358	365.06(0.1201)	H $\rightarrow$ L (89%)	449.45(0.2190)	H $\rightarrow$ L (81%)
DMSO		224.17(0.3806)	H $\rightarrow$ L+3 (45%) H $\rightarrow$ L+2 (24%) H-1 $\rightarrow$ L+2(17%)	234.41(0.2437)	H $\rightarrow$ L+3 (77%) H-6 $\rightarrow$ L (6%)
	284	276.33(0.1877)	H-2 $\rightarrow$ L (67%) H-4 $\rightarrow$ L (16%)		
	316	324.40(0.6040)	H-1 $\rightarrow$ L (83%)	334.65(0.6353)	H-1 $\rightarrow$ L (81%) H-2 $\rightarrow$ L (6%)
	360	365.44(0.1274)	H $\rightarrow$ L (89%)	451.33(0.2299)	H $\rightarrow$ L (81%)

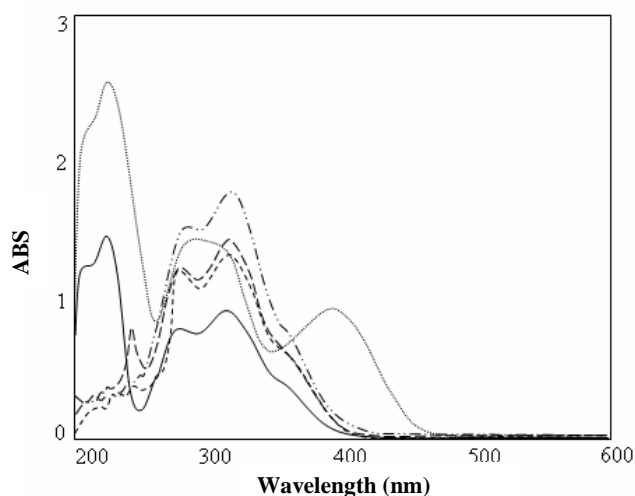
## Molecular and Computational Structure Characterizations of



**Fig. 7.** The molecular orbitals of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol for enol form and keto form in EtOH.

bands of the molecule in EtOH, DMSO, Benzene and  $\text{CHCl}_3$  are given in Table 7. Representative spectra are shown in Fig. 8. The absorption band is observed at 316 nm followed by a shoulder at 360 nm in all solvents. The influence of the solvent is important for intramolecular hydrogen bonds. Some solvents such as DMF and DMSO show hydrogen bond breaking effect. Such an effect by the solvent, leads to the destruction of intramolecular hydrogen bond and subsequently to the formation of anion [30,31].

Therefore, we have recorded the UV-Vis spectrum in EtOH by adding NaOH so that we can understand whether the anion of the title compound exists or not. A new absorption band in basic media appeared at 395 nm (Fig. 8). This shows that the absorption band at 360 nm does not arise from forming of anion of the title compound. This can be explained by the fact that the compound has a very strong intramolecular hydrogen bond and the title compound does not convert to anion even by DMSO [30]. In addition, the second band at 360 nm can be formed by the molecules rendering intramolecular proton transfer from enol form to keto form possible. In the calculated excitation energies, one can see that the HOMO  $\rightarrow$  LUMO transition for keto form occurs above 449 nm. But in the experimental spectra, there is no absorption in this region (Fig. 6). This indicates that the compound (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol is not in keto form in



**Fig. 8.** The solvent effect on UV-Vis spectra of (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol in (---) DMSO, (—) EtOH, (--)  $\text{CHCl}_3$ , (-.-) Benzene, (.....) EtOH+NaOH.

solution.

In view of TD-DFT calculations for enol form, four excitation energies at 224 nm, at 276 nm, at 323 nm and at 365 nm arise from HOMO  $\rightarrow$  LUMO+3(43%), HOMO-1  $\rightarrow$  LUMO+2(18%); HOMO-2  $\rightarrow$  LUMO(66%); HOMO-1  $\rightarrow$

**Table 8.** Thermodynamic Properties of Title Compound at Different Temperature

T (K)	$H_m^0$ (Kcal mol <sup>-1</sup> )	$S_m^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$C_{p,m}^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
100	1.813	86.481	26.106
200	5.589	111.877	45.694
298.15	11.267	134.704	66.058
300	11.393	135.126	66.438
400	19.228	157.533	85.861
500	28.857	178.951	102.180

LUMO(82%) and HOMO→LUMO(89%) transitions, respectively. These transitions were experimentally observed as bands at 224 nm, at 278 nm, at 314 nm and a shoulder at 358 nm. The results obtained by the calculation for enol form are in reasonable agreement with the experimental as seen in Fig. 6 and the compound adopts enol form in solution.

### Thermodynamic Properties

The heat capacity ( $C_{p,m}^0$ ), entropy ( $S_m^0$ ) and enthalpy ( $H_m^0$ ) that are the standard thermodynamic functions were performed using DFT/B3LYP method with 6-311G(d,p). The results are shown in Table 8. The heat capacities, entropies and enthalpies were obtained by increasing the temperature from 100 K to 500 K. According to the results, the increase of temperature increases heat capacities, entropies and enthalpies due to increasing intensities of molecular vibration.

The correlation equations between heat capacities, entropies, enthalpies and temperature are shown below and can be used for analyzing heat capacities, entropies and enthalpies at different temperatures.

$$C_{p,m}^0 = 3.61284 + 0.2262T - 5.64766 \times 10^{-5}T^2, R^2 = 0.99918$$

$$S_m^0 = 60.47976 + 0.26761T - 6.16926 \times 10^{-5}T^2, R^2 = 0.99995$$

$$H_m^0 = -0.06255 + 0.00873T + 9.8323 \times 10^{-5}T^2, R^2 = 0.99998$$

### CONCLUSIONS

The compound (*E*)-2-ethoxy-6-[(4-fluorophenylimino)methyl]phenol was synthesized and the corresponding molecular structure was experimentally characterized by means of X-ray Diffraction, IR and UV-Vis spectroscopy techniques. It was concluded that this compound is in enol

form in the solid state both on the basis of X-ray and IR spectroscopic data. UV-Vis spectra of the title compound were recorded in various solvents. Whether the title compound was in the keto or enol forms was also examined utilizing UV-Vis spectroscopic measurements conducted in different solvents. The results show that the molecule exists only in enol form even in solvent media. In addition, DFT/B3LYP optimization was performed based on X-ray geometry. TD-DFT calculations starting from optimized geometry were carried out in both gas and solution phase to calculate excitation energies of enol and keto tautomers. Vibrational frequency analysis was performed at the optimized geometry with the same level of theory. 6-311G(d,p) basis set was applied throughout the calculations. The results obtained by the calculation for enol form showed a satisfactory consistency with the experimental data.

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