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Spectroscopic, molecular structure characterizations and quantum chemical computational studies of (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol

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1. Introduction

o-Hydroxy Schiff bases derived from the condensation of primary amines with carbonyl compounds have a strong intramolecular hydrogen bond. These compounds are of interest because of their thermochromism and photochromism in the solid state, which can involve reversible the intramolecular proton transfer from an oxygen atom to the neighboring nitrogen atom. Intramolecular proton transfer mechanism of both excited state and ground state is still the subject of intensive research. On the basis of thermochromic and photochromic Schiff bases, it was proposed that molecules exhibiting thermochromism are planar, while molecules exhibiting photochromism are non-planar [1,2]. Photochromic compounds are used as optical switches and optical memories, variable electrical current, ion transport through membranes [3]. In addition, they have widespread usage as ligands in the field of coordination chemistry [4] as well as in diverse fields of chemistry and biochemistry owing to their biological activities [5]. o-Hydroxy Schiff bases can exist in two tautomeric structures as enol and keto forms in the solid state [6,7]. o-Hydroxy Schiff bases were studied in solvent media and found to exist as both enol and keto form. While the absorption band at wavelength greater than 400 nm is observed in polar solvents, this band is not observed in apolar sol-

ABSTRACT

The molecular structure and spectroscopic properties of (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol were characterized by X-ray diffraction, IR and UV/Vis spectroscopy. These properties of title compound were also investigated from calculative point of view. Geometry optimization in gas phase was performed using DFT method with B3LYP applying 6-311G(d,p) basis set and geometry optimizations in solvent media were performed with the same level of theory by the polarizable continuum model (PCM). TD-DFT calculations starting from optimized geometry were carried out in both gas and solution phase to calculate excitation energies of title compound. In addition, while the non-linear optical properties were computed, thermodynamic properties were obtained at the optimized geometry with the same level of theory. The intramolecular proton transfer process from enol form to keto form was investigated using DFT method with B3LYP applying 6-311G(d,p) basis set. Transition state structure in EtOH was performed with the same level of theory by the polarizable continuum model (PCM).

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vents. The absorption band at greater than 400 nm was found to belong to the keto form of o-hydroxy Schiff bases [8,9].

In recent years, among the computational methods to calculate the electronic structure, excitation energies of molecular systems, DFT and TD-DFT are of particular interest steadily owing to give satisfactory results with experiment by costing low computational demands among the computational methods calculating [10,11].

A new (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol compound was synthesized and its spectroscopic properties were studied both experimental and theoretical insight. The crystal structure of title Schiff base compound was determined by single crystal X-ray diffractometry. The structure of (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol was experimentally characterized by IR, UV/Vis spectroscopy, investigated by using density functional theory DFT and excitation energies were carried out using TD-DFT calculations starting from optimized geometry. Also, intramolecular proton transfer process of (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol was investigated for ground state in gas phase and EtOH.

2. Experimental and computational methods

2.1. Synthesis

The compound (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino) methyl]phenol was prepared by refluxing a mixture of a solution



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containing 5-(diethylamino)-2-hydroxybenzaldehyde (Alfa Aesar, 99%, 0.5 g, 2.59 mmol,) in 20 mL ethanol (Kimetsan, 96%) and a solution containing 2-fluoroaniline (Alfa Aesar, 99%, 0.29 g, 2.59 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (E)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol suitable for X-ray analysis were obtained by slow evaporation from acetone (Alfa Aesar, 99.5+%, yield 76%; m.p. 367–369 K).

2.2. Instrumentation

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. The solvents used for UV/ Vis studies are benzene (Carlo Erbaa, 99.8+%), CHCl₃ (Alfa Aesar, 99.5+%) DMSO (Alfa Aesar, 99.9+%).

2.3. X-ray crystallography

A suitable sample of $0.2 \times 0.2 \times 0.2 \text{ mm}^3$ size was selected for the crystallographic study. All diffraction measurements were performed at 130 K using graphite monochromated Mo K α radiation and a Xcalibur diffractometer. Absorption correction was achieved by Semi-empirical from equivalents. The structure was solved by direct methods using SHELXS-97 [12]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms. All non-hydrogen atom parameters were refined anisotropically and all H atoms were located in a difference Fourier map, and their coordinates and Uiso(H) values were refined freely. The data collection conditions and parameters of refinement process are listed in Supplementary data.

2.4. Computational procedure

All computations were performed using Gaussian 03W program package running under Windows XP [13]. Full geometry optimization of the title molecule was performed by using DFT method with Becke's three-parameters hybrid exchange-correlation functional (B3LYP) [14] employing 6-311G(d,p) basis set [15–17] as implemented in Gaussian 03W. Crystallographically obtained geometrical data of the molecule was used for the optimization. Total molecular energy, and dipole moment were obtained from the optimization output. The ground state geometry optimization of the title compound for gas phase was calculated at using DFT method with B3LYP adding 6-311G(d,p). Solution phase geometry optimizations were performed with the same level of theory by the polarizable continuum model (PCM). The polarizable continuum model (PCM) family of solvation models is among the most widely used [18,19]. TD-DFT calculations starting from gas phase and solution phase optimized geometry using same level of theory were carried out in both gas and solution phase to calculate excitation energies of title compound. Calculated electronic transitions of the title compound were obtained by TD-DFT excited state calculation. Also gas-phase vibrational frequencies for title compound were performed, the non-linear optical properties were computed and thermodynamic properties were obtained at the optimized geometry with the same level of theory. The ground state geometry optimizations of the title compound in gas phase and solution phase for TS structure were performed with the same level of theory.

3. Results and discussion

3.1. Structure determination

The crystal data and refinement details of (E)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol compound are given in Supplementary data. Selected bond lengths and angles are given in Table 1. The molecular structure of title compound is shown in Fig. 1 with the atom numbering scheme. As it can be seen in Fig. 1, the molecule adopts *E* configuration about the C=N double bond.

o-Hydroxy Schiff bases show tautomerism by intramolecular proton transfer from oxygen atom to nitrogen atom. As a result of this, o-hydroxy Schiff bases can exist in two tautomeric structures as enol and keto forms in the solid state. As shown Fig. 2, depending on their forms, two types of intramolecular hydrogen bonds are possible (a) $O-H \cdots N$ in enol form and (b) $N-H \cdots O$ in keto form. For title compound, enol form is favoured over the keto form in the solid state. The C7–N1 bond length of 1.2939(17) Å and C2-O1 bond length of 1.3542(16) Å are consistent with the distances of the C-N double bond and the C-O single bond as presented in related compounds previously studied [20-22]. A significant intramolecular interaction is noted involving phenolic atom O1 and nitrogen atom N1 and constitutes a six-membered ring S(6) [23]. The O1 \cdots N1 distance of 2.5778(14) Å is indicative of strong intramolecular hydrogen bonding (Table 2). This length is clearly shorter than the sum of the van der Waals' radii for N and O [24].

While N2–C4 bond length is 1.3689(17) Å, N1–C8 bond length is 1.4117(16) Å. N2 atom has two unpaired electrons. The contraction of N2–C4 bond length shows that the unpaired electrons of nitrogen atom do not reside entirely on nitrogen atom but are spread over the aromatic ring, overlap with π electron of aromatic ring.

The intermolecular hydrogen bonded geometry and details of C—H···O interactions for the title compound are listed in Table 2. The molecules are linked by intermolecular C—H···O interactions and C—H··· π interactions between π electrons of aromatic ring and aromatic hydrogen as shown in Fig. 3.

The optimized parameters for title compound were obtained by using the B3LYP/6-311G(d,p). Selected bond lengths and angles for the optimized structure and X-ray geometry of the molecule are listed in Table 1. Superimposition of X-ray and optimized structures of title compound is shown in Supplementary data. As it can be seen from Table 1, C2—O1 and C7—N1 distances for enol form at the optimized geometry are 1.338 Å and 1.295 Å. N2—C4 distance for optimized structure is 1.379 Å. The results obtained from the optimization for enol form are in agreement with the experimental ones. But the experimental bond lengths are slightly different from optimization ones. These differences are because the theoretical calculations are performed for gas phase while experimental results belong to solid phase.

3.2. Non-linear optical (NLO) properties

The non-linear optical properties play an important role for design of materials in modern communication technology, signal processing and optical switchs and optical memory devices [25]. The organic molecules that contain π electron cloud movement from donor group to acceptor group are known as non-linear optical materials. The donor and acceptor groups have an important role in the polarizability and first hyperpolarizability. If the donor and acceptor groups are powerful, delocalization of π electron cloud of molecules increases and as a result of this, the polarizability

Table 1
The selected bond lengths, angles and torsion angles (Å, °).

	X-ray	DFT/B3LYP enol form	DFT/B3LYP keto form
N1-C7	1.2939(17)	1.295	1.341
01–C2	1.3542(16)	1.338	1.258
N1-C8	1.4117(16)	1.397	1.395
C1C7	1.4301(18)	1.435	1.383
C1-C2	1.4150(18)	1.425	1.476
C2-C3	1.3795(18)	1.392	1.429
C3–C4	1.4078(19)	1.409	1.390
C4—C5	1.4195(19)	1.426	1.451
C5–C6	1.3667(19)	1.376	1.358
C1-C6	1.4101(18)	1.408	1.428
N2-C4	1.3689(17)	1.379	1.379
F1-C13	1.3629(16)	1.349	1.351
C7-N1-C8	121.66(11)	121.59	127.35
N1-C7-C1	121.52(12)	122.37	122.86
N1-C8-C9	126.25(12)	124.78	124.88
N1-C8-C13	117.52(12)	118.20	117.88
01-C2-C1	120.14(11)	121.51	121.05
01–C2–C3	118.56(12)	118.11	122.25
C8-N1-C7-C1	178.35(11)	177.10	-179.29
C7-N1-C8-C9	-2.4(2)	-33.42	4.06
C7-N1-C8-C13	177.96(12)	149.62	-176.12
C7-C1-C2-01	1.80(19)	0.15	-0.29
C6-C1-C2-01	-179.27(12)	-179.83	179.46
C14-N2-C4-C5	173.46(12)	179.84	-178.77
N1-C8-C13 01-C2-C1 01-C2-C3 C8-N1-C7-C1 C7-N1-C8-C9 C7-N1-C8-C13 C7-C1-C2-O1 C6-C1-C2-O1 C14-N2-C4-C5	$\begin{array}{c} 117.52(12)\\ 117.52(12)\\ 120.14(11)\\ 118.56(12)\\ 178.35(11)\\ -2.4(2)\\ 177.96(12)\\ 1.80(19)\\ -179.27(12)\\ 173.46(12) \end{array}$	118.20 121.51 118.11 177.10 -33.42 149.62 0.15 -179.83 179.84	117.88 121.05 122.25 -179.29 4.06 -176.12 -0.29 179.46 -178.77



Fig. 1. A view of title compound, with the atom numbering scheme.

and first hyperpolarizability of organic molecules increase [26]. Quantum chemical calculations can be used to describe the relationship between the electronic structure of molecules and their non-linear optical properties. The increase of π electron delocalization of molecules and the strengthen of donor and acceptor groups increase polarizability and first hyperpolarizability. The energy gap between HOMO and LUMO is important in getting polarizability of a molecule [27]. The molecules having a small energy gap are more polarizable than molecules having a large energy gap. Also, UV–Vis spectra can be used to correlate with polarizability. A small HOMO–LUMO gap means small energy gap are shifted toward the visible.

Table 2 Hydrogen bonding geometry (Å,°).

O1—H18…N1 0.950(19) 1.692(18) 2.5778(14) 153.6(13) C11—H11…O1 ⁱ 0.964(15) 2.509(15) 3.4590(18) 168.5(12) C10—H10…Cg1 ⁱⁱ 0.940(15) 2.971(15) 3.8018(16) 148.0(12) Calculated O1—H18…N1 0.994 1.735 2.629 147.49	D—H····A	D—H	$H{\cdots}A$	$D{\cdots}A$	$\langle D {-\!\!\!-} H {\cdot} {\cdot} {\cdot} A$
	01—H18…N1	0.950(19)	1.692(18)	2.5778(14)	153.6(13)
	C11—H11…O1 ⁱ	0.964(15)	2.509(15)	3.4590(18)	168.5(12)
	C10—H10…Cg1 ⁱⁱ	0.940(15)	2.971(15)	3.8018(16)	148.0(12)
	Calculated O1—H18…N1	0.994	1.735	2.629	147.49

Symmetry code: (i) 1/2 - x, -1/2 + y, 3/2 - z; (ii) 3/2 - x, -1/2 + y, 3/2 - z. Cg1 is the centroid of C1–C6 ring.

The total static dipole moment μ , the average linear polarizability α , and the first hyperpolarizability β can be calculated by using the Eqs. (1), (2), (3), respectively [25].

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{1}$$

$$\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\beta = \left[\left(\beta_{\text{xxx}} + \beta_{\text{xyy}} + \beta_{\text{xzz}} \right)^2 + \left(\beta_{\text{yyy}} + \beta_{\text{xxy}} + \beta_{\text{yzz}} \right)^2 + \left(\beta_{\text{zzz}} + \beta_{\text{xxz}} + \beta_{\text{yyz}} \right)^2 \right]^{1/2}$$
(3)

The dipole moment, polarizability and the first hyperpolarizability were calculated using polar = ENONLY at the level of B3LYP/6-311G(d,p) and the results obtained from calculation were given in Table 3.



Fig. 2. Enol and keto tautomeric forms of title compound.



Fig. 3. A partial packing diagram for title compound, with C-H··· π and C-H···O hydrogen bonds shown as dashed lines [symmetry codes: (i) 1/2 - x, -1/2 + y, 3/2 - z; (ii) 3/2 - x, -1/2 + y, 3/2 - z].

Table 3								
Calculated	dipole	moments	(D),	polarizability	and	first	hyperpolarizability	
components (a.u.) for the title compound.								

μ_x	-3.24	β_{xxx}	5397.4
μ_{v}	-2.92	β_{xxy}	-673.5
μ_z	0.02	β _{xyy}	-365.2
		β_{yyy}	-82.7
α_{xx}	454.2	β_{xxz}	46.9
α_{xy}	-4.2	β_{xyz}	-113.3
α_{yy}	198.2	β_{yyz}	11.1
α_{xz}	10.5	β_{xzz}	-112.2
α_{yz}	-3.5	β_{yzz}	-28.7
a _{zz}	116.5	βzzz	18.8

The calculated dipole moment μ_{tot} , polarizability α and first hyperpolarizability β for title compound are 4.36 D, 37.94 Å³ and 43.06 × 10⁻³⁰ cm⁵/esu respectively. The first hyperpolarizability of title compound is greater than those of 2-methyl-6-[2-[trifluorormethyl]phenyliminomethyl]phenol [28], 4-(2,3,4-trihydroxybenzylidene amino)antipyrine [29]. The energy gap between HOMO and LUMO of title compound is 3.75 eV for gas phase. Absorption band of title compound is at 380 nm. The decrease of the energy gap between HOMO and LUMO shows that title compound has a smaller energy gap than related compounds [28,30] and as a result of this, absorption band is shifted toward the visible. These results show that title compound can be used as a good non-linear optical material.

3.3. 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 obtained from the basis of vibrational analysis are shown in Supplementary data. The heat capacities, entropies and enthalpies were obtained by increasing temperature from 100 K to 500 K. As results, 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 in different temperature.

$$\begin{split} C^0_{p,m} &= 5.49806 + 0.24645T - 4.18785 \times 10^{-5}T^2, \quad R^2 = 0.99935 \\ S^0_m &= 62.6245 + 0.30408T - 6.86279 \times 10^{-5}T^2, \quad R^2 = 0.99992 \\ H^0_m &= -0.04742 + 0.00948T + 1.12845 \times 10^{-4}T^2, \quad R^2 = 0.99999 \end{split}$$

3.4. IR spectroscopy

IR spectrum of the title compound was shown in Supplementary data. The strong intramolecular hydrogen bonding occurs in title compound. The absorption band in 2000–3000 cm⁻¹ region is attributed to the v(O-H) stretching frequencies which broaden owing to the formation of strong intramolecular hydrogen bonding $O-H\cdots N$. The absorption band at 1629 cm⁻¹ is attributed to v(C=N) stretching. The IR spectrum of the molecule shows also the presence of v(C-F) stretching at 1132 cm⁻¹. These values are in accordance with the literature [31].

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 [32]. Vibrational bands have been made by using Gaussview. The experimental and the calculated vibrational frequencies are given in Supplementary data. The results obtained by the calculation for title compound have shown a satisfactory consistency with the experimental data.

3.5. UV/Vis absorption spectra

We have calculated the total energy, dipole moment and frontier molecular orbital energies by using DFT/B3LYP method with 6-311G(d,p) basis set by adding the polarizable continuum model (PCM) in solvent media. Results obtained from used solvents having different polarities are shown in Table 4. As it is shown in Table 4, the total energies decrease with increase of the polarity of the solvent, in other words stability of molecule increases. While the energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital (LUMO) decreases, dipole moment increases with increase of the polarity of the solvent. HOMO and LUMO called Frontier molecular orbitals (FMO) are the most important orbitals because they play Table A

	Gas phase	Benzene	CHCl ₃	EtOH	DMSO
Enol form					
E _{total} (a.u.)	-944.064280	-944.070248	-944.074691	-944.079151	-944.079682
E _{LUMO} (eV)	-1.60	-1.64	-1.68	-1.72	-1.74
E _{HOMO} (eV)	-5.35	-5.36	-5.38	-5.40	-5.41
$\Delta E (eV)$	3.75	3.72	3.70	3.68	3.67
μ (D)	4.36	5.10	5.66	6.24	6.32
Keto form					
E _{total} (a.u.)	-944.057234	-944.065392	-944.071571	-944.077830	-944.078580
E _{LUMO} (eV)	-1.36	-1.93	-1.97	-2.01	-2.02
E _{HOMO} (eV)	-3.42	-5.41	-5.49	-5.55	-5.56
$\Delta E (eV)$	2.06	3.48	3.52	3.54	3.54
μ(D)	4.28	5.15	5.88	6.68	6.78

lculated total energies.	frontier orbital energies	and dipol moments of	f title compound for en	ol and keto form.

important roles in reactions between molecules and in UV/Vis spectra of a molecule. The energy gap between HOMO and LUMO is important to influence the stability of a molecule and determines the chemical reactivity, kinetic stability, polarizability and chemical hardness-softness of a molecule [27]. The molecules having a large energy gap are stable molecules as chemical. Hard molecules have a large energy gap and they are more stable than soft molecules having a small energy gap. Because soft molecules have a small energy gap, they are more polarizable and more reactive than hard molecules. The energy gap between HOMO and LUMO of title compound is 3.75 eV for gas phase. The energy gap between HOMO and LUMO of title compound is smaller than that of related compounds [28,30]. This result indicates that title compound is more polarizable, more reactive and more soft molecule than related compound. The frontier molecular orbitals for enol and keto forms of the title molecule are shown in Supplementary data.

Also, the first 10 spin-allowed singlet–singlet excitations for title compound were calculated by TD-DFT approach. TD-DFT calculations were started from gas phase and solution phase optimized geometry using same level of theory and carried out in both gas and solution phase to calculate excitation energies. The percentage contributions of molecular orbitals to formation of the bands were extracted from output by using SWizard Program [33]. For title compound, wavelength (λ), oscillator strength (f) larger than 0.5, major contributions of calculated transitions are given in Table 5.

The UV/Vis spectra of title compound in various organic solvents (EtOH, DMSO, benzene and CHCl₃) were recorded within 200–500 nm range. The characteristic UV/Vis absorption bands of the molecule in EtOH, DMSO, benzene and CHCl₃ are given in Table 5. The UV/Vis spectra are shown in Supplementary data. The absorption band is observed at 380 nm in DMSO, CHCl₃ and benzene. This transition is attributed $\pi \rightarrow \pi$ transition. However, the compound shows new absorption bands in EtOH but these

absorption bands are not observed in DMSO, CHCl₃ and benzene. The theoretical calculations and experimental studies show that the new absorption bands belong to the keto form of o-hydroxy Schiff bases [8,30]. In EtOH, title compound exists both enol and keto form. This can not be explained as the polarity of solvent. If it depended on the polarity of solvent, keto form would have observed in DMSO. The fact that keto structure did not formed in DMSO shows that the solvent polarity is not effective on the proton transfer and instead it depends on the H-donor-acceptor property of solvent. EtOH is a polar and protic solvent and this property causes both enol and keto forms to be stable in solvent.

3.6. Intramolecular proton transfer process

DFT calculations with B3LYP adding 6-311G(d,p) have been performed to investigate the tautomeric equilibrium for both enol form and keto form. This compound in the solid state exists enol form. Selected geometric parameters for enol, keto and TS structures are given in Table 6. The tautomerization energies in gas phase and EtOH were calculated as a difference in energies between enol form and TS structure. Fig. 4 is a schematic representation of the potential energy curve at ground state indicating enol, keto and TS structure in gas phase and EtOH. For title compound enol form is more stable than keto form in gas phase. The keto form energy is found at 4.42 kcal/mol above enol form. The activation energy needed to overcome the barrier of intramolecular proton transfer reaction is 6.2 kcal/mol in gas phase. The geometric optimizations of enol and keto forms and TS structure in EtOH were performed with the same level of theory by the polarizable continuum model (PCM). The energies of enol, keto and TS structures were calculated to determine the effect of solvent on tautomerization. As seen in Fig. 4, enol form in EtOH is also more stable than

Table	5
Table	J

	For enol	and keto	forms	wavelength	oscillator	strength	maior	contributions	of	calculated	transition
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	Experimental			Calculated	
	λ (nm)	Enol form λ (nm) (f)	Major contribution	Keto form λ (nm) (f)	Major contribution
Gas phase	_	353.87 (1.0421)	$H \rightarrow L (80\%)$	366.53 (1.102) 423.36 (0.016)	H−1 → L(74%), H → L(+5%) H → L(+79%), H−1 → L(8%)
Benzene	378	369.59 (1.2361)	$\mathrm{H} \rightarrow \mathrm{L} \ (84\%)$	383.12 (1.2872) 421.54 (0.0296)	$H-1 \rightarrow L(79\%)$ $H-L(83\%) H-1 \rightarrow L(6\%)$
CHCl ₃	378	370.4 (1.2321)	$H \rightarrow L (84\%)$	382.08 (1.2905) 415.32 (0.0245)	H-1 → L(65%) H → L(18%) H → L(67%) H-1 → L(21%)
EtOH	358 388 430	369.37 (1.2161) - -	H → L (83%) - -	- 379.63 (1.2808) 408 (0.021)	H → L(79%) H−1 → L(87%)
DMSO	386	372.33 (1.2464)	$H \rightarrow L (84\%)$	382.61 (1.3084) 408.06 (0.0263)	$H \rightarrow L(80\%)$ H-1 $\rightarrow L(87\%)$

Table 6
Selected bond lengths (Å) and angles (°), energies and dipole moments for enol, keto and TS structures.

	Gas phase			EtOH		
	Enol	TS	Keto	Enol	TS	Keto
E _{total} (a.u.)	-944.064280	-944.054402	-944.057234	-944.079151	-944.069245	-944.077830
μ (D)	4.36	4.01	4.28	6.24	6.03	6.68
N1-H18	1.735	1.195	1.043	1.709	1.229	1.036
01-H18	0.994	1.300	1.711	0.998	1.256	1.755
N1···01	2.629	2.421	2.592	2.615	2.418	2.622
N1-C7	1.295	1.322	1.341	1.298	1.318	1.338
C1C7	1.435	1.402	1.383	1.434	1.409	1.388
01–C2	1.338	1.289	1.258	1.348	1.308	1.273
C1-C2	1.425	1.454	1.476	1.425	1.447	1.470
C2-C3	1.391	1.411	1.429	1.389	1.403	1.422
C3–C4	1.409	1.399	1.390	1.415	1.409	1.399
C4–C5	1.426	1.441	1.451	1.428	1.439	1.449
C5-C6	1.376	1.366	1.358	1.376	1.369	1.360
N1-H18-01	147.49	151.96	139.14	148.84	153.38	138.40
H18-01-C2	107.47	104.15	104.62	106.79	103.76	103.90
H18-N1-C8	99.31	105.41	111.59	99.39	104.77	112.17



Fig. 4. Schematic energy profile of intramolecular proton transfer in gas phase and EtOH for ground state. Energies relative to enol form in EtOH are given in kcal/mol.

keto form. The energy gap between enol form and keto form decreases from gas phase to solution phase. This shows that tautomerization in polar solvent occurs more easily than in gas phase. The dipole moment of keto form is less than that of enol form in gas phase but the dipole moment of keto form is more than that of enol form in benzene, CHCl₃ EtOH and DMSO (Table 4). Keto form is easily stabilized by solvent and as a result of this, the energy of keto form decreases. The stability of TS structure and the energy gap between enol form and TS structure slightly increases from gas phase to EtOH due to dielectric constant of solvent. If nonpolar reactant generates a nonpolar transition state, solvation

does not have an important role during reaction. But if there are significant changes in charge distribution during the reaction the solvent plays a more important role. If the TS is more polar than reactants it will be stabilized by polar solvents [34]. As seen in Table 6, the results obtained from calculation show that enol form is more polar than TS. Because enol form is more polar than TS, it will be stabilized by polar solvents. Energies of both enol form and TS structure decrease with the increase of polarity of solvent but decrease of energy for enol form is more than that for TS. So energy needed to overcome the barrier between enol form and TS slightly increase with increase of polarity of solvent. Because energy of enol form in gas phase and all solvents is less than that of keto form, enol form is favored. UV/Vis spectra of title compound showed the tautomeric equilibrium favored the enol form in benzene, CHCl₃ and DMSO. But in EtOH title compound tends to shift toward the keto form. Experimentally, while in EtOH new absorption bands 358 nm and 430 nm are observed, in benzen, CHCl₃ and DMSO it is not. This result clearly shows that not only the polarity of solvent but also hydrogen donor-acceptor properties of solvent influence the equilibrium. The results obtained from theoretical calculations show that the strong hydrogen bond interaction decreases activation energy between enol form and TS [35,36]. Benzene and CHCl₃ are solvents with low polarity and DMSO is polar and aprotic solvent but EtOH is polar and protic solvent acting as both hydrogen donor and acceptor. Because intramolecular proton transfer from enol form to keto form occurs in Transition state, protic solvents as EtOH can facilitate proton transfer. Therefore, molecules are strongly solvated by EtOH. TS structure of title compound will be stabilized by hydrogen bond involving EtOH and activation energy needed to overcome the barrier of intramolecular proton transfer between enol form and TS structure will decrease. The decrease of activation energy experimentally causes the formation of keto form in EtOH.

4. Conclusions

The compound (*E*)-5-(diethylamino)-2-[(2-fluorophenylimino)methyl]phenol was experimentally characterized by means of IR and UV/Vis spectroscopy techniques. It has been determined 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 different organic solvents. The results show that molecule exists only enol form in DMSO, CHCl₃ and benzene but in EtOH molecule exists as both enol and keto form. Also, 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 title compound. In addition, The intramolecular proton transfer process from enol form to keto form was investigated using DFT method with B3LYP applying 6-311G(d,p) basis set. Transition state structure in gas phase and EtOH have been performed with the same level of theory by the polarizable continuum model (PCM). Solvent effects on intramolecular proton transfer have been examined.

Appendix A. Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 776183. 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.09.030.

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