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HIGHLIGHTS

A detailed interpretation of FT-IR spectra and the effect of various organic solvents with different polarities on the UV-vis spectra has been studied.
Mulliken population method, natural population analysis (NPA) and NBO were performed.

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ABSTRACT

The molecular structure and spectroscopic properties of (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol were investigated by X-ray diffraction, FT-IR and UV-vis spectroscopy. The vibrational frequencies calculatedusing DFT/B3LYP/6-31G(d,p) method. Results showed better agreement with the experimental values. The electronic properties was studied and the most prominent transition corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Two types of intramolecular hydrogen bonds are strong O–H···N interactions in enol-imine form and N–H···O interactions in keto-amine form are compared by using density functional theory (DFT) method with B3LYP applying 6-31G(d,p) basis set. Both enol-keto tautomers engender six-membered ring due to intramolecular hydrogen bonded interactions.

Geometry optimizations in solvent media were performed with the same level of theory by the polarizable continuum model (PCM). The effect of solvents on the tautomeric stability has been investigated. Stability of the molecule arises from hyperconjugative interactions, charge delocalization and intramolecular hydrogen bond has been analyzed using natural bond orbital (NBO) analysis. Molecular electrostatic potential (MEP) of the titled compound was studied for predicting the reactive sites. Mulliken population method and natural population analysis (NPA) have been studied. Population methods and MEP generally provides information regarding the chemical reactivity regions and charge distributions. Additionally, Frontier Molecular Orbitals analysis hasbeen performed from the optimized geometry. These orbitals also related to ionization potential, electron affinity, kinetic stability and hyperpolarizability of the molecule. The molecule exhibited good nonlinear optical (NLO) activity and first order hyperpolarizability. The predicted nonlinear optical properties of the title compound are 18 times greater than ones of urea.

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1. Introduction

Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activity [1,2] and can be classified according to their photochromic or thermochromic properties

* Corresponding author. Tel.: +90 362 312 1919. E-mail address: zeynep.kelesoglu@omu.edu.tr (Z. Demircioğlu). [3,4]. From observations on some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar [5,6]. o-hydroxy Schiff base ligands are of interest mainly because of the existence of typical hydrogen bonds and tautomerism between the O–H···N in enol-imine and N–H···O in keto-amine forms [7,8]. This compound undergoes tautomerism by proton transfer between the hydroxy O atom



and the imine N atom, namely the phenol-imine tautomer. Schiff bases are used as starting materials in the synthesis of important drugs such as antibiotics, antiallergics, antitumors and antifungals because of their biological activities [9,10]. In addition, their nonlinear properties have an importance for the design of various molecular electronic devices such as optical switches and optical data storage devices [11,12]. For Schiff bases, NLO studies provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [13–15].

A new (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol compound was synthesized and it was determined by single crystal X-ray diffraction technique. In the present study, it is planned to have a joint experimental and theoretical investigation of FT-IR and UV-vis spectra. According to X-ray, FT-IR and UV-vis results, the compound shows the enol-imine form, as well the theoretical results reveal the structure is more stable state in enolimine form rather than keto-amine form. Electronic absorption spectra of the title compound were predicted for enol-imine and keto-amine states by using TD-DFT (time-dependent density functional theory) [16–18] in the calculation of electronic excitation energies for gas and solution phases (different solvent media). The excitation energies, dipole moments, oscillator strengths and total energies were also obtained at TD-DFT level at the optimized geometry. Additionally, it was also planned to illuminate theoretical determination of the optimized molecular geometries, HOMO-LUMO energy gap, MEP, NLO, Mulliken charges, NPA and NBO analysis of the title compound by using density functional theory (DFT) with B3LYP/6-31G(d,p) basis set. In addition, the electronic properties of the titled molecule were calculated. The other important quantities such as ionization potential (I), electron affinity (A), electrophilicity index (w), chemical potential (μ), electronegativity (χ), hardness (η), and softness (S) are also evaluated in the way of molecular orbital framework. In the paper, all calculations are valuable for providing insight into molecular properties of Schiff base compounds.

2. Experimental and computational methods

2.1. Synthesis

For the preparation of (E)-2-([(3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol compound, the mixture of 2-hydroxy-6-methoxybenzaldehyde (0.5 g, 3.3 mmol) in ethanol (20 ml) and 3,4-dimethylaniline (0.4 g, 3.3 mmol) in ethanol (20 ml) was stirred for 2 h under reflux. The crystals suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield; 72%, m.p.; 364–366 K).

2.2. Instrumentation

The FT-IR spectrum of the title compound was recorded in the 4000–400 $\rm cm^{-1}$ region with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets. Absorption spectra were determined on Unicam UV–vis spectrometer.

2.3. Crystal structure determination

The single-crystal X-ray data were collected on a STOE IPDS II image plate diffractometer at 296 K. Graphite-monochromated MoK α radiation (λ = 0.71073 Å) and the ϖ -scan technique were used. The structure was solved by direct methods using SHELXS-97 [19] and refined through the full-matrix least-squares method using SHELXL-97 [20], implemented in the WinGX [21] program suite. Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were located in a difference Fourier map and were refined isotropically. Data collection: Stoe X-AREA [21], cell refinement: Stoe X-AREA [21], data reduction: Stoe XRED [22]. The general-purpose crystallographic tools PLATON [23] and ORTEP-3 [21] were used for the structure analysis and presentation of the results. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

2.4. Computational details

The molecular structure optimization of the titled compound and corresponding vibrational harmonic frequencies were calculated using B3LYP exchange correlation functional [24–30] which consist of the Lee–Yang–Parr correlation functional in conjunction with a hybrid exchange functional first proposed by Becke. The three-parameter hybrid exchange–correlation functional (B3LYP) [31] employing 6-31G(d,p) basis set [32–34] as implemented in Gaussian 03 package [35]. Gaussian 03 program package [36] was used without any constraint on the geometry with the double split valence basis set along with polarization functions; 6-31G(d,p).

By combining the results of the GAUSSVIEW [37] program with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy and the vibrations match quite well with the motions observed using the GAUSSVIEW program.

For calculating the excitation energies, dipole moments, oscillation strengths (*f*), wavelengths (λ) and energy gaps of the molecule, TD-DFT calculations started from gas phase and solution phases optimized geometries were carried out using the same level of theory. Theoretical UV-vis spectra of the titled compound in enol and keto forms were also obtained by TD-DFT excited state calculation. These calculations are also very important in determining solvent polarity effect on tautomerism. Solvent effects play an important role in absorption spectrum of the compound, in this paper, the integral equation formalism polarizable continuum model (PCM) [38,39] dealing with solvent effect was chosen in total energies, excitation energies, oscillator strengths, dipole moments and frontier orbital energies. The calculated values for solvents which are different dielectric constants, as well as two tautomers of enol-keto forms have also compared with experimental UV-vis spectrum results.

Table I			
Crystal data and	structure	refinement	parameters.

Chemical formula	C ₁₆ H ₁₇ N ₁ O ₂
Color/shape	Orange/Plate
Formula weight	255.31
Temperature	296 K
Crystal system	Monoclinic
Space group	P21/c
Unit cell parameters	a = 7.1788(14) Å
	b = 25.560(3) Å
	<i>c</i> = 7.4256(13) Å
	$\beta = 97.231(15)^{\circ}$
Volume	1351.7(4) Å ³
Z	4
Density	$1.255 { m Mg} { m m}^{-3}$
Absorption coefficient	0.083 mm^{-1}
Diffractometer/meas. meth.	STOE IPDS $2/\varpi$ -scan
θ range for data collection	1.6–27°
Unique reflections measured	2908
Total reflection/observed reflections	7617/1730
Goodness of fit on F^2	0.959
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.046, wR_1 = 0.116$
R indices (all data)	$R_2 = 0.088$, $wR_2 = 0.135$

HOMO-LUMO analysis has been used to clarify the information regarding charge transfer within the molecule. HOMO-LUMO energy gap provides important information about stability of the structure and non-linear optical properties. The polarizability (α), hyperpolarizability (β) and the electric dipole moment are calculated. Ionization potential (I), electron affinity (A), electrophilicity index (ω), chemical potential (μ), electronegativity (χ), hardness (η) , and softness (S) are calculated for determining the chemical reactivity.

The natural bond orbital (NBO) [40] analysis is being performed to estimate the delocalization pattern of electron density between the principal occupied Lewis-type (bond or lone pair) orbitals and unoccupied non-Lewis (antibond or Rydberg) orbitals.

Molecular electrostatic potential (MEP) analysis has been used to find the reactive sites of the compound. In addition, in this paper the net charges are calculated with Mulliken population method and natural population analysis (NPA). The calculated natural atomic charge values from the natural population analysis procedures are obtained from NBO analysis.

3. Results and discussion

3.1. Crystal structure and optimized geometry

The optimized molecular structure of the Schiff base with atom numbering scheme adopted in this study. The X-ray (experimental) and optimized (theoretical) geometry parameters, namely bond lengths and bond angles were calculated by B3LYP/6-31G(d,p) method.

The tautomerism appears in o-hydroxy Schiff bases as a result of intramolecular proton transfer from oxygen atom to nitrogen atom. This proton transfer resulted in two tautomeric structures in the solid state. These tautomeric forms are related to two types of intramolecular hydrogen bonds as O-H····N in enol-imine form and $N-H\cdots O$ in keto-amine form (Fig. 1).

Our X-ray investigations show that the (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol indicates double bond character of the C9=N1 and of C1-C2, C2-C3, C4-C5 and C1–C6 compared with the normal values for the aromatic benzene ring and the observed O1-C11 bond length is consistent with O-C single bond. Furthermore, the H1 atom is located on atom O1, thus the title compound exists in the enol form in the solid state.

The C=N double bond and C-O single bond lengths compare well with previously reported values for similar compounds [41– 43]. It is found that the molecule adopts E configuration about the C=N double bond.

As a result of enol-imine form, the molecule has strong O1-H1...N1 intramolecular hydrogen bonding (Fig. 2).

A significant intramolecular interaction (O1–H1···N1) is noted involving phenol atom O1 and nitrogen atom N1 and constitutes a six-membered ring S(6) [44]. The crystal packing of the title compound is mainly stabilized by C2–H2···O1ⁱ [symmetry code (i): 1 + x, y, z inter-molecular hydrogen bonding (Table 2). As can be seen in Fig. 3, molecules are linked with C-H--O chains.



Fig. 2. Ortep 3 diagram for (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol, with the atom numbering scheme. Dashed lines are show the O1-H1...N1 intra molecular hydrogen bonds.

Table 2	
Hydrogen bonding geometry for the titled compound	d.

D—H···A	D—H	H···A	D···A	D—H···A
01-H1···N1	0.94(3)	1.71(3)	2.579(2)	151(2)
C2-H2···02 ⁱ	0.93	2.6	3.336	137

D: donor; A: Acceptor (symmetry code: (i): 1 + x, y, z).

As an another way of confirming if title molecule exists in enol form, the harmonic oscillator model of aromaticity (HOMA) index is calculated by using Eq. (1) for benzene rings [45,46].

$$HOMA = 1 - \left[\frac{\alpha}{n} \sum_{i=1}^{n} (R_i - R_{opt})^2\right]$$
(1)

n is the number of bonds in ring, α is the constant equal to 257.7 and R_{opt} is equal to 1.388 Å for C–C bonds. For the purely aromatic compounds HOMA index is equal to 1 but, for non-aromatic compounds it is equal to 0. We calculated HOMA index of C1-C6 and C7-C12 rings. The calculated HOMA indices for C1-C6 and C10-C15 rings are 0.98 and 0.95, respectively. These results also indicate that the rings are the aromatic. X-ray results show that the dihedral angle between the planes of two aromatic rings is 24.68(5)° and in optimized geometry is 33.56°. The possibility for the title compound to exhibit thermochromic or photochromic properties is related to its planar or non-planar geometry. X-ray results shows the molecular structure of the compound is nearly planar. In addition, the dihedral angle between the nearly planar S(6) ring with C1-C6 and C9-C14 aromatic rings are 23.96(16)° and 0.83(15)°, respectively. The selected bond lengths, bond angles and torsion angles for the optimized structure in enol and keto forms of the molecule are listed in Table 3. As expected, the results show a little differences in experimental and computational processes. The differences observed between the experimental and calculated parameters are due to the ignored effects. These effects are



Fig. 1. Enol-imine and keto-amine tautomeric forms of titled compound.



Fig. 3. A partial packing diagram with C2–H2···O2ⁱ intermolecular hydrogen bonds shown as dashed lines [symmetry code: (i): 1 + x, y, z].

Table 3		
Bond lengths (Å), bond angles (°) and di	ihedral angles (°) obtained by X-ray	and DFT/B3LYP/631G(d,p).

Bond lengths (Å), bond angles (°) and torsions (°)	Experimental	DFT/631G(d,p) enol-imine	DFT/631G(d,p) keto-amine
C1N1	1.42(2)	1.408	1.40
N1-C9	1.28(2)	1.29	1.33
01–C11	1.35(2)	1.33	1.26
C9–C10	1.44(2)	1.44	1.39
C15–O2	1.36(2)	1.36	1.36
02–C16	1.41(2)	1.42	1.42
C4—C7	1.50(3)	1.51	1.50
C5—C8	1.51(3)	1.51	1.50
C1-C2	1.37(3)	1.40	1.39
C11–C12	1.39(3)	1.40	1.44
01-H1	0.94(3)	1.00	1.64
N1—H1	-	1.67	1.05
N1-C9-C10	122.44(17)	121.61	121.95
C9–C10–C15	120.39(16)	120.50	119.99
C15–O2–C16	118.46(15)	118.56	118.21
01–C11–C12	118.61(18)	118.54	122.05
01–C11–C10	120.57(17)	121.25	121.38
C6-C1-N1	117.95(18)	117.67	117.33
C8–C5–C4	120.9(2)	120.78	120.85
C7–C4–C3	120.3(2)	120.40	120.47
N1-C1-C2-H2	2.1(3)	-1.48	0.002
C10-C9-N1-C1	178.51(15)	117.18	-179.99
C6-C1-N1-C9	155.69(17)	149.38	180.008
C8–C5–C6–C1	178.36(19)	179.23	-179.99
C7–C4–C3–C2	179.42(17)	179.89	-180.00
C10-C15-02-C16	179.9(15)	-179.81	179.98
N1-C9-C10-C11	1.8(3)	-0.25	0.002
C9–C10–C11–O1	-0.3(3)	0.11	-0.002

the molecular interactions which the theoretical methods cannot take into account. While the experimental results belong to the solid state, the calculated results belong to the isolated gaseous phase.

Namely, the optimized geometry with B3LYP is preferred more planar conformation than X-ray geometry. The structural discrepancies between the optimized molecule and crystallographically observed geometry can be analyzed quantitatively by r.m.s. overlay. The r.m.s. fit of the atomic positions of experimental and calculated geometries are 0.105 Å and 0.289 Å, indicating the two geometries for enol-imine and keto-amine form, respectively. Fig. 4 shows the enol-imine form of overlay. Keto-amine geometry has bigger deviations than enol-imine, because of stretching and shortening the characteristic bonds.

As can be seen clearly from the results of the optimized molecular structure parameters that the effects of the intramolecular



Fig. 4. Superimposition of the X-ray structure (red) and calculated structure (black) of the titled molecule. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

proton transfer on the molecular geometry can be seen better via examining the changes in bond lengths for both forms. Table 3 shows that the changes occurred in the lengths of C11—O1 single and C9=N1 double bonds with the transfer process from enol form to keto form. While bond lengths of C11—O1 and N1—C9 for enol tautomer were found as 1.33 Å and 1.29 Å, these lengths for the keto tautomer were 1.26 and 1.33 Å, respectively. The intramolecular proton transfer affects the single and double characters of these indicative bonds.

3.2. Vibrational spectra

Vibrational wavenumbers were calculated based on the optimized geometries by using B3LYP level with the 6-31G(d,p) basis set. Experimental and calculated FT-IR spectrum of the title compound was given in Fig. 5 and vibration frequencies of compound are compared in Table 4. None of the predicted vibrational spectra have any imaginary frequency prove that optimized geometry is located at the lowest point on the potential energy surface. However, it is well known that DFT levels overestimate the vibrational frequencies due to the systematical errors. So, the vibrational frequencies were scaled by 0.9627 [47]. The frequencies obtained by theoretical method is in accordance with the observed FT-IR spectrum. Depending on the X-ray and IR results, the compound in the solid state exists in enol form.

The OH stretching vibration is very sensitive to inter- and intramolecular hydrogen bonds and lies in the region 3000–3500 cm⁻¹ in FT-IR spectrum. It gives rise to the three vibrations as stretching, in plane bending and out of plane bending vibrations. In 1700– 3000 cm⁻¹ region, the absorption band is attributed to the v(O-H) stretching vibration which broaden owing to the formation of strong intramolecular hydrogen bonding O1–H1…N1 in the structure. Generally, the $\gamma(O-H)$ rocking vibrations of phenols lie in the region 1300–1400 cm⁻¹. The band observed at 1493.56, 1403.57, 1348.28 cm⁻¹ was assigned to OH rocking vibration for the title compound. The absorption band located at 1616.72 cm⁻¹ for the title compound is attributed to v(C=N) stretching vibration.

The aromatic C—H stretching, C—H in plane bending and C—H out of plane bending vibrations appear in 3000–3100 cm⁻¹,

 $1100-1500 \text{ cm}^{-1}$ and $800-1000 \text{ cm}^{-1}$ frequency ranges, respectively. The absorption band at 3010.42 cm^{-1} corresponds to the aromatic C-H symmetric stretching vibrations of the title compound. In addition, in plane bending and out of plane C-H vibrations were observed at 1440.15-1566.47 cm⁻¹ and 821.88 cm⁻¹, respectively. The asymmetric and symmetric stretching vibrations of the C–H₃ group of the title compound were observed at 2960 and 2837.63 cm⁻¹. The C–O stretching vibrations in phenols are expected to appear as a strongest band in 1300-1100 cm⁻¹ frequency ranges. The absorption band observed at 1188.86 cm⁻¹ for the title compound was assigned to O–C stretching mode of vibration. The absorption bands at $1600-1400 \text{ cm}^{-1}$ are due to C-C stretching vibrations of the aromatic compounds. The C-C stretching modes of aromatic rings of the title compound were observed at 1599.22 cm⁻¹, which agree well with the literature data [48]. The other vibrational frequencies can be seen in Table 4. The calculated results show slight deviations from experimental values due to the intramolecular hydrogen bond between N and O atoms and other hydrogen bonding interactions.

3.3. Analysis of Frontier Molecular Orbitals (FMOs)

The highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are named as Frontier Molecular Orbitals (FMOs). The FMOs play an important role in the optical and electric properties, as well as in quantum chemistry and UV-vis spectra. HOMO, LUMO energy characterizes the ability of electron accepting. When we are dealing with interacting molecular orbitals, the two that interact are generally the highest energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the compound. These orbitals are a pair of orbitals in the compound, which allows them to interact more strongly. These orbitals are sometimes called the frontier orbitals, because they lie at the outermost boundaries of the electrons of compound. The frontier orbital gap helps characterize the chemical reactivity and the kinetic stability of the molecule. A molecule with a small frontier orbital gap is generally associated with high chemical reactivity and low kinetic stability and is also termed as soft molecule [49]. In addition, the FMOs



Fig. 5. Experimental (red) and theoretical DFT/B3LYP/631G(d,p) (black) FT-IR spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4

Experin	nental a	and c	alculate	ed vibr	ationa	l fre	quen	cies	(cn	n ⁻¹).	
											1

Experimental IR with KBr	DFT/B3LYP/631-G(d,p)	Assignments
1188.86	1092.23	v(C-02)
	1232.25	
3010.42	3082.18	υ symmetric (C–H) R1, R2
	3102.44	
	3116.98	
3000-3100	3055.1	υ asymmetric (C—H) R1, R2
	3070.65	
	3068.81	
1440.15	1506.25	β in plane (C—H) R1, R2
1566.47	1567.38	
	1594.75	
821.88	796.98	β out of plane (C—H) R1, R2
	858.79	
	871.67	
1460.88	1463.34	β out of plane (C—H ₃)
	1450.5	
3000-3500	2921.12	v(O1-H1)
	2926.01	
1493.56	1455.6	γ(O1-H1)
1403.57	1506.25	
1348.28	1567.38	
	1614.04	
2837.63	2911.25	υ symmetric (C–H ₃)
		methoxy
1616.72	1567.38	υ (N=C)
	1594.75	
	1614.04	
	1618.76	
2960.14	2974.14	υ asymmetric (C—H ₃)
		methoxy
	3012.4	
	3007.17	
	3034.8	
1348.26	1613.48	$\gamma(N=C-H)$
	1614.04	
	1343.81	
2900-3000	3007.3	υ(C9—H9)
2950.02	2970.74	v asymmetric (C—H ₃)
		methyl
	2965.24	
2800-2900	2921.91	v symmetric (C–H ₃) methyl
	2917.78	
1599.22	1618.76	υ(C—C) R1, R2
	1594.23	

^a ν, stretching; γ , rocking; β , bending. *Abbreviations*: R1, C1–C6; R2, C9–C14 phenyl ring.

are important in determining the ability of a molecule to absorb light.

The calculated energy values in the event of enol-imine form of HOMO and LUMO in gas phase are -5.55 eV and -1.45 eV, respectively, and the frontier orbital energy gap value is 4.09 eV. The calculations indicate that the titled compound has 68 occupied molecular orbitals. HOMO and LUMO energies and surfaces can be seen in Fig. 6.

The narrow energy gap between HOMO and LUMO facilitates intramolecular charge transfer which makes the material to be NLO active. In addition, FMOs are directly related to chemical hardness and softness of molecules. We will discuss each of these capabilities in detail later in this paper.

3.4. Molecular orbital theory studies

Quantum chemical calculations are used to determine electronegativity of pure s-, p- and d-states. Then, to obtain the atom's electronegativity, they are summarized according to the degree of atom orbital hybridization [50]. Mulliken was introduced a different formulation in terms of two other periodic properties,



Fig. 6. Molecular orbital surfaces and energies for the HOMO and LUMO.

namely the ionization potential and the electron affinity, and enabled the extension of this concept to molecules. Electron affinity refers to the capability of legend to accept precisely one electron from a donor. However in many kinds of bonding viz. covalent hydrogen bonding, partial charge transfer takes places. Considering the chemical hardness, large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of the molecule to hardness, which means that the molecule with least HOMO-LUMO gap is more reactive. According to optimized geometry, the ionization energy (I) and electron affinity (A) can be obtained from FMOs as, $I = -E_{HOMO}$ and $A = -E_{LUMO}$. Mulliken electronegativity (χ) can be calculated as follows: $\chi = (I + A)/2$. Softness (*S*) is a property of the molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness $S = 1/2\eta$. It is defined as the reciprocal of hardness (η) and $\eta = (I - A)/2$ [51]. The electrophilicity index (ω), $\omega = (-\gamma^2/2\eta)$ [52] is a measure of energy lowering due to maximal electron flow between donor and acceptor. The values of electronegativity, chemical hardness, softness, and electrophilicity index are 3.50 eV, 2.04 eV, 0.24 eV, -2.99 eV in gas phase, respectively, for the title molecule.

3.5. Molecular electrostatic potential (MEP) surface

The MEP surface generally provides information regarding the chemical reactivity of a molecule. The electrostatic potential generated in space around a molecule by the charge distribution is help-ful to understand electrophilic or nucleophilic properties [53]. The electrostatic potential V(r) at any point in space around a molecule by charge distribution is given by

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr'$$
(2)

where the summation runs over all the nuclei *A* in the molecule and polarization and reorganization effects are neglected. Z_A is the charge of the nucleus *A*, located at R_A and $\rho(r')$ is the electron density function of the molecule.

In the present study, 3D plots of molecular electrostatic potential (MEP) has been drew in Fig. 7. The MEP is a plot of electrostatic potential mapped onto the constant electron density surface.

The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The color code of these maps is in the range between -0.04676 a.u. (deepest red) and 0.04676 a.u. (deepest blue) in compound, where blue shows the



Fig. 7. Total electron density mapped with molecular electrostatic potential surface of (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol.

strongest attraction and red shows the strongest repulsion. Regions of negative V(r) are usually associated with the lone pair of electronegative atoms. According to MEP map results, the negative regions of whole molecule is located on donor oxygen atom and acceptor nitrogen atom (red coded region). Besides, the positive regions (blue encoded regions) of whole molecule are located on methyl group and the methoxy group attached to the carbonyl group and concentrated on the hydrogen atoms around. The negative potential regions are mainly over the electronegative N1 and O1 atoms. In addition, O2 atom is almost electron-poor region with orange color code. The MEP contour results show that the regions having the negative potential are over the electronegative atoms and the regions having the positive potential are over the hydrogen atoms. However, the H1 atom which is providing the proton transfer in the 6-membered ring has higher values than on the all other H atoms. As can be seen in Fig. 7, deepest red¹ on O1 atom is strongest attraction rather than the most blue region of H1 atom. So that we could not seen blue codes on H1 atom, effectively. As expected, it appears in yellow code. After all, red and blue areas in the MEP map refer to the regions of negative and positive potentials and correspond to the electron rich and electron-poor regions, respectively, whereas the green color signifies the neutral electrostatic potential. The MEP surface provides necessary information about the reactive sites

3.6. Mulliken population analysis and natural population analysis

The effective atomic charges calculation which depicts the charges of the every atom in the molecule distribution of positive and negative charges are vital to increase or decrease in bond length between the atoms. Atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity-basicity behavior and lot of properties of molecular system and electrostatic potential surfaces [54–57].

The total atomic charges of the Mulliken population analysis and the natural population analysis (NPA) are listed in Table 5. The Mulliken population analysis and NPA are obtained from optimized geometry and NBO [58] results, respectively. The two methods predict the same tendencies. As can be seen in results that all the hydrogen atoms have a net positive charge, the obtained atomic charge shows that the H1 atom has bigger positive atomic charge (0.33e; 0.51e) than the other hydrogen atoms. This is due to the presence of O1—H1…N1 strong intramolecular hydrogen bond.

|--|

Calculated net charges by Mulliken population method and natural population analysis (NPA).

Atom	B3LYP/6-31G(d,p) Mulliken charges	B3LYP/6-31G(d,p) (NPA) natural charges
C1	0.25	0.14
C2	-0.05	-0.25
C3	-0.09	-0.22
C4	0.04	-0.03
C5	0.03	-0.01
C6	-0.08	-0.22
C7	-0.34	-0.70
C8	-0.34	-0.70
C9	0.24	0.12
C10	-0.02	-0.23
C11	0.26	0.40
C12	-0.04	-0.31
C13	-0.05	-0.18
C14	-0.09	-0.36
C15	0.29	0.36
C16	-0.04	-0.32
N1	-0.60	-0.52
01	-0.55	-0.69
02	-0.55	-0.52
H1	0.33	0.51
H2	0.04	0.23
H3	0.03	0.23
H6	0.03	0.24
H7A	0.12	0.24
H7B	0.10	0.24
H7C	0.12	0.24
H8A	0.10	0.24
H8B	0.12	0.24
H8C	0.12	0.24
H9	0.08	0.22
H12	0.05	0.25
H13	0.05	0.24
H14	0.04	0.24
H16A	0.11	0.20
H16B	0.11	0.20
H16C	0.11	0.23

N1, O1 and O2 atoms are most negative atomic charges (-0.60e; -0.52e), (-0.55e; -0.69e), (-0.55e; -0.52e). Moreover, Mulliken atomic charges and natural population charges also show that the methyl group of C7 and C8 atoms has bigger negative atomic charges (-0.34e; -0.70e), (-0.34e; -0.70e) because of the steric effects.

According to these results, NBO's net charges are slightly longer than Mulliken charges. The intention is to accurately model partial charge magnitude and location within a molecule. Mulliken population analysis is a good way to account for differences in electronegativities of atoms within the molecule and frequently uses for supporting the MEP contour map. MEP and Mulliken population method can be used for interpreting and predicting the reactive behavior of a wide variety of chemical systems in both electrophilic and nucleophilic reactions.

3.7. UV-vis absorption spectra

TD-DFT at B3LYP/6-31G(d,p) level by adding polarizable continuum model (PCM) calculations were started from gas phase and solution phase. The energies of FMOs, absorption wavelengths (λ), oscillator strengths (f), and excitation energies of the compound were also determined from TD-DFT method and compared with the experimental values for enol–keto tautomerism.

The UV-vis spectra of the title compound in various organic solvents (benzene, chloroform, EtOH and DMSO) were recorded within 200–800 nm range (Fig. 8). The theoretical UV-vis absorption bands of the molecule for enol-imine and keto-amine forms

 $^{^{1}\,}$ For interpretation of color in Fig. 7, the reader is referred to the web version of this article.



Fig. 8. The solvent effect on UV-vis spectra of the titled compound in DMSO, ethanol and chloroform and benzene.

in gas phase, ethanol, DMSO, chloroform and benzene are comparatively given in Table 6. Absorbance values can be used to determine the concentration of a chemical or biological molecule in a solution using the Beer-Lambert Law. Beer's Law states that absorbance of a sample depends on the molar concentration (c), light path length in centimeters (L), and molar extinction coefficient (ε) for the dissolved substance at the specified wavelength (λ). Absorbance is also determined with *abs* = εcL equation. The resulting extinction coefficient values will be accurate for spectrophotometer, allowing the function as an accurate reference standard for samples of unknown concentration. Our concentration samples have different dielectric constants and dipole moments; benzene $\varepsilon = 2.3$, $\mu = 0$ D; chloroform $\varepsilon = 4.9$, $\mu = 1.04$ D; EtOH ε = 24.3, μ = 1.69 D and DMSO ε = 46.7, μ = 3.96 D, respectively. The greater the dielectric constant, the greater the polarity (in this paper; DMSO = high, gas phase = low). The second one comes from directly measuring the dipole moment. Protic solvents have O-H or N-H bonds. These solvents are important because protic solvents can participate in hydrogen bonding, which is a powerful intermolecular or intramolecular force. Additionally, these O-H or N-H bonds can serve as a source of protons (H+). Aprotic solvents may have hydrogens on them somewhere, but they lack O-H or N-H bonds, and therefore cannot hydrogen bond with themselves. Therefore, we give priority to these solvents because of chloroform and benzene is a nonpolar solvent, DMSO is a polar aprotic solvent. Besides, ethanol is a polar protic solvent acting as both hydrogen donor and acceptor. In light of this, as can be seen in Table 6, ethanol solution of title molecule's wavelength and excitation energy was increased sharply with decreasing polarity. Increasing values of total energies, energy gaps and dipole moments with the increasing polarity of the solvents were observed in the form of both enol-imine and keto-amine. Charge delocalization of the molecule increases with the increasing polarity of solvents, therefore, induces the dipole moments raised. However, excitation energies (λ) and oscillator strengths (f) were not changed linearly with increasing polarity. Furthermore, deviations from linearity are likely related to chemical properties for solvents and the other reasons have described above. (see Table 7).

With increasing polarity, $n \rightarrow \pi^*$ transitions are shifted to lower wavelengths and decreasing orbital energy. These shifts are due to unpaired electrons. In addition to these, with increasing polarity, $\pi \rightarrow \pi^*$ transitions are often (not always) shifted to higher wavelengths. As can be seen in Fig. 8, experimental electronic spectra involve all contributions to the transitions and the simulated spectra were given in graphical abstract. However, in this paper, we are interested in major contribution of first transition from HOMO to LUMO level. In addition, this first strict transition clarifies the enol-keto tautomerism. With respect to this, the first strong

Table 6

Electronic properties of calculated energies, excitation energies, oscillator strengths, dipole moments and frontier orbital energies for the enol-imine and keto-amine tautomerism.

	Gas phase	Benzene	Chloroform	Ethanol	DMSO
E _{TOTAL} (a.u.) Enol-imine form	-825.1828	-825.1771	-825.1798	-825.1818	-825.1819
E _{TOTAL} (a.u.) Keto-amine form	-825.1820	-825.1739	-825.1775	-825.1841	-825.1805
$E_{\rm HOMO}$ (eV)	-5.746	-5.663	-5.7108	-5.7462	-5.7519
E_{HOMO} (eV) Keto-amine form	-5.377	-5.239	-5.317	-5.375	-5.385
E_{LUMO} (eV) Epol-imine form	-1.631	-1.549	-1.5973	-1.6326	-1.6498
ELUMO (eV) Keto-amine form	-1.9237	-1.8325	-1.8910	-1.9335	-1.9427
ΔE (eV) Epol-imine form	4.1152	4.1130	4.1135	4.11357	4.1127
ΔE (eV) Keto-amine form	3.453	3.406	3.426	3.441	3.442
Excitation energy (nm)	342.24	345.07	344.08	342.74	344.25
Enol-imine form Excitation energy (nm)	412.89	420.71	417.93	414.92	416.74
Keto-amine form					
Experimental wavelength (nm)	-	319	308	231	318
Oscillator strength (f)	0.606	0.6035	0.6152	0.6026	0.6611
Enol-imine form Oscillator strength (f)	0.2384	0.2568	0.2486	0.236	0.2528
Keto-amine form					
μ (D) Enol-imine form	4.2454	3.6774	3.9492	4.1729	4.1910
μ (D) Keto-amine form	5.8190	4.8834	5.3203	5.6830	5.7154

absorption bands 319 nm, 308 nm and 318 nm are caused by $n \rightarrow \pi^*$ and the other one of moderately intense band 231 nm is due to $\pi \rightarrow \pi^*$ transitions. The strong absorption bands are correspond to less energy and the longer wavelengths.

In the UV-vis spectra of o-hydroxy Schiff base compounds, the presence of an absorption band at less than 400 nm indicates the enol imine tautomeric form. On the other hand, compounds adopt keto-amine tautomeric form show a new absorption band at greater than 320 nm [59,60]. It is clear from experimental results that there is no absorption band observed at greater than 400 nm region in any solvent for the title compound. UV-vis results supported that the molecule adopts the enol-imine form rather than keto-amine form. Theoretical UV-absorption spectra in different solvents were investigated and give results nearly similar to our experimentally measured ones.

The transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aromaticity of the benzene ring. The evaluation of the results was based on the oscillator strengths (*f*) which is greater than 0.6 and 0.2 in enol-imine form and keto-amine form, respectively. It is well known that $\pi \rightarrow \pi^*$ transition is shifted to long wavelength and low energy with increasing the solvent polarity. The reason of this shifting, the dipole moment of solvent is produced dipole moment over the solute matter.

On the other hand, the energy gap (ΔE) between the HOMO, LUMO and dipole moment increases with the polarity of the solvent. The energy gap (ΔE) is important to influence the stability

Table 7

Second order perturbation theory analysis of Fock matrix in NBO basis for (E)-2-([3,4-dimethylphenyl)imino]methyl)-3-methoxyphenol.

					-			
Donor(<i>i</i>) (occupancy)	Туре	ED _A (%) ED _B (%)	Acceptor(<i>j</i>) (occupancy)	Туре	ED _A (%) ED _B (%)	$E^{(2)a}$ (kcal/mol)	$E_j - E_i^{\mathbf{b}}$ (a.u.)	$F(ij)^{c}$ (a.u.)
BD C1-C2	σ	50.57	BD*C2–C3	σ^*	49.87	2.77	1.28	0.053
(1.97514)		49.43	(0.01378)		50.13	0.00		
RD C1-C2	σ	50.57	BD"C1-C6	σ^{*}	49.30	3.69	1.26	0.061
(1.97514)		49.43	(0.02247)		50.70			
BD C1–C2	π	49.10	BD*C3–C4	π^*	49.78	20.63	0.29	0.069
(1.64539)		50.9	(0.34444)		50.22			
BD C1-C2	π	49.10	BD*C5-C6	π^*	50.94	17.79	0.29	0.065
(164539)		50.9	(0.32312)		49.06			
BD C1-C2	π	49.10	BD*C9-N1	π^*	62.40	9.00	0.26	0.045
(164520)	70	50.0	(0.21709)	70	27.60	5.00	0.20	0.045
(1.04359)	_	50.9	(0.21708)	_*	57.00	2.15	1.20	0.057
BD CI-NI	σ	40	BD C9-C10	σ	51.53	3.15	1.28	0.057
(1.98335)		60	(0.02468)		48.47			
BD C1—N1	σ	40	BD*C1–C6	π^*	49.30	1.33	1.35	0.038
(1.98335)		60	(0.02247)		50.70			
BD C2-C3	σ	50.13	RY*C1	-	-	1.64	1.90	0.5
(1.97693)		49.87	(0.00704)					
BD C2–C3	σ	50.13	RY*C1	_	_	0.5	1.71	0.026
(197693)		49.87	(0.00579)					
BD C2-C3	G	50.13	BD*C4-C7	G *	50.67	3 21	1 1 1	0.053
(1.07602)	0	40.97	(0.02001)	0	40.22	5.21	1.11	0.033
(1.97093)		49.67	(0.02091)		49.55	4.20		0.000
BD C2-C3	σ	50.13	BD*CI—NI	σ^*	60	4.38	1.14	0.063
(1.97693)		49.87	(0.02821)		40			
BD C3-C4	σ	49.33	RY*C2	-	-	1.06	1.95	0.041
(1.97561)		50.67	(0.00384)					
BD C3-C4	σ	49.33	RY*C2	_	-	0.95	1.50	0.34
(197561)		50.67	(0.00264)					
BD C3-C4	π	50.07	BD*C1-C2	π^*	50.9	19.95	0.28	0.067
(1 (5 (2)	70	40.79	(0.20108)	Л	40.1	13.33	0.20	0.007
(1.03893)		49.76	(0.59108)	_*	49.1	20.0	0.20	0.000
BD C3-C4	π	50.22	BD-C5-C6	π^{-}	50.94	20.0	0.29	0.068
(1.65893)		49.78	(0.32312)		49.06			
BD C4-C7	σ	50.54	BD*C5-C6	σ^*	49.37	2.59	1.21	0.050
(1.98384)		49.46	(0.01885)		50.63			
BD C5-C6	σ	50.63	RY*C4	-	-	0.81	2.02	0.036
(1.97414)		49.37	(0.00480)					
BD C5-C6	σ	50.63	RV*C4	_	_	0.86	17	0.034
(1.97414)	0	10.37	(0.00337)			0.00	1.7	0.051
	~	45.57	(0.00557) RD*C4_C5	~ *	50.07	2 70	1.26	0.062
BD C5-C6	0		BD C4-C5	0	50.07	3./8	1.20	0.062
(1.97414)			(0.03035)		49.93			
BD C5-C6	π	49.06	BD*C3-C4	π^*	49.78	19.18	0.28	0.066
(1.67476)		50.94	(0.34444)		50.22			
BD C5-C6	π	49.06	BD*C1–C2	π^*	50.9	21.06	0.28	0.069
(1.67476)		50.94	(0.39108)		49.1			
BD C6-H6	σ	62.21	BD*C1–C2	σ^*	49.43	4.18	1.08	0.06
(1 97997)	-	37 79	(0.02952)	-	50.57			
(1.57557) PD C6_H6	æ	62.21	(0.02332) PD*C4	G *	50.07	1 7 1	1.09	0.061
	0	02.21	BD (4-C3	0	30.07	4.24	1.06	0.001
(1.97997)		37.79	(0.03035)		49.93	0.00		
BD C7—H7A	σ	62.17	BD*C3-C4	π^*	49.78	3.02	0.54	0.040
(1.98069)		37.83	(0.34444)		50.22			
BD C7—H7B	σ	62.12	BD*C4—C5	σ^*	50.07	4.03	1.08	0.059
(1.99069)		37.88	(0.03035)		49.93			
BD C7—H7C	σ	62.19	BD*C3–C4	π^*	49.78	2.95	0.54	0.039
(1.98072)	-	37 81	(0.34444)		50.22			
BD C9-C10	σ	48.4	BD*C1—N1	σ^*	60	42	1 13	0.062
(1.07426)	0	-101 51 50	(0.02921)	0	40	7.2	1.15	0.002
(1.97420)	_	31.33	(U.U2021) DV#C1		40	0.01	2.00	0.022
BD C9-NI	σ	39.91		-	-	0.61	2.08	0.032
(1.98706)		60.09	(0.00704)					
BD C9-N1	σ	39.91	RY*C1	-	-	2.57	1.9	0.059
(1.98706)		60.09	(0.00579)					
BD C9-N1	σ	39.91	BD*C1-N1	σ^*	60	1.71	1.33	0.043
(1.71811)		60.09	(0.02821)		40			
BD C9-N1	π	37.6	BD*C1-C2	π^*	50.9	11.21	0.37	0.062
(191173)		62.4	(0.39108)		49.1		,	0.002
BD (0-N1	π	27.6	BD*C10-C11	TF *	30.42	614	0.35	0.046
DD C9-INI (1.01172)	π	57.0		n	59.45	0.14	0.55	0.040
(1.911/3)		62.4	(0.45663)		60.57			
BD C10-C11	σ	51.45	BD*C15-02	σ^*	67.64	3.11	1.05	0.051
(1.97361)		48.55	(0.02783)		32.36			
BD C10-C11	π	60.57	BD*C9-N1	π^*	62.4	24.2	0.26	0.075
(1.59930)		39.43	(0.21708)		37.6			
BD C10-C11	π	60.57	BD*C12-C13	π^*	45.49	12.82	0.28	0.055
(1 59930)		39.43	(0.31952)		54 51			
PD C10_C11	-	55. 4 5	PD*C14_C15	# *	12 51	26.90	0.27	0.077
(1,50020)	л	20.37	DD C14-C13	n	45.34	20.09	0.27	0.077
(1.59930)		39.43	(0.38259)		56.46			
BD C10-C15	σ	50.79	BD*C14-C15	σ^*	50.46	3.39	1.26	0.059

Table 7	(continued)
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	Donor(<i>i</i>) (occupancy)	Туре	ED _A (%) ED _B (%)	Acceptor(<i>j</i>) (occupancy)	Туре	ED _A (%) ED _B (%)	E ^{(2)a} (kcal/mol)	$E_j - E_i^{b}$ (a.u.)	<i>F</i> (<i>ij</i>) ^c (a.u.)
BD C11-C12σ50.54RY 010.661.940.032BD C11-C12σ50.54BD C10-C11σ'48.552.921.230.054(1.97783)σ62.65BD C10-C11σ'48.554.371.050.061(1.97783)σ62.65BD C10-C11σ'48.554.371.050.061(1.97783)π53.51BD C10-C11σ'48.554.370.050.077(1.71850)π54.51BD C10-C11σ'35.40.320.056BD C12-C13π54.51BD C10-C11σ'66.123.520.056(1.71850)σ45.49(0.32259)66.123.521.100.056(1.97373)50.11(0.0777)38.80.570.6650.670.665(1.97533)50.44(0.0278)767.6450.21.050.065(1.97533)50.44(0.0278)7743.541.320.280.054(1.97533)50.44(0.0276)749.541.930.280.054(1.97533)50.44(0.0276)749.541.920.0560.75(1.97533)50.45BD C10-C11π'39.431.930.280.054(1.9956)780.5160.46BD C10-C1560.57749.541.370.056(1.9956)783.31(0.002.8)76.541.99 <td>(1.96814)</td> <td></td> <td>49.21</td> <td>(0.02487)</td> <td></td> <td>49.54</td> <td></td> <td></td> <td></td>	(1.96814)		49.21	(0.02487)		49.54			
(1.97783) 9.46 (0.00152) BD C11-C12 σ 49.46 (0.03441) 51.45 BD C12-C112 σ 62.65 BD C10-C11 σ' 48.55 4.37 1.05 0.061 (1.97783) 7.35 (0.03441) 51.45 1.45	BD C11-C12	σ	50.54	RY*O1	_	-	0.66	1.94	0.032
BD C11-C12 σ 50.54 BD C10-C11 σ' 48.55 2.92 1.23 0.054 BD C12-H12 σ 62.65 BD C10-C11 σ' 48.55 4.37 1.05 0.061 (1.9793) 73.5 (0.03441) - - 0.27 0.077 (1.9791) 7.5 (0.03441) - - 0.27 0.076 BD C12-C13 π 54.51 BD C10-C11 π' 39.43 24.72 0.27 0.056 (1.71830) - 45.49 (0.38259) - 56.46 - - - - 0.056 - 0.056 - - 0.056 - 0.057 - - 0.057 - 0.056 - 0.056 - 0.057 - 0.057 - 0.056 - 0.057 - 0.057 - 0.057 - 0.057 - 0.057 - 0.057 - 0.057 - 0.057 <t< td=""><td>(1.97783)</td><td></td><td>49.46</td><td>(0.00152)</td><td></td><td></td><td></td><td></td><td></td></t<>	(1.97783)		49.46	(0.00152)					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C11-C12	σ	50.54	BD*C10-C11	σ^*	48.55	2.92	1.23	0.054
BD C12-H12 σ 62.65 BD C10-C11 σ' 44.55 4.37 1.05 0.061 (1.9791) 37.35 (0.03441) π' 39.43 24.72 0.27 0.071 (1.71850) 45.49 (0.45663) π' 39.43 24.72 0.27 0.057 (1.71850) 45.49 (0.32259) 56.46 - - 0.057 (1.71850) - 45.49 (0.32259) 56.46 - - 0.056 (1.97537) - 50.1 (0.01787) 33.88 - - - 0.056 (1.97537) - 50.44 (0.02783) 3.38 - </td <td>(1.97783)</td> <td></td> <td>49.46</td> <td>(0.03441)</td> <td></td> <td>51.45</td> <td></td> <td></td> <td></td>	(1.97783)		49.46	(0.03441)		51.45			
	BD C12-H12	σ	62.65	BD*C10-C11	σ^*	48.55	4.37	1.05	0.061
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.97911)		37.35	(0.03441)		51.45			
	BD C12-C13	π	54.51	BD*C10-C11	π^*	39.43	24.72	0.27	0.077
BD C12-C13 π 54.51 BD C14-C15 π' 43.54 13.82 0.27 0.056 (1.71850) - 56.49 - 56.49 -	(1.71850)		45.49	(0.45663)		60.57			
	BD C12-C13	π	54.51	BD*C14-C15	π^*	43.54	13.82	0.27	0.056
BD C12-C13 σ 49.9 BD C11-O1 σ' 6.12 3.52 1.10 0.056 (1.97878) 50.1 (0.01787) 33.88 -	(1.71850)		45.49	(0.38259)		56.46			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C12-C13	σ	49.9	BD*C11-O1	σ^*	66.12	3.52	1.10	0.056
BD C13-C14 σ 9.56 BD C15-O2 σ [*] 67.64 5.02 1.05 0.065 (1.97533) 50.44 (0.02783) 32.36 30.75	(1.97878)		50.1	(0.01787)		33.88			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C13-C14	σ	49.56	BD*C15-02	σ^*	67.64	5.02	1.05	0.065
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.97533)		50.44	(0.02783)		32.36			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C14-C15	σ	49.54	BD*C10-C15	σ^*	49.21	4.00	1.25	0.063
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.98055)		50.46	(0.02676)		50.79			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C14-C15	π	56.46	BD*C10-C11	π^*	39.43	11.93	0.28	0.054
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.70374)		43.54	(0.45663)		60.57			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C14-C15	π	56.46	BD*C12-C13	π^*	45.49	23.54	0.3	0.075
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.70374)		43.54	(0.31952)		54.51			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C16-02	σ	31.63	BD* C10-C15	σ^*	49.21	2.80	1.37	0.056
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.99287)		68.37	(0.02676)		50.79			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C16-H16A	σ	61.09	RY* 02	-	-	0.68	1.59	0.029
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.99568)		38.91	(0.00228)					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C16-H16B	σ	61.07	RY* 02	-	-	0.68	1.59	0.029
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.99567)		38.93	(0.00228)					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BD C16-H16C	σ	61.73	BD*C15-02	σ^*	67.64	3.44	0.9	0.05
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.99077)		38.27	(0.02783)		32.36			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	CR C2	-	-	RY*C1	-	-	2.39	11.07	0.145
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.99903)			(0.00579)					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	LP O1	n	-	BD*C10-C11	π^*	39.43	41.39	0.32	0.109
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1.79518)			(0.45663)		60.57			
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	LP O2	n	-	BD*C14-C15	π^*	43.54	31.6	0.35	0.099
BD*C9-N1 π* 62.40 BD*C1-C2 π* 50.9 55.52 0.02 0.055 (0.21708) 37.60 (0.39108) 49.1	(1.96220)			(0.38259)		56.46			
(0.21708) 37.60 (0.39108) 49.1 BD*C10C11 π^* 39.43 BD*C12C13 π^* 45.49 236.94 0.01 0.083 (0.45663) 60.57 (0.31952) 54.51 64.51 64.51	BD*C9-N1	π^*	62.40	BD*C1-C2	π^*	50.9	55.52	0.02	0.055
BD*C10—C11 π* 39.43 BD*C12—C13 π* 45.49 236.94 0.01 0.083 (0.45663) 60.57 (0.31952) 54.51 54.51 54.51	(0.21708)		37.60	(0.39108)		49.1			
(0.45663) 60.57 (0.31952) 54.51	BD*C10-C11	π^*	39.43	BD*C12-C13	π^*	45.49	236.94	0.01	0.083
	(0.45663)		60.57	(0.31952)		54.51			
BD [*] C14C15 π [*] 43.54 BD [*] C12C13 π [*] 45.49 220.47 0.01 0.079	BD*C14-C15	π^*	43.54	BD*C12-C13	π^*	45.49	220.47	0.01	0.079
(0.38259) 56.46 (0.31952) 54.51	(0.38259)		56.46	(0.31952)		54.51			

Percentage electron density over bonded atoms (ED_{A,B}, %).

^a $E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).

^b Energy difference between donor (*i*) and acceptor (*j*) NBO orbitals.

^c F(i,j) is the Fock matrix element between *i* and *j* NBO orbital.

of a molecule and determines the chemical reactivity, kinetic stability, polarizability and chemical activity of a molecule [61]. If the molecule has a large energy gap, they are more stable molecule as a chemical activity. As a known fact that hard molecules have large energy gap and soft molecules have small energy gap, so soft molecules are more polaritable and more reactive than hard molecules. With respect to these results, title compound is more polarizable, more reactive and more soft molecule as related compounds [62,63].

3.8. Natural bond orbital (NBO) analysis

Natural bond orbital analysis provides an efficient method of studying intra- and intermolecular bonding and interaction among bonds and provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [64]. The bonding–anti bonding interaction can be quantitatively described in terms of the NBO approach that is expressed by means of second-order perturbation interaction energy $E^{(2)}$ [65–68]. This energy represents the estimate of the off-diagonal NBO Fock matrix element. The stabilization energy $E^{(2)}$ associated with $i(\text{donor}) \rightarrow j(\text{acceptor})$ delocalization is estimated from the second-order perturbation approach as given below:

$$E^{(2)} = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i} \tag{3}$$

where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) and F(i,j) is the off-diagonal Fock matrix element. 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 long pair) NBO orbitals and formally unoccupied (antibonding and Rydgberg) non-Lewis NBO orbitals corresponds to a stabilizing donor–acceptor interaction. The effect of substitution on the hydrogen bond strength, the charge distributions, steric effects, and electron delocalization can be also investigated by NBO method.

NBOs are localized electron pair orbitals for bonding pairs and lone pairs. The hybridization of the atoms and the weight of each atom in each localized electron pair bond are calculated in the idealized Lewis structure. If the occupancy is not 2, then there are deviations from an ideal Lewis structure. Strong electron delocalization in best Lewis structure will also show up as donor–acceptor interactions. Our calculation has done by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs. As a result of our study, the structure is a type of Lewis structure with 97.241% (core, 99.958%; valance Lewis, 96.188%) and non Lewis with 2.759% (Rydberg non-Lewis, 0.16%; valance non-Lewis, 2.599%).

As can be seen from these results, the π -conjugation/resonance due to π -electron delocalization is involved due to the $\pi \to \pi^*$ interactions, whereas the primary hyperconjugative interactions due to the various types of orbital overlaps such as $\sigma \to \pi^*$, $n \to \pi^*$, $n \to \sigma^*$ and secondary hyperconjugative interactions due to the orbital overlap $\sigma \to \sigma^*$. In theoretical calculations, all interactions can be observed successfully. However, only $\pi \to \pi^*$ and $n \to \pi^*$ interactions are also possible according to experimental results.

The interactions $\pi(C1-C2)$, $\pi(C3-C4)$, $\pi(C5-C6)$, $\pi(C10-C11)$, $\pi(C12-C13)$, $\pi(C14-C15)$ and their antibonding π^* interactions are responsible for conjugation of respective π -bonds in benzene rings. The electron density at the conjugated π bonds (1.59–1.91) of benzene rings and π^* bonds (0.32–0.45) of benzene rings indicates strong π -electron delocalization within ring leading to a maximum stabilization of energy ~26.89 kcal/mol. The charge transfer interactions are formed by the orbital overlap between bonding (π) and antibonding (π^*) orbitals, which results in intramolecular charge transfer (ICT) causing stabilization of the system. The movement of π -electron cloud from donor to acceptor i.e. ICT can make the molecule more polarized and it must be responsible for the NLO properties of molecule. Therefore, the titled molecule can be ideal material for non-linear optical applications in future.

The primary hyperconjugative interactions $\sigma(C1-N1) \rightarrow \pi^*$ (C1–C6), σ (C7–H7A) $\rightarrow \pi^*$ (C3–C4) and σ (C7–H7C) $\rightarrow \pi^*$ (C3–C4) are responsible for hydrogen interactions as O1-H1...N1 and methoxy groups steric interactions. The other primary hyperconjugative interactions lone pair NBO orbitals of $n(O1) \rightarrow \pi^*(C10-C11)$ and $n(O2) \rightarrow \pi^*(C14-C15)$ are stabilized to the molecule up to 41.3 kcal/mol and 31.6 kcal/mol, respectively. As can be seen from calculated results, the energetic contribution (\sim 0.5–2.5 kcal/mol) of hyperconjugative interaction is weak and the $E^{(2)}$ value is chemically significant and can be used as a measure of the intramolecular delocalization. The other important interaction energies of $\sigma \rightarrow \sigma^*$ denotes slightly contribution to the stability of the molecule. Thereby, hyperconjugative interaction values are around the (~1.1–4.39 kcal/mol). The energies for the interaction π^* (C9–N1) → $\pi^{*}(C1-C2), \pi^{*}(C10-C11) \rightarrow \pi^{*}(C12-C13) \text{ and } \pi^{*}(C14-C15) \rightarrow \pi^{*}(C14-C15)$ π^* (C12–C13) are 55.52, 236.94 and 220.47 kcal/mol, respectively. In addition to these, strong intramolecular hydrogen bond and sp³ hybridization at O2 atom which is bound to methyl group leads to an enormous stabilization energy. Besides, the higher stabilization of $E^{(2)}$ energy is related to the resonance in benzene rings. The efficient $\pi \to \pi^*$ and $n \to \pi^*$ interactions significantly influence crystal packing with titled molecule.

3.9. Nonlinear optical effects (NLO)

Molecule-based second-order nonlinear optical (NLO) materials have recently attracted much interest because they involve new scientific phenomena and because they offer potential applications in emerging optoelectronic technologies, telecommunications, information storage, optical switching and signal processing [69].

The output from GAUSSIAN03W provides 10 components of the $3 \times 3 \times 3$ matrix as β_{xxx} ; β_{xxy} ; β_{xyy} ; β_{yyy} ; β_{xxz} ; β_{yyz} ; β_{yyz} ; β_{yzz} ; β_{zzz} ; respectively, from which the *x*; *y* and *z* components of β are calculated as described earlier [70]. When reporting a single value of β ; one of the common formats is to simply treat the three independent values for β as a quasi Pythagorean problem and solve for the average β by the following equation.

$$\beta_{top} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \tag{4}$$

Table 8

Calculated dipole moments (μ), polarizability (α) and first hyperpolarizability (β) components for the title compound.

$\mu_x = -0.13$ a.u.	$\beta_{xxx} = -781.45 \text{ a.u.}$
$\mu_y = 1.22 \text{ a.u.}$	$\beta_{xxy} = 89.581$ a.u.
$\mu_z = 0.24$ a.u.	$\beta_{xyy} = 6.291$ a.u.
μ_{tot} = 1.26 Debye	$\beta_{yyy} = -35.76 \text{ a.u.}$
	$\beta_{xxz} = 82 \text{ a.u.}$
$\alpha_{xx} = 347.09 \text{ a.u.}$	$\beta_{xyz} = 13.14 \text{ a.u.}$
$\alpha_{xy} = 8.311$ a.u.	$\beta_{yyz} = -27.86 \text{ a.u.}$
$\alpha_{yy} = 192.98$ a.u.	$\beta_{xzz} = 9.43 \text{ a.u.}$
α_{xz} = 2.26 a.u.	$\beta_{yzz} = 29.23 \text{ a.u.}$
$\alpha_{yz} = -7.38$ a.u.	$\beta_{zzz} = 33.66 \text{ a.u.}$
$\alpha_{zz} = 90.04 \text{ a.u.}$	β_{tot} = 6.71 × 10 ⁻³⁰ cm ⁻⁵ /esu
$\alpha_{tot} = 31.12 \text{ Å}^3$	

The total static dipole moment μ , the average linear polarizability α , and the first hyperpolarizability β can be calculated by using Eqs. (5)–(7), respectively.

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^2 \tag{5}$$

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2 \tag{6}$$

$$\beta_{\text{tot}} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx} \right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy} \right)^2 \right]^{1/2}$$
(7)

The dipole moment, polarizability and the first hyperpolarizability were calculated using polar = ENONLY at the level of B3LYP/6-31G(d,p) and the results obtained from calculation. As can be seen in Table 8, calculated values of electronic dipole moment (μ), polarizability (α), and the first hyperpolarizability (β) are 1.26 Debye, 31.12 Å³ and 6.71 × 10⁻³⁰ cm⁵/esu, respectively. These results are greater than those of urea (α and β of urea of 3.83 Å³ and 0.37 × 10⁻³⁰ cm⁵/esu), respectively [71]. We can determine that the studied structure exhibited good nonlinear optical activity and first hyperpolarizability was 18 times greater than that of urea.

The small HOMO–LUMO energy gap for the title compound indicates that molecular charge transfer occurs in the compound. Energy gap is small and it is easy to notice that they can be sensitive to the influence of the polar environment. Determination of the energy gap, the dipole moment, the polarizability and the first hyperpolarizability explain that NLO analysis shows that the molecule is a material which can be used as an effective NLO material.

4. Conclusion

In the present work, the compound is experimentally characterized by means of X-ray diffraction, FT-IR and UV–vis spectroscopic techniques. It is concluded on the basis of X-ray and FT-IR investigations that the title compound exists in enol form in the solid state. All theoretical calculations is performed with DFT/B3LYP/6-31G(d,p). The theoretically calculated values of both bond lengths and bond angles of the structure of the minimum energy were investigated and then enol–keto tautomers were compared with X-ray crystallographic data.

The vibrational frequencies of the fundamental modes of the compound have been precisely assigned and analyzed, and the theoretical results were compared with the experimental vibrations. The net charge distribution of title compound was calculated by the Mulliken population method and natural population analysis with B3LYP/6-31G(d,p) basis set. The MEP map contour shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. The electronic absorption spectrum was calculated by TD-DFT method for enol-imine and keto-amine tautomers. Molecular orbital coefficient analyses suggest that the electronic spectrum corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. In order to understand electronic transitions of the molecule, TD-DFT calculations on electronic absorption spectra in several solvents and gas phase were performed comparatively. Computational and experimental UV-vis studies for various organic solvents of different polarities indicate that the stability of the molecule increases upon an increase in the polarity of solvent. The experimental results show that the molecule exists enol form even in solvent media. Solvent effects on intramolecular proton transfer have been examined. The movement of π -electron cloud from donor to acceptor i.e. intramolecular charge transfer can make the molecule more polarized and the HOMO-LUMO energy gap must be responsible for the NLO properties of molecule. The title compound exhibited good NLO property and was much greater than that of urea. We can conclude that the titled molecule is an attractive object for future studies of non-linear optical properties. The values of electronegativity, chemical hardness, softness, and electrophilicity index have been calculated. According to stability of the molecule to softness, which means that the molecule with least HOMO-LUMO gap and means that it is more reactive molecule. Natural bond orbital (NBO) calculations reveal the delocalization or hyperconjugation interaction, intramolecular charge transfer and stabilization energy of molecule. According to NBO results, we can determine the ideal Lewis type structure. This ideality has also been arised percentage of valence hybrids of the atoms and the weight of each atom in each localized electron pair bond, clearly. We hope all conclusions of this study will help researchers to analyze and synthesize new materials.

Supplementary material

CCDC 965354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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