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Research Article

Combined X-Ray, IR, Intramolecular Proton Transfer and Quantum Chemical Studies on (E)-2-Bromo-4-Methoxy-6-[(P-Tolylimino)Methyl]Phenol

(E)-2-Bromo-4-Metoksi-6-[(P-Tolilimino)Metil]Fenol Üzerine X-Işını, IR, Molekül İçi Proton Transferi ve Kuantum Kimyasal Hesaplamalar

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Abstract

In this work, molecular structure of (E)-2-Bromo-4-methoxy-6-[(p-tolylimino) methyl] phenol which is an o-hydroxy Schiff base derivative was characterized by X-ray single crystal diffraction, IR spectroscopy. In the quantum mechanical calculations, the density functional theory (B3LYP) with 6-31G (d, p) was used to support our studies. According to the X-ray crystallographic data, it was observed that adopts the phenol-imine tautomeric form of the compound in solid state.

The two possible tautomeric forms of the title compound were investigated using DFT method with B3LYP applying 6-31G(d, p) basis set. A relaxed potantial energy surface (PES) scan was performed based on the optimized geometry of the OH tautomeric form and O–H bond distances were used as the redundant internal coordinate. PES scan process helped us for understand the effects of transfer on the molecular geometry. At the same time, in this study, nonlinear optical properties (NLO) of the molecule were investigated.

Keywords: Density functional theory (DFT), Nonlinear optical properties (NLO), Schiff base, Tautomerism

Öz

Bu çalışmada, o-hidroksi Schiff Bazı türevi olan (E)-2-Bromo-4-metoksi-6-[(p-tolilimino)metil]fenol molekülünün moleküler ve kristal yapısı tek kristal X-ışını kırınımı ve IR spektroskopileri ile karakterize edildi. Kuantum mekaniksel hesaplamalarda Yoğunluk Fonksiyoneli Teorisi B3LYP/6-31G(d,p) baz seti kullanılarak çalışmalarımız desteklendi. X-ışını kristalografisi verilerine göre bileşiğin katı halde fenol-imin tautomerik formu benimsediği gözlenmiştir.

Molekülün iki tautomerik formu da DFT/B3LYP/6-31G(d,p) yöntemi kullanılarak incelenmiştir. Potansiyel enerji yüzeyi (PES) taraması OH tautomerik formun optimize geometrisi üzerinden gerçekleştirilmiştir ve içsel koordinat olarak O–H bağ uzunluğu kullanılmıştır. PES süreci, bizlere moleküler geometri üzerinde proton transferi etkilerini anlamak için yardımcı olur. Aynı zamanda bu çalışmada, molekülün doğrusal olmayan optik (NLO) özellikleri de incelenmiştir.

Anahtar Kelimeler: Yoğunluk fonksiyoneli teorisi (DFT), Doğrusal olmayan optik özellikler (NLO), Schiff bazı, Tautomerizasyon

1. Introduction

o-Hydroxy Schiff bases derived from the reactions of *o*-hydroxyaldehydes with aniline have been examined extensively (Calligaris et al. 1972, Maslen and Waters,1975). Schiff bases play a major role in many fields, e.g., as ligands in the field of coordination chemistry (Garnovskii et al. 1993, Calligaris and Randaccio 1987), as starting materials in synthesis of important drugs (antibiotics, antiallergics, antitumors and antifungals) in pharmacy (Lozier et al. 1975, Das et al. 1999, Ren et al. 2002, Ren et al. 2000), as new organic materials in nanotechnology (Hadjoudis et al. 1987, Hadjoudis 1995). The Schiff base compounds have been under investigation for several years because of their potential application to optical communications and because many of them can be suitable non-linear optical (NLO) active materials (Jalali-Heravi et al. 1999, Nicoud and Twieg 1987, Tanak and Toy 2013).

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Schiff bases exist in two possible tautomeric forms known as phenol-imine (OH) and keto-amine (NH) (Fig. 1). Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O–H···N in phenol-imine (Petek et al. 2007, Yüce et al. 2004) and N–H···O in keto-amine (Şahin et al. 2005) tautomers.

The presence of *ortho* hydroxyl group, photo- and thermochromism may involve reversible proton transfer from the hydroxy O atom to the imine N atom and this process associated with a change in π-electron configuration under the influence of light or temperature (Cohen et al. 1964, Moustakali-Mavridis et al. 1978, Hadjoudis et al. 1987). The proton transfer process shows that position of the tautomeric equilibrium also depends on the electronic structure of the molecule with its conformation.

To the best of our knowledge, neither the synthesis nor the theoretical studies on the compound of (*E*)-2-Bromo-4-methoxy-6-[(*p*-tolylimino)methyl] phenol have been available until now. We believe that our paper will be useful for the design and synthesis of new materials.

2. Material and Methods

2.1. Synthesis

For the preparation of (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino)methyl]phenol compound the mixture of 3-bromo-2-hydroxy-5-methoxybenzaldehyde (0.5 g, 2.16 mmol) in ethanol (20 ml) and 4-methylaniline (0.23 g, 2.16 mmol) in ethanol (20 ml) was stirred for 1 h under reflux. The crystals suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield 72% ; m.p. 275-277 K).

2.2. Instrumentation

The FT-IR spectrum of the title compound was recorded in the 4000-400 cm^{-1} region with a Bruker Vertex 80V FT-IR spectrometer using KBr pellets.

2.3. Crystal Structure Determination

The single-crystal X-ray data were collected on a STOE IPDS II image plate diffractometer at room temperature (296 K). Graphite-monochromated Mo K_α radiation (λ = 0.71073 A) and the w-scan technique were used. The structure was solved by direct methods using SHELXS-97 (Sheldrick 2008) and refined through the full-matrix least-squares method using SHELXL-97 (Sheldrick 2008), implemented in the WinGX (Farrugia 1999) program suite. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atom H1 was located in a difference Fourier map and refined isotropically, and the other H atoms were positioned geometrically and treated using a riding model. Data collection: Stoe X-AREA (Stoe 2002), cell refinement: Stoe X-AREA, data reduction: Stoe X-RED32 (Stoe 2002). The general-purpose crystallographic tool ORTEP-3 (Farrugia 1997) was 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 Procedure

All quantum chemical calculations were performed with the Gaussian 09W software package (Gaussian09 2009) and GaussView visualization program (Dennington et al. 2009) on a personel computer. Starting coordinates of the title molecule were taken from the X-ray geometry. In order to perform geometrical optimization and theoretical calculations of the title molecule, DFT method with Becke's three parameters hybrid exchange-correlation functional (B3LYP) (Lee et al. 1988, Becke 1993) at 6-31G(d,p) basis set (Schlegel 1982, Hehre et al. 1972) was used. The vibrational frequencies of the optimized molecule were also calculated at the same level of the theory and achieved frequencies were scaled by 0.9627 (Merrick et al. 2007). A relaxed potential energy surface (PES) scan was performed on the basis of the optimized geometry of the

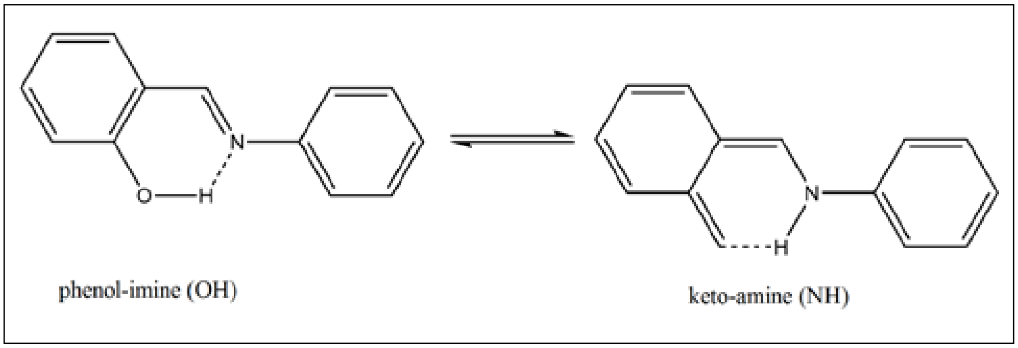

Figure 1. Enol-imine (OH) and keto-amine (NH) forms of *o*-hydroxy Schiff bases.

Table 1. Crystal data and refinement parameters of the title compound.

Formula	$C_{15}H_{14}Br_1N_1O_2$
Formula weight	320.18
Crystal color	Fire brick
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
Z	4
a, b, c	9.6367 (9), 14.1722 (11), 10.4610 (10)
α, β, γ	90°, 105.790°, 90°
Volume	1374.8 (2) Å^3
Radiation type	MoKα
μ	2.99 mm^{-1}
T_{max}, T_{min}	0.4487, 0.1825
Measured reflections	9184
Independent reflections	2847
Reflections with $I>2\sigma(I)$	1863
Number of parameters	176
θ_{max}, θ_{min}	26.50°, 2.02°
Scan range	-12 < h < 12, -17 < k < 17, -13 < l < 12
$R[F^2 > 2\sigma(F^2)]$	0.049
$wR(F^2)$	0.088
S	1.038
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.339, -0.292

OH tautomeric form by varying O1-H1 bond distance as a redundant internal coordinate from 0.99 to 1.85 Å with 18 steps of 0.05 Å. In the PES scan process, all of the remaining internal coordinates were fully optimized. Furthermore, NLO was performed at the same level of theory.

3. Results and Discussion

3.1. Description of the Crystal Structure

An ORTEP- 3 view of the compound indicating atom numbering scheme with thermal ellipsoids at 30% probability is shown in Fig. 2 and crystal data collection and refinement details of the compound are listed in Table 1. Selected bond lengths, bond angles and torsion angles obtained from X-ray diffraction are listed in Table 2.

The title compound contains the six membered rings (C1/C6 and C9/C14) and the imine frame. Acording to the X-ray results, the molecular geometry of the compound is non-planar with the dihedral angle between the aromatic rings of 28.66°. It is also known that Schiff bases may show thermochromism and photochromism depending on the planarity or non-planarity, respectively (Hadjoudis et al.1987, Moustakali-Mavridis et al. 1980). Therefore, it can be said that the title compound displays photochromic tendency.

In general, *o*-hydroxy Schiff bases exhibit two possible tautomeric forms in the solid state, namely, phenol-imine (OH) that is a tautomeric form has O–H···N intramolecular hydrogen bond and keto-amine (NH) that is the other tautomeric form has N–H···O intramolecular hydrogen

Table 2. Selected bond lengths (Å), angles and torsion angles (°) obtained from X-ray diffraction.

Parameters		Parameters	
C8 C9	1.456 (5)	C8 N1 C1	120.8 (3)
N1 C8	1.276 (4)	N1 C1 C2	123.9 (3)
N1 C1	1.421 (4)	O1 C10 C9	122.6 (3)
C10 O1	1.345 (4)	C10 C11 Br1	118.5 (3)
C11 Br1	1.890 (4)	C10 O1 H1	102.0 (3)
C13 O2	1.371 (4)	O1 H1 N1	157.0 (4)
C15 O2	1.398 (4)	N1 C8 C9 10	0.5 (6)
O1 H1	0.804 (1)	C2 C1 N1 C8	-26.7 (6)
O1 N1	2.587 (4)	C9 C8 N1 C1	176.1 (4)
N1 H1	1.830 (2)	O1 C10 C11 Br1	-2.1 (5)
C8 C9 N1	121.5 (4)	C8 C9 C10 O1	3.1 (5)
C8 C9 C10	120.4 (3)		

bond. As it can be seen in Fig. 2 and Table 2, the molecule has adopted the phenol- imine tautomeric form due to the position H1 atom which is located on atom O1. Furthermore, the C10–O1 [1.345(4)Å], C8–C9 [1.456(5)] and C8–N1 [1.276(4)Å] bonds are the most sensitive indicators of the tautomeric form of the title molecule. These bond distances are in good agreement with literature values (Karadayı et al. 2003, Yazıcı et al, 2009).

In order to investigate the aromaticity of the both rings which must be aromatic in the phenol- imine form, HOMA (harmonic oscillator model of aromaticity) index for the rings of the molecule is defined by the following equation (Kruszewski and Krygowski 1972, Krygowski 1993):

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

where n is the number of bonds in ring, α is the normalization constant is equal to 257.7 and R_{opt} is equal to 1.388 Å for C-C bonds. The HOMA index is equal to 0 for non-aromatic systems and 1 for the purely aromatics. We calculated HOMA index of C1/C6 and C9/C14 rings. The calculated HOMA indices for C1–C6 and C9–C14 are 0.98 and 0.97, respectively.

These results also indicate that the rings are the aromatic and (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] exists in phenol- imine form.

In the molecule, atom H1 bonded to O1 forms a strong intramolecular hydrogen bond with atom N1 [D···A=2.587(4) Å] and this hydrogen bond which is quite common between the *o*-hydroxysalicylidene systems generates an S(6) ring motif (Table 3). The distance between the O1 and N1 atoms is meaningfully shorter than the sum of the van der Waals radii for O and N [3.07 Å] (Bondi 1964). The neighboring molecules interact with each other via weak van der Waals interactions in three dimensions.

3.2. Optimized Geometries of Tautomers and Intramolecular Proton Transfer Process

The geometric parameters for (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] were calculated at B3LYP/6-31G (d,p) level of the theory in gas phase and listed in Table 4. As can be seen from Table 2 and Table 4, experimental and theoretical parameters of phenol-imine (OH) form are in good agreement except for some minor differences. These differences are due to the ignored effects in the gas phase. In the theoretical studies are not taken into account the intermolecular interactions in the crystal. Since these interactions are ignored, the planarity of the molecule is also affected. The dihedral angle between the aromatic rings is 33.28° for optimized OH tautomer. Due to the absence of the strong intermolecular interactions in the title molecule experimental end theoretical dihedral angles are not very different from each other.

To determine the conformational harmony between the observed and calculated geometries these geometries are superimposed (Fig. 3) and RMSE (the root mean square error) is found to be about 1.9 x 10^{-1} Å.

Table 3. Hydrogen bonding geometry for the titled compound (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
O1-H1···N1	0,804(2)	1,83 (2)	2,587(4)	157(4)

***D:** donor; **A:** Acceptor.*

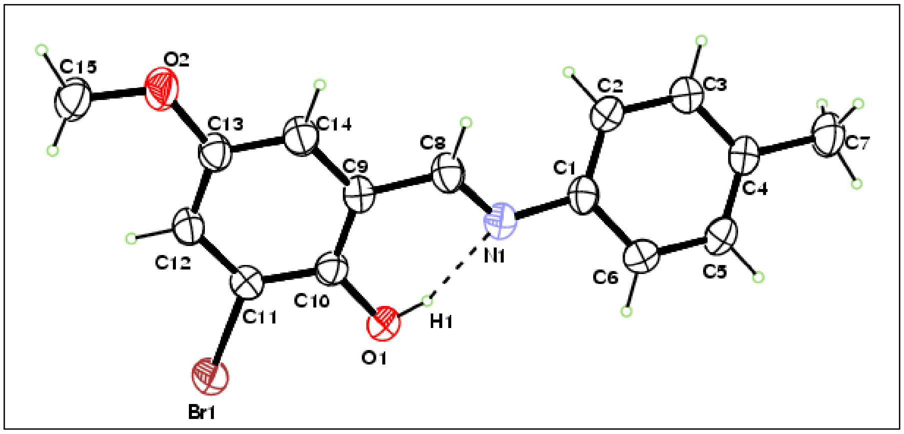

Figure 2. Ortep 3 diagram for (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl], with the atom numbering scheme. Dashed lines are show the O1-H1···N1 intra molecular hydrogen bonds.

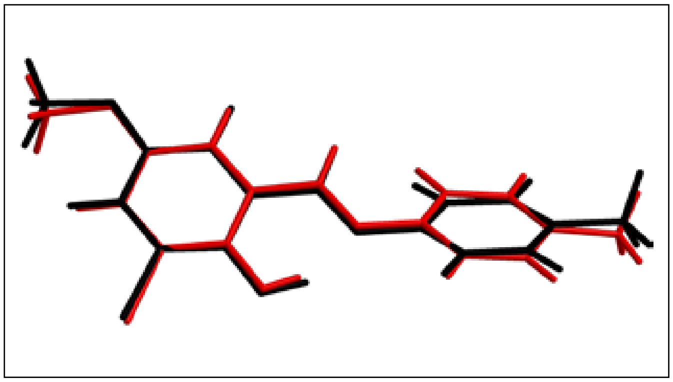

Figure 3. Superimposition of the X-ray structure (red) and calculated structure (black) of the title molecule.

The total energies, frontier orbital energies and dipole moments of phenol and keto forms of the title molecule in vacuo and in various solvents are tabulated in Table 5. When we examined the energetic behavior of both tautomeric forms of (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl], we saw that the total molecular energies and dipole moments of the tautomers increase with the rising polarity of the solvent.

As can be seen in Table 5, OH form is stable than NH form in gas phase with an energy differences of 4.393 kcal/mol. This result is assosiated with that the phenol form has two aromatic rings and the *o*-hydroxy Schiff bases are generally

Table 4. Selected bond lengths (Å), angles and torsion angles (°) in gas phase and various solvents obtained from the DFT/B3LYP/6-31G(d,p) calculations.

Parameters	Gas		$CHCl_3$		EtOH		H_2O	
	OH	NH	OH	NH	OH	NH	OH	NH
C8 C9	1.453	1.403	1.455	1.405	1.456	1.412	1.456	1.401
N1 C8	1.291	1.330	1.292	1.320	1.292	1.323	1.292	1.321
N1 C1	1.408	1.405	1.410	1.411	1.410	1.411	1.410	1.409
C10 O1	1.338	1.263	1.342	1.270	1.343	1.272	1.343	1.276
C11 Br1	1.905	1.904	1.912	1.915	1.913	1.917	1.914	1.915
C13 O2	1.368	1.372	1.368	1.371	1.368	1.373	1.367	1.370
C15 O2	1.419	1.417	1.423	1.424	1.425	1.423	1.425	1.426
O1 H1	0.998	1.639	1.004	1.683	1.006	1.687	1.006	1.681
O1 N1	2.618	2.555	2.599	2.590	2.593	2.588	2.593	2.586
N1 H1	1.714	1.051	1.685	1.042	1.676	1.044	1.675	1.048
C8 C9 N1	122.2	122.3	121.6	121.9	121.4	122.3	121.3	121.9
C8 C9 C10	120.6	118.9	120.6	118.7	120.6	119.6	120.6	118.8
C8 N1 C1	121.5	128.5	121.8	127.2	121.9	128.5	121.9	128.2
N1 C1 C2	123.5	123.4	123.5	123.4	123.6	123.1	123.6	123.0
O1 C10 C9	122.3	122.5	122.0	122.5	121.9	122.7	121.9	122.3
C10 C11 Br1	118.9	117.3	118.7	117.2	120.6	117.0	118.7	117.3
C10 O1 H1	106.8	103.2	106.2	102.1	106.1	102.6	106.1	103.7
O1 H1 N1	148.4	142.7	149.3	140.9	149.5	141.5	149.5	141.1
N1 C8 C9 C10	-0.2	0.0	-0.8	0.0	0.1	-0.0	-0.1	0.0
C2 C1 N1 C8	-32.6	-3.7	-30.8	-4.2	-29.7	-4.6	-29.6	-3.0
C9 C8 N1 C1	177.4	179.8	177.8	178.7	178.1	179.7	177.8	179.7
O1 C10 C11 Br1	-0.1	-0.1	-0.0	-0.2	-0.2	-0.1	-0.1	-0.0
C8 C9 C10 O1	0.2	0.0	-0.3	0.1	0.1	0.1	0.1	0.0

chose the phenol form (Albayrak et al. 2013). In order to investigate the effects on the molecular structure of the intramolecular proton transfer a PES scan process was carried out for the title compound in the gas phase at the B3LYP/6-31G(d,p) level. The scan process was started from optimized enol geometry by selecting O-H bond as redundant internal coordinate. Dependency of the relative energy of the title compound against the O-H bond distance is given in Fig. 4.

The energy values were calculated relative to the energy of stable phenol form. As can be seen from the Fig. 4. there are two minima representing the stable forms. One of them is a local minima refers to the NH form of the compound, second and deeper one is a global minima represents the stable phenol form. The potential energy needed for the transition from phenol form to keto form was determined as 5.810 kcal/mol.

The effects of the intramolecular proton transfer on the molecular geometry can be seen better via examining the changes in HOMA index of C9/C14 ring and indicative bond lengths for every step in the scan process. During the proton transfer, in the indicative bond lengths (C8=N1, C9–C8 and C10–O1) the changes are observed (Fig.5). These

Table 5. Calculated energies, frontieer orbital energies and dipole moments in gas phase and various solvents.

	Gas	$CHCl_3$	EtOH	H_2O
OH				
E_{total} (a.u.)	-3356.948	-3356.959	-3356.961	-3356.962
E_{LUMO} (eV)	-1.8558	-1.8738	-1.8890	-1.8839
E_{HOMO} (eV)	-5.5010	-5.6159	-5.6272	-5.6307
ΔE (eV)	3.6452	3.7421	3.7382	3.7468
μ (D)	3.5586	4.7598	5.1158	5.1791
NH				
E_{total} (a.u.)	-3356.941	-3356.955	-3356.959	-3356.960
E_{LUMO} (eV)	-2.1707	-2.2256	-2.2448	-2.2343
E_{HOMO} (eV)	-4.9572	-5.1253	-5.1410	-5.1732
ΔE (eV)	2.7865	2.8996	2.8963	2.9388
μ (D)	4.6537	6.3986	7.0331	7.4932

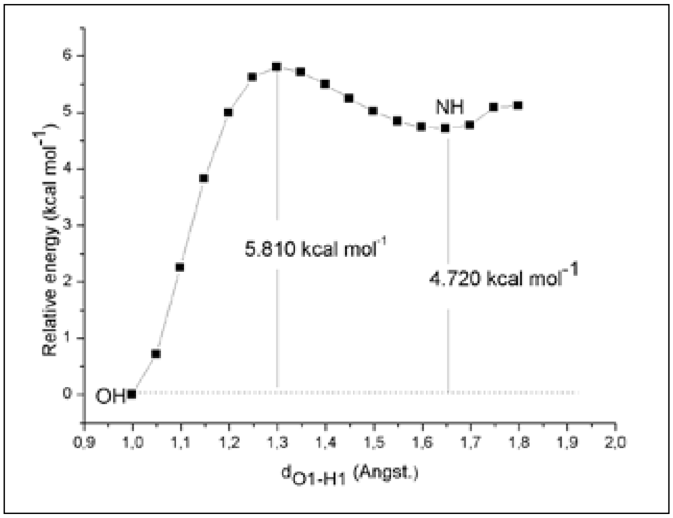

Figure 4. Relative energy versus the redundant coocrdinate in PES scan process.

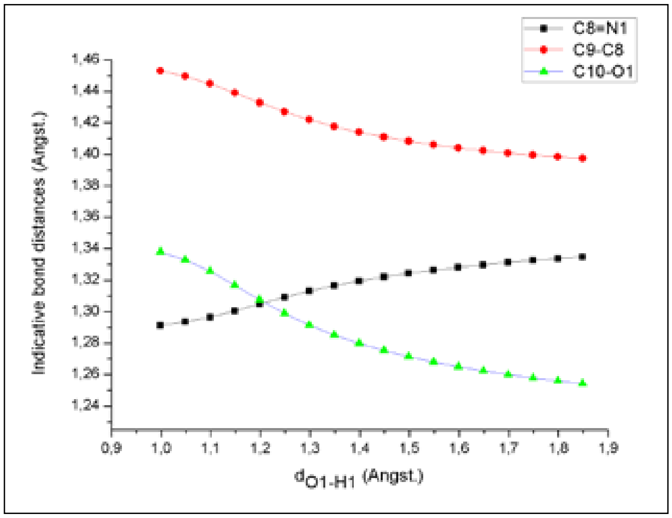

Figure 5. Indicative bond lengths versus the redundant coordinate in PES scan process.

changes are due to the changed electronic distrubition of the molecule in the transfer process. Bond lengths of stable phenol form, C8=N1 (1.291 Å), C9–C8 (1.453 Å) and C10–O1 (1.338 Å) were found as 1.330, 1.403, and 1.263 Å at the eighteenth step of scan where the stable keto tautomer was observed. The figure shows that the intramolecular transfer process affects the double and single characters of these indicative bonds.

The changes of HOMA index of C9/C14 and C1/C6 rings were calculated at every step of the scan process and they are illustrated in Fig 6. As seen in the figure, while the aromaticity level of phenol ring (C9/C14) involving proton transfer decreases, the aromaticity level of C1/C6 ring is not changed with the scan coordinate from 0.99 to 1.85 Å.

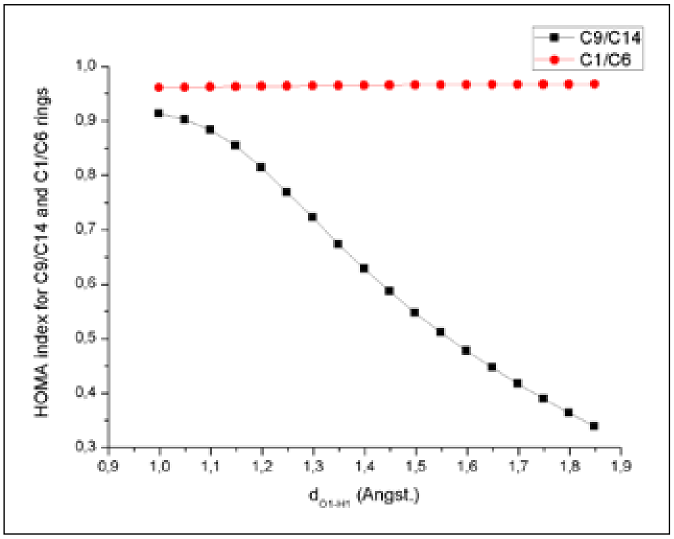

Figure 6. HOMA indexes of C1/C6 and C9/C14 rings versus the redundant coordinate in PES scan process.

3.3. Vibrational spectra

The harmonic vibrational frequencies of (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] phenol have been calculated by using DFT method at 6-31G (d, p) level. It is known that there is a systematic error in the calculated harmonic vibrational frequency when it is compared to the experimental fundamental vibrational frequency (Scott and Radom 1996). Because the quantum mechanical calculations are neglected anharmonicity and can not explain properly the electron-electron interactions. As a result of the frequency calculations, there are no imaginary values for any frequencies, this means is that the molecule has the minimum energy structure at this level of theory. In order to improve the agreement between the theoretical results and the experimentally observed values of those, all of the calculated frequencies are scaled by 0.9627 for B3LYP/6-31G (d,p).

Experimental and theoretical FT-IR spectra of the molecule are shown in Figure 7. Table 6 also summarizes the experimental and calculated vibrational frequencies and their assignments. Since O–H stretching vibrations is sensitive to intramolecular hydrogen bonding this mode of (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] were observed at 2000-3000 cm^{-1} as a broad peak owing to the formation of strong intramolecular O–H···N hydrogen bond in the structure. Its value obtained by DFT calculations is 3156 cm^{-1}. The C=N stretching vibration band was calculated at 1687 cm^{-1} with the same level of the theory while that was observed at 1638 cm^{-1} experimentally. A peak observed at 858 cm^{-1} in the theoretical spectrum was assigned to C–Br stretching vibration. As can be seen from the Figure 7 these bands show the best agreement with their experimental values.

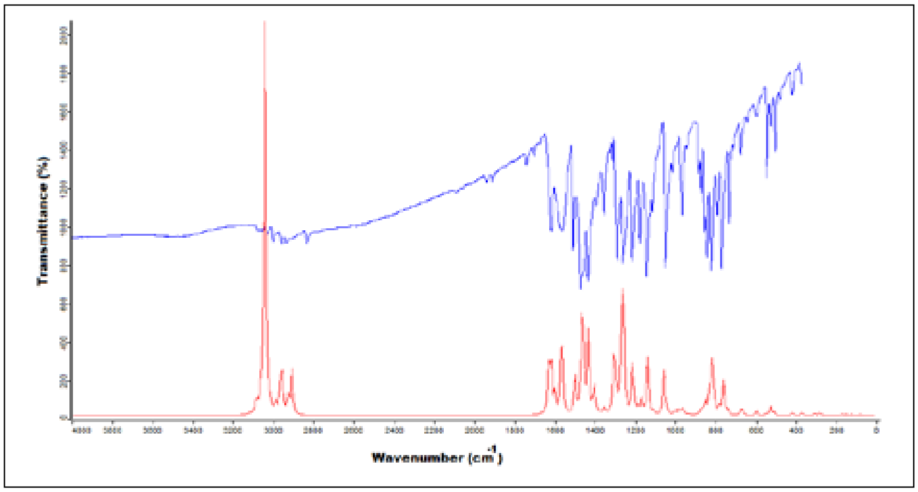

Figure 7. Experimental (blue) and theoretical DFT/B3LYP/6-31G(d,p) (red) FT-IR spectrum.

Table 6. The experimental and the calculated vibrational frecuencies (cm^{-1}) of the molecule.

Assignments	Experimental	DFT/B3LYP/6-31G (d, p)
O–H str.	2000-3000	3156
N=C–H (imino) str.	2998	3065
C=C str. + O–H bend.	1560	1617-1624
C–H (aromatic) str.	3058	3173-3243
N=C–H (imino) bend.	1432	1395
C–H (CH3) str.	2954-2934	3013-3129
C=N str. + C=C str.	1638	1687
O–H bend. + C–H (aromatic) bend.	1352	1349
C–Br str.	820	858

***str.:** stretching; **bend.:** bending.*

3.6. Nonlinear Optical Effects (NLO*)*

There is currently an immense interest in NLO properties of materials, since they provide valuable information about important aspects of matter. For example, they are related to electronic and vibrational structures as well as to intra- and intermolecular interactions. On the other hand, NLO properties are of great practical importance for the design of materials and devices, which have numerous and important applications (e.g. optical devices for the transfer and storage of data) (Papadopoulos et al. 2006). The polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field. Electric polarizability is a fundamental characteristic of atomic and molecular systems.

The first hyperpolarizability (β) is a third-rank tensor that can be described by a 3x3x3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Klein man symmetry (Kleinman 1962). The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes:

$$E = E^0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta} F_\alpha F \beta - 1/6\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \ldots \qquad (2)$$

where E^0 is the energy of the unperturbed molecules, F_α, the field at the origin and μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ, polarizability α, mean polarizability α_0 and the mean first hyperpolarizability β_0, using the x, y, z components are defined as follows (Rajamani and Muthu 2013):

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^2 \qquad (3)$$

$$\alpha = 2^{-1/2}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2\right]^{1/2} \qquad (4)$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2 \qquad (5)$$

$$\beta_0 = \begin{bmatrix} (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + \\ (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \end{bmatrix} \qquad (6)$$

The dipole moment, polarizability and the first hyperpolarizability were calculated with the level of B3LYP/6-31G(d,p). Because the values of the polarizabilities α and hyperpolarizability β of output data are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α: 1 a.u. = 0.1482x10^{-24} esu; β: 1 a.u. = 8.6393x10^{-33} esu).

The studied molecular results of μ, α ve β are 4.0461 Debye, 32.840 Å^3 and 7.7596x10^{-31} cm^5/esu, respectively. When it is compared with the related Schiff base compounds in the literature, the calculated value of β of the title compound is greater than that of (*E*)-4-methoxy-2-[(*p*-tolylimino) methyl]phenol (β = 4.516x10^{-30} cm^5/esu calculated with B3LYP/6-31G(d,p) method) (Koşar and Albayrak 2011) and (*E*)-2-[(2-hydroxy-6-methoxybenzylidene)amino] benzonitrile (β = 6.927x10^{-30} cm^5/esu calculated with B3LYP/6-31G(d,p) method) (Demircioğlu et al. 2015). So, it can be said that (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] is a good candidate as second order NLO material.

4. Conclusion

In the present work, we have investigated molecular and structural properties of (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] with X-ray diffraction, FT-IR and DFT calculations. The comparison between the theoretical and experimental data indicates that B3LYP/6-31G (d, p) method shows a good harmony. The PES scan process in gas phase shows that the potential energy needed for the transition from phenol form to keto form is 5.810 kcal/mol. This intramolecular proton transfer affects the molecular geometry because of changing the aromaticity of C1/C6 ring and lengths of the indicative bonds. The investigation of non-linear optical properties suggests that (*E*)-2-bromo-4-methoxy-6-[(*p*-tolylimino) methyl] can be a good applicant as a non-linear material due to the high values of the second order polarizability of the title molecule.

We hope the results of this study will be helpful for new researchers to synthesis new materials.

5. Supplementary Data

CCDC 921283 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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