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STRUCTURE OF ORGANIC COMPOUNDS

A Close Look at the Molecular Structure, Prototropic Behavior and Supramolecular Architecture of (*E*)-4-Bromo-2-[(phenylimino)methyl]-5-methoxyphenol by Spectroscopic, Crystallographic, and Computational Methods

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Abstract—In this study, the molecular structure, prototropic behavior and supramolecular architecture of a new Schiff base have been studied in depth using spectroscopic (UV-vis), crystallographic (XRD) and computational (HOMA and DFT) methods. Regarding the molecular structure and prototropy, the XRD, DFT and HOMA results show that the compound exists in phenol-imine form. The HOMA indices for the structural evaluation show that the compound has a pure aromatic structure in solid state. UV-vis spectra of the compound dissolved in four different solvents were investigated in order to determine which tautomeric form of the compound is dominant in the solution. It is found that the compound prefers only phenol-imine form in apolar solvents while both phenol-imine and keto amine forms appear in polar solvents. This is because polar solvent decrease the activation energy, and thus, it becomes possible to observe both forms in the solution. For an energetic approach, the tautomeric conversion between two forms of the compound was investigated by a PES scan process and close energy values were obtained for two tautomers. Investigation of non-covalent interactions underlines the active roles of C–H···O H-bonds and C···Br interactions in constructing the supramolecular network of the compound.

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INTRODUCTION

The *o*-Hydroxy Schiff bases are one of the classes of organic compounds capable of showing photochromism and thermochromism. Practical applicability of these properties such as in information storage, electronic imaging systems, optical switching devices, ophthalmic glasses, and so on [1–5] has been the motivation of many researchers from various fields [6–22]. The occurrence of photochromic and thermochromic phenomena in an *o*-Hydroxy Schiff base is mainly related to the tautomeric conversion between the phenol-imine and keto-amine forms of the candidate compound. However, recent studies have also showed that there is a relevance with the molecular geometry (planarity) and the crystal packing of the compound [5, 23]. Therefore, the investigation of an *o*-Hydroxy Schiff base from the point of non-covalent interactions and the changes in molecular geometry is as important as the evaluation of tautomeric process. In this study, a new *o*-hydroxy Schiff base, (*E*)-4-bromo-2-[(phenylimino)methyl]-5-methoxyphenol, has been synthesized. The molecular structure, supramolecular architecture and the prototropy-related-changes in the compound have been investigated in detail by using X-ray diffraction technique (**XRD**), Harmonic Oscillator Model of Aromaticity (**HOMA**) and Density Functional Theory (**DFT**). In addition, the solvent effect on tautomerism has been examined by UV-vis spectroscopy using different types of solvent media.

EXPERIMENTAL

Synthesis

The solution of 5-bromo-2-hydroxy-4-methoxybenzaldehyde (0.20 g; 0.87 mmol) and ethanol (20 ml) was added to solution of aniline (0.081 g; 0.87 mmol) and ethanol (20 ml). The mixture was refluxed by stirring for 1 h. The yellow precipitate was filtered, washed and dried. The single crystals of (*E*)-4-bromo-2-[(phenylimino)methyl]-5-methoxyphenol for X-ray diffraction were obtained by slow evaporation of the ethyl alcohol (Yield: 78%, M.p.= 76–78°C).

Computational Studies

All calculations were performed by Gaussian 03W [24]. GaussView program was used for molecular visu-

Table 1. Crystallographic characteristics and the X-ray-data collection and structure-refinement parameters for the title compound

Formula	$C_{14}H_{12}BrNO_2$
Formula weight	306.15
T, K	298
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	4
a, b, c, Å	4.1450(3), 27.1290(19), 11.1910(9)
α, β, γ, deg	90, 90, 90
V, Å^3	1258.43(16)
Radiation type	MoK_α
μ, mm^{-1}	3.259
θ_{max}, θ_{min}	28.5, 3.00
h, k, l ranges	$-5 < h < 5$, $-35 < k < 36$, $-14 < l < 14$
R ($F^2 > 2\sigma(F^2)$)	0.053
wR (F^2)	0.091
Goodness-of-fit on F^2(S)	1.123
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.57, −0.57

alization of calculated structures [25]. The geometry optimizations of two tautomers for gas phase were carried out at DFT level by using the hybrid functional B3LYP (Becke's three-parameter hybrid functional with LYP correlation functional) [26] with 6-311G (d,p) basis set [27]. To characterize tautomerism related to the intramolecular proton transfer in the compound, the potential energy surfaces (**PES**) scan has been performed using the optimized geometry of phenol-imine form. The O–H distance has been selected as a redundant internal coordinate from 0.9 to 1.80 Å with step size of 0.05 Å [28].

Crystallographic Studies

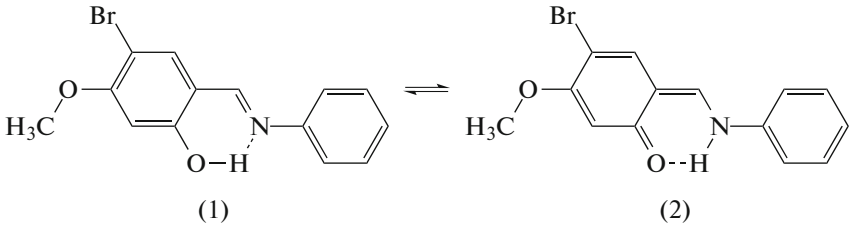
The crystal structure of the compound has been solved by direct methods using SHELXT-2014/4 [29]. All non-hydrogen atoms have been refined anisotropically by full matrix least-squares methods using SHELXL-2018/3 [30]. All H atoms except for the H1 have been located geometrically and refined by a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H_{methyl}) = 1.5U_{eq}(C)$. The H1 atom has been located from difference Fourier map since its position identifies the tautomeric form of the compound. Coordinates of H1 and $U_{iso}(H)$ values were refined freely. The WinGX (Version 2018.3) [31], ORTEP-3 [32] and MERCURY [33] softwares have been used to obtain the figures and other materials related to the molecular structures. Experimental conditions and other details are given in Table 1 and crystallographic information file (CCDC 1883212).

RESULTS AND DISCUSSION

Experimental and Computational Investigation of Molecular Geometry

The *o*-Hydroxy Schiff bases can exist in two different tautomeric structures [34–36] which can easily convert into each other by the transfer of the proton from oxygen atom to nitrogen atom. The phenol-imine form refers to the structure in which the tautomeric proton is on the phenolic oxygen atom while the keto-amine form has the proton on the imino nitrogen atom. The possible tautomeric structures of the compound are illustrated in the Scheme 1.

The XRD analysis reveals that the hydrogen atom (H1) is located on the oxygen atom (Fig. 1). Significant changes in the bond length of the aromatic ring occur when the proton migrates from oxygen atom to the nitrogen atom: the C–O bond, which has a single bond character in phenol-imine form, extends to a double bond length when the keto-amine form is adopted by the compound. In addition, the double length of C–N bond in the phenol imine form changes to a single bond length in the keto-amine form [37–39]. The C1–O1 and C7–N1 bond lengths in molecule are 1.342(6) and 1.302(6) Å. These results suggest a single bond character for the C–O bond and double bond character for the C–N bond. In addition, the bond lengths of C1/C6 ring (Table 2), which are other characteristic bond distances for tautomeric conversion, correspond to those of an aromatic compound and consistent with previously reported values [37–39].



(1) (2)

Scheme 1. The possible tautomeric forms of (*E*)-4-bromo-2-[(phenylimino)methyl]-5-methoxyphenol: phenol-imine form (1) and keto-amine form (2).

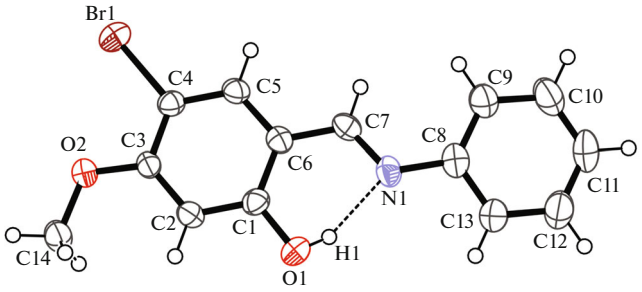


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Hydrogen atoms are represented with small spheres of arbitrary radii.

The Harmonic Oscillator Model of Aromaticity (**HOMA**) indices have been calculated to obtain information about aromaticity of rings [40, 41]. HOMA indices of C1/C6 rings where tautomerism occurs and C8/C13 for compound are 0.989. Considering that HOMA index is 1 in a pure aromatic system and approaches 0 with reduced aromaticity, we can say that the both rings constitute pure aromatic systems.

For more insight on the molecular structure of the compound, possible phenol-imine and keto-amine forms were optimized in the gas phase. Computationally (DFT) obtained bond lengths are given in Table 2. Based on the tautomerism-related bond lengths, the following geometric changes were found for a conversion from the phenol-imine form to the keto-amine form: the single bond length C1–O1 begins to shorten, having a double bond length (1.33569 → 1.25675 Å) while the C7=N1 double bond gains a single bond character (1.28985 → 1.33265 Å). In addition, there seem a shortening in the bond length of the C6–C7 (1.44441 → 1.39118 Å) and significant changes in the bond lengths of aromatic ring (C1/C6). Of two possible tautomeric forms, the optimized phenol-imine form of the compound contains more consistent results with experimental geometry.

Table 2. Selected experimental and computational bond lengths (Å) for the compound

Experimental (XRD)		Computational (DFT)	
		phenol-imine form	keto-amine form
N1–C7	1.302(6)	1.28985	1.33265
O1–C1	1.342(6)	1.33569	1.25675
C6–C7	1.439(6)	1.44441	1.39118
C1–C2	1.386(6)	1.39840	1.43740
C2–C3	1.388(6)	1.39347	1.37419
C3–C4	1.381(6)	1.41534	1.44262
C4–C5	1.385(6)	1.37568	1.35829
C5–C6	1.399(6)	1.40769	1.42713
C6–C1	1.396(6)	1.41942	1.46986
N1–C8	1.426(6)	1.40781	1.40429
C3–O2	1.359(5)	1.34681	1.34556
C4–Br1	1.891(4)	1.91141	1.91194

Description of Supramolecular Networks

The title compound has intra-molecular O–H···N hydrogen bonds which can be characterized by the distances of 2.566 Å between the nitrogen and the oxygen atoms. The geometry of all non-covalent interactions is given in the Table 3. In the crystal packing, the molecules are linked by two hydrogen bonds (C14–H14C^{i}···O1 and C14–H14C···O1^{ii}), thus, an H-bonded 1D polymeric chain is constructed propagating along the direction [100] in a herringbone pattern (Fig. 2a).

It is also seen that this arrangement of H-bonds opens a channel down to the *a* axis (Fig. 2b). In the 2D supramolecular network of the compound, these H-bonded chains are inter-connected by C7···Br1^{iii} (iii: $1/2 + x$, $1/2 - y$, $-z$), Br1···C7^{iv} (iv: $-1/2 + x$, $1/2 - y$, $-z$) short contacts between the imino carbon and bromine atoms (Fig. 3), forming a herringbone-type layer in (010) plane. The non-covalent interaction angle between all bromine and carbon atoms (C–X···C) is 128.87°. This means that the lateral regions of the bromine atom, that is, the lone pair electrons, are used in the interaction. Topologically, the resulted 2D network can be defined as (4,4) in Wells nomenclature or ($4^4.6^8$) in Schläfli notations [42].

The 2D layer in (010) and adjacent parallel layers are connected to each other along [010] with C11^{v}–H11^{v}···O2 (v: $1 - x$, $1/2 + y$, $1/2 - z$) and C11–H11···O2^{vi} (vi: $1 - x$, $-1/2 + y$, $1/2 - z$) hydrogen bonds between the aromatic hydrogen and methoxy oxygen atoms, forming the 3D supramolecular structure shown in Fig. 4.

Table 3. The geometry of non-covalent interactions in the title compound

D–H	*A*	*D*–H, Å	H···*A*, Å	*D*···*A*, Å	*D*–H···*A*, deg
O1–H1	N1	0.80(4)	1.85(5)	2.566(7)	148(4)
C14–H14C^{i}	O1	0.96	2.648	3.550	156.64
C14–H14C	O1^{ii}	0.96	2.648	3.550	156.64
C7	Br1^{iii}			3.529	128.87
Br1	C7^{iv}			3.529	128.87
C11–H11^{v}	O2	0.93	2.58	3.501(6)	170.99
C11–H11	O2^{vi}	0.93	2.580	3.501	170.99

Symmetry codes: (i) $1/2 + x$, $1/2 - y$,$1 - z$; (ii) $-1/2 + x$, $1/2 - y$, $1 - z$; (iii) $1/2 + x$, $1/2 - y$, $-z$; (iv) $-1/2 + x$, $1/2 - y$, $-z$; (v) $1 - x$, $1/2 + y$, $1/2 - z$; (vi) $1 - x$, $-1/2 + y$, $1/2 - z$.

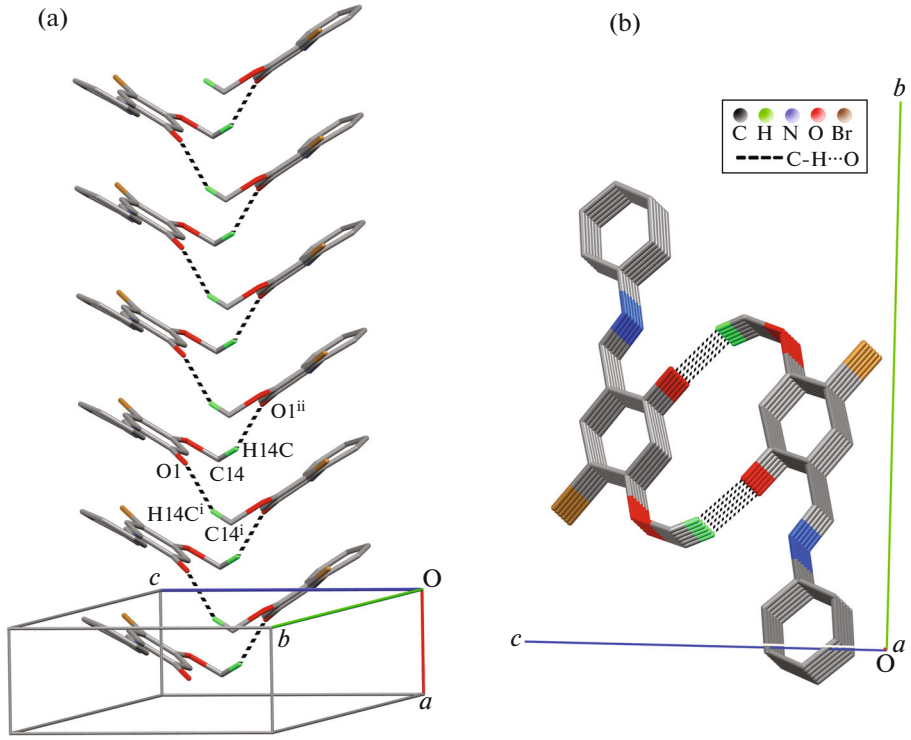


Fig. 2. One dimensional H-bonded polymeric chain formed by C–H···O type interactions in the crystal packing of the compound (a) and the chain propagates along the direction [100] and encloses a channel down to the *a* axis (b).

Experimental and Computational Studies on Tautomerism

Previous studies show that the tautomerism in Schiff bases is affected by the type of solution [43, 44]: these compounds may exist in both phenol-imine and keto-amine forms with increase of solvent polarity. However, they prefer only phenol-imine form in apolar solvents. This is explained by the fact that polar sol-

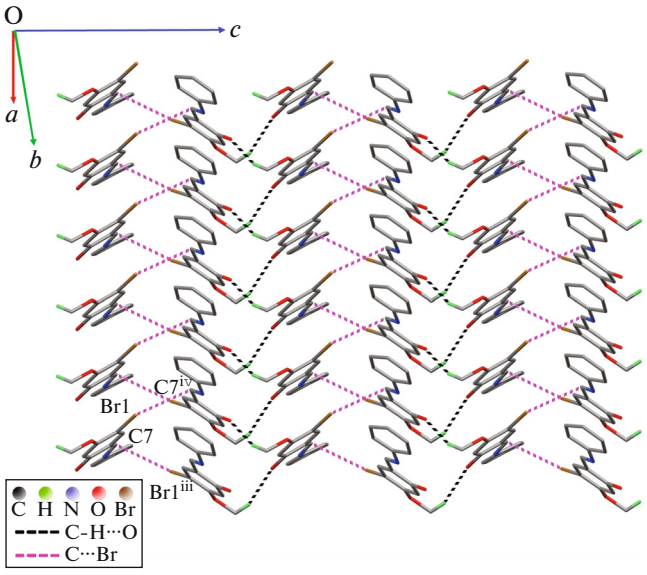


Fig. 3. The 2D structure through the carbon-halogen contacts (C7···Br1).

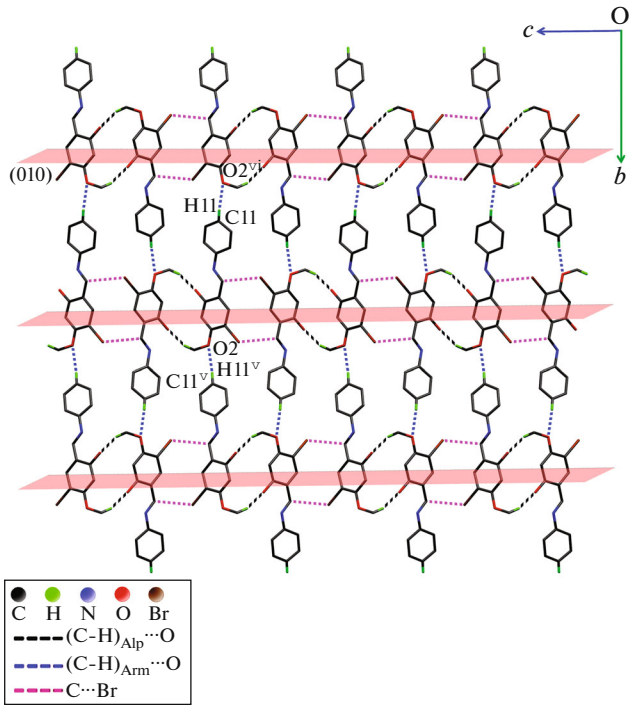


Fig. 4. The 3D supramolecular architecture of the compound formed by the connection of 2D layers in (010) with the C–H···O hydrogen bonds through [010].

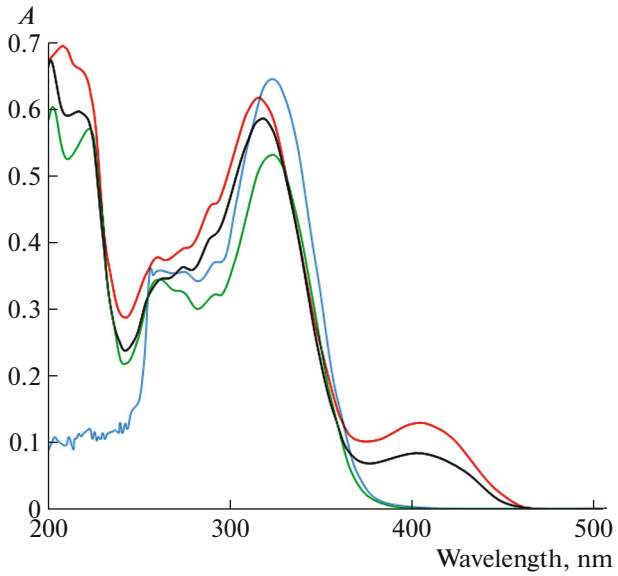


Fig. 5. UV-vis spectra of the compound in the solvents of different polarities (black) EtOH; (red) DMF; (blue) toluene; (green) hexane.

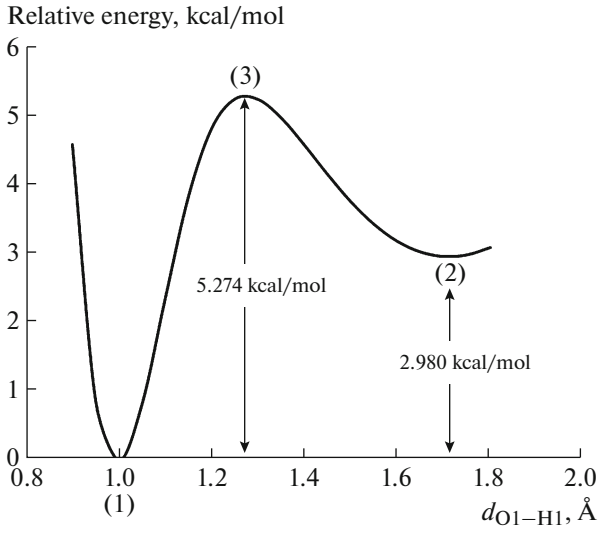


Fig. 6. Relative energy profile during the proton transfer process. The energy values were calculated relative to the energy of stable phenol-imine form: (1) phenol-imine form, (2) keto-amine form, (3) transition state.

vents can stabilize the keto-amine form. In addition, UV-vis spectroscopy studies suggest that the characteristic absorption band of phenol-imine form is between 300–400 nm while that of the keto-amine form appears over 400 nm [43, 44]. To investigate the tautomeric behavior of the title compound in solvent media, UV-vis spectra were recorded for four solvents of different polarities (Fig. 5). It is seen that the spectra of the compound in EtOH and DMF have two absorption bands between 300–500 nm while there is only a single absorption band between 300–400 nm in the case of toluene and hexane. The absorption band at about 320 nm corresponds to the phenol-imine form of the compound while the band at 404 nm belongs to the keto-amine form. That is, the title compound prefers only the phenol-imine form in nonpolar solvents such as toluene and hexane while it contains two tautomeric forms in polar solvents such as EtOH and DMF.

In this study, the PES scan has been performed starting from the optimized geometry of the phenol-imine form and the energy levels of the tautomers have been calculated in order to evaluate the tautomeric process and its effects on the molecular structure from another point of view. In the relative energy graph (Fig. 6), the global minimum is related to the optimized phenol-imine form while the local minimum corresponds to the optimized keto-amine form. It is seen that the phenol-imine form is more stable than the keto-amine form by 2.98 kcal/mol. This lower energy of phenol-imine form is related with its aromatic character. The activation energy required for a proton transfer from phenol-imine to keto-amine form was calculated as 5.274 kcal/mol for the gas phase. The previous quantum chemical studies show that the proton transfer is easier in polar solvents such as EtOH and DMF since the activation energy reduces in these media [45]. Therefore, it is possible to see both tautomeric forms of the compound in the UV-vis spectra recorded for polar solvents.

CONCLUSIONS

On the basis of the X-ray results, the title compound has phenol-imine form adopting the *trans* configuration with respect to the imino group. The calculated HOMA indices show that the compound has pure aromatic character. The weak hydrogen bond and carbon-halogen interactions are more effective in the design of crystal packing. According to UV-vis studies in different solvent media, the compound only prefers phenol-imine form in nonpolar solvents (toluene and hexane) while it exists in both phenol-imine and keto-amine forms in the polar solvents (ethyl alcohol and DMF) which facilitate the proton transfer process by reducing the activation energy.

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