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STRUCTURE OF ORGANIC COMPOUNDS

Investigation of the Molecular Structure of (*E*)-2-Bromo-6-[(4-bromo-2-methylphenylimino)methyl]-4-chlorophenol

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Abstract—In this study, the molecular structure of (*E*)-2-bromo-6-[(4-bromo-2-methylphenylimino)methyl]-4-chlorophenol has been investigated using crystallographic (XRD), spectroscopic (UV-vis, NMR), and computational (DFT, HOMA) methods. The refinement parameters in XRD study supports the preference of phenol-imine form by the compound in solid state. The analysis of HOMA indices indicates that C1/C6 ring (tautomeric ring) deviates slightly from the aromaticity while the C8/C13 ring preserves its aromaticity in solid state. For the solvent-media dependence of the tautomerism, UV-vis and NMR spectra of the compound were investigated. It is found that the compound prefers only phenol-imine form in solvent media as in the case of solid state.

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INTRODUCTION

Salicylidenanilines are considered as an important class of organic compounds due to their various practical applications [1–5] which are mainly related to the tautomeric process involving the imino and hyrdroxyl groups in these compounds. The tautomeric conversion forms two structural isomers called phenol-imine and keto-amine. In this study, (*E*)-2-bromo-6-[(4-bromo-2-methylphenylimino)methyl]-4-chlorophenol has been successfully synthesized. The molecular structure of the compound has been investigated using X-ray diffraction technique (**XRD**), Harmonic Oscillator Model of Aromaticity (**HOMA**) and Density Functional Theory (**DFT**). In addition, the existence of possible tautomers in solvent media has been examined with UV-vis and NMR spectroscopies.

EXPERIMENTAL

Synthesis

The ethanolic solution (20 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (0.25 g; 1.06 mmol) and 2-methyl-4-bromoaniline (0.20 g; 1.06 mmol) were stirred by heating for 1 h. The resulted yellow solid was filtered, washed and dried, then dissolved in 20 ml of absolute ethanol. The single crystals of (*E*)-2-bromo-6-[(4-bromo-2-methylphenylimino)methyl]-4-chlorophenol were obtained by slow evaporation at room temperature (yield: 77%, M.p.= 158–159°C).

Computational and Spectroscopic Studies

The geometry optimization of the phenol-imine form of compound was performed using Gaussian 03W [6] and visualized with GaussView program [7]. The geometry optimization for gas phase were carried out at DFT level using the hybrid functional B3LYP (Becke's three-parameter hybrid functional with LYP correlation functional) [8] with 6-31+G (*d*,*p*) basis set [9]. UV-Vis spectrum and NMR spectra of the compound were recorded with SHIMADZU UV-2600 spectrometer and 400 MHz Brucker AVANCE III spectrometer, respectively.

Crystallographic Studies

The crystal structure of the compound has been solved by direct methods using SHELXT-2014/4 [10]. All non-hydrogen atoms have been refined anisotropically by full matrix least-squares methods using SHELXL-2018/3 [11]. All H atoms 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 WinGX (Version 2018.3) [12] and ORTEP-3 [13] softwares have been used to obtain the figures and other materials related to the molecular structure of the compound. Experimental conditions and other details are given in Table 1 and crystallographic information file (CCDC 1899023).

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

Formula	$C_{14}H_{10}Br_2ClNO$
Formula weight	403.50
T, K	298
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, b, c, Å	23.3097(13), 3.8751(2), 15.6543(9)
α, β, γ, deg	90, 108.084(2), 90
V, Å^3	1344.16(13)
Radiation type	MoK_α
μ, mm^{-1}	6.22
θ_{max}, θ_{min}	28.3, 3.2
h, k, l ranges	$-30 < h < 27$, $-5 < k < 4$, $-19 < l < 20$
R ($F^2 > 2\sigma(F^2)$)	0.066
wR (F^2)	0.192
Goodness-of-fit on F^2(S)	1.07
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.85/–2.25

RESULTS AND DISCUSSION

Experimental and Computational Investigation of Molecular Geometry

The molecular structure of the compound obtained from XRD analysis is given in Fig. 1. Based on the refinement parameters, the tautomeric form of the compound is the phenol-imine form in which the tautomeric proton (H1) is located on the phenolic oxygen atom (O1). The distance of 2.560 Å between the nitrogen and the oxygen atoms shows that the compound has strong O–H···N intra-molecular hydrogen bond. The molecular structure deviates from planarity with a dihedral angle of 18.22° between the two aromatic rings. The steric effect of methyl group causes C8/C13 ring to twist slightly while the C1/C6 ring is planar with the effect of intramolecular hydrogen bonding. The C1–O1, C7–N1, and C6–C7 bond lengths in the molecule are 1.324(8), 1.282(10), and 1.466(9) Å. These results suggest a single bond character for the C–O and C6–C7 bonds and double bond character for the C–N bond [14–16] as expected from a phenol-imine structure.

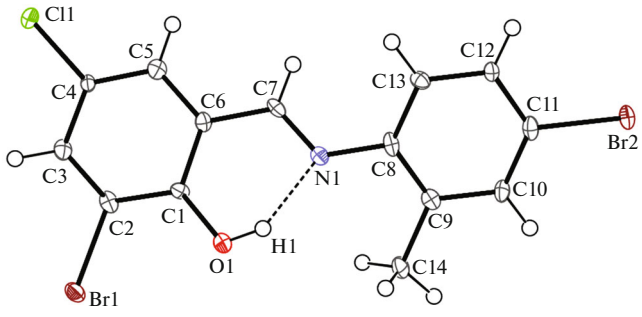

Fig. 1. The molecular structure of the compound. Displacement ellipsoids are drawn at the 40% probability level for non-hydrogen atoms. Hydrogen atoms are represented with small spheres of arbitrary radii.

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

Bond	Experimental (XRD)	Computational (DFT)
N1–C7	1.283(10)	1.292
O1–C1	1.324(8)	1.336
C6–C7	1.464(10)	1.454
C1–C2	1.409(10)	1.407
C2–C3	1.372(10)	1.390
C3–C4	1.406(10)	1.399
C4–C5	1.385(10)	1.385
C5–C6	1.393(10)	1.408
C6–C1	1.438(9)	1.422
N1–C8	1.424(10)	1.409
C2–Br1	1.885(7)	1.894
C4–Cl1	1.740(7)	1.757

The Harmonic Oscillator Model of Aromaticity (**HOMA**) indices [17, 18] have been calculated in order to investigate the molecule from the point of aromaticity in its ring systems. HOMA indices of rings C1/C6 (tautomeric ring) and C8/C13 in the compound are 0.852 and 0.955, respectively. Considering that HOMA index is 1 in a pure aromatic system and approaches 0 with reduced aromaticity, we can propose that the C8/C13 ring constitute a pure aromatic system while the C1/C6 ring deviates slightly from aromaticity.

The molecular structure of the compound has been probed by geometrically optimizing the phenol-imine form for the gas phase. Computationally (DFT) obtained bond lengths are given in Table 2. The C1–O1, C7–N1,

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
Experimental (XRD)	O1–H1	N1	0.80(4)	1.85(5)	2.566(7)	148(4)
Computational (DFT)	O1–H1	N1	1.00102	1.70743	2.61232	148.252

and C6–C7 bond lengths in the molecule are 1.336, 1.292, and 1.454 Å. The DFT study also proposes a twisted molecular structure for the compound with a dihedral angle between the two aromatic rings (35.00°). For the intra-molecular O–H···N hydrogen bond of the optimized structure, the distance of between the nitrogen and the oxygen atoms is 2.612 Å. The geometry of non-covalent interactions in the title compound is given in Table 3. In all aspects, the optimized phenol-imine structure of the compound contains consistent results with experimental geometry.

Spectroscopic Studies

Previous studies show that salicylidenanilines can exist in both phenol-imine and keto-amine forms in solvent media. 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 [19, 20]. To investigate the tautomeric behavior of the title compound in solvent media, UV-vis spectrum was recorded in ethyl alcohol (Fig. 2). It is seen that the spectrum of the compound in EtOH has absorption bands between 300–400 nm while there is no absorption band above 400 nm. The absorption bands between 300–400 nm correspond to the phenol-imine form of the compound. That is, the title compound prefers only the phenol-imine form in EtOH.

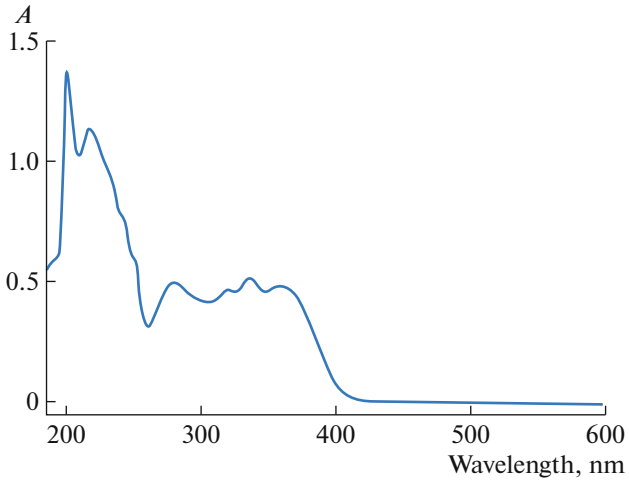

Fig. 2. The UV-vis spectrum of the compound in EtOH.

In addition, ^{1}H NMR spectrum was recorded in $CDCl_3$. When the ^{1}H NMR spectrum of the compound (Fig. 3) is examined, the tautomeric proton H1 resonates at 14.22 ppm while the H7 imino proton appears at 8.48 ppm as a single peak. The fact that these two protons cannot be observed as a doublet indicates that the compound prefers the phenol-imine form in $CDCl_3$. If the keto-amine form existed in $CDCl_3$, H1 and H7 protons would be neighbor to each other and observed as a doublet. Signals of H3 and H5 protons appear at 7.64 (*d*, $^{4}J_{3,5} = 2.4$ Hz) and 7.37 ppm (*d*, $^{4}J_{5,3} = 2.4$ Hz), respectively. The observation of tautomeric ring protons (H3, H5) as doublets is another evidence for the compound in phenol-imine form. As for the signals of the C8/C13 aromatic ring protons, the H10 proton appears at 7.44 ppm (*d*, $^{4}J_{10,12} = 1.6$ Hz), the H12 proton at 7.41 ppm (*dd*, $^{3}J_{12,13} = 8$ Hz, $^{4}J_{12,10} = 1.6$ Hz) and the H13 proton at 7.01 ppm (*d*, $^{3}J_{13,12} = 8$ Hz).

The ^{13}C NMR spectrum of the compound was recorded in $CDCl_3$. In the ^{13}C NMR spectrum, there is only one resonance peak for each carbon (Fig. 4). This is possible only if the compound adopts one tautomeric structure (phenol-imine) in solution.

CONCLUSIONS

On the basis of the X-ray results, the title compound has the *trans* configuration with respect to the imino group. The compound has a strong intramolecular hydrogen bond and deviates slightly from the planarity due to the steric effect of the methyl group. The key geometric parameters in characterizing the tautomeric structure of the compound, namely, C–O, C–N and aromatic ring bonds from XRD and DFT, propose the phenol-imine form in solid state. According to UV-vis and NMR studies, the compound prefers phenol-imine form in solvent media as well as in solid state.

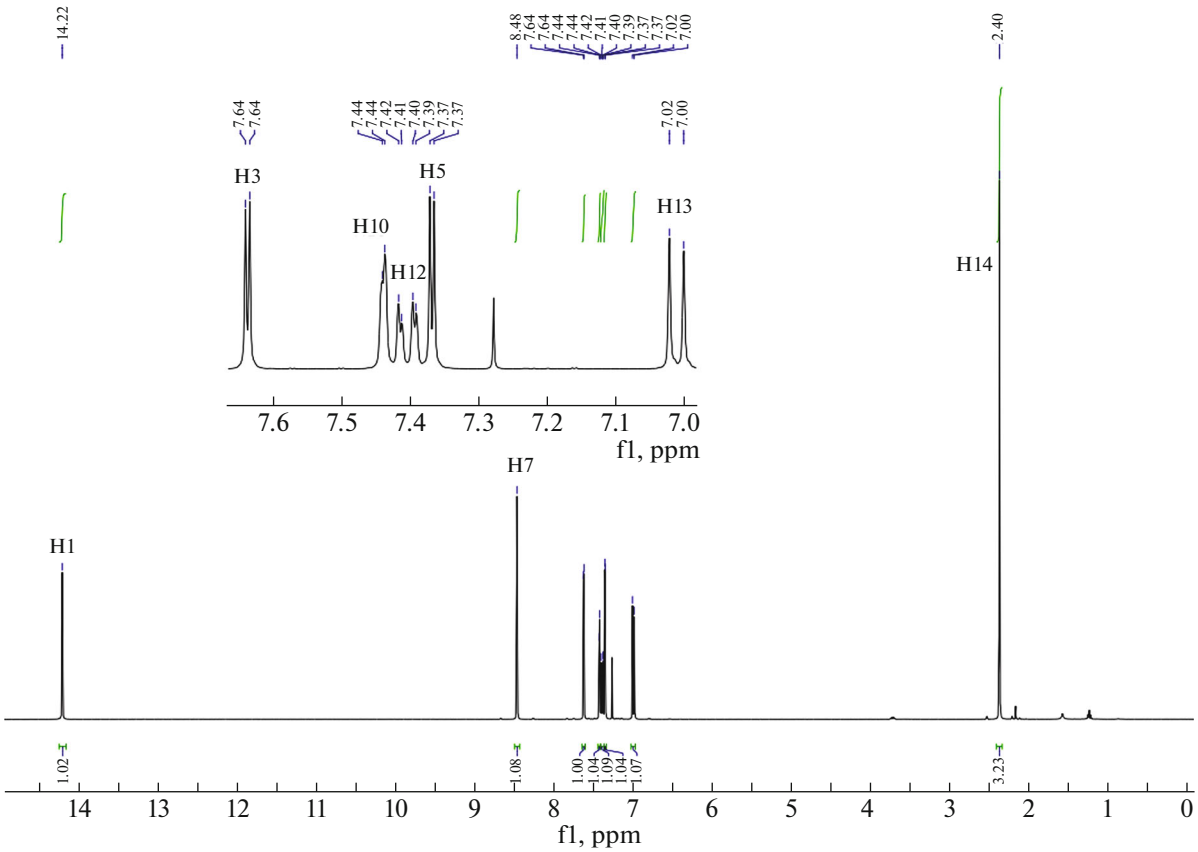

Fig. 3. The ^{1}H NMR spectrum of the compound in $CDCl_3$.

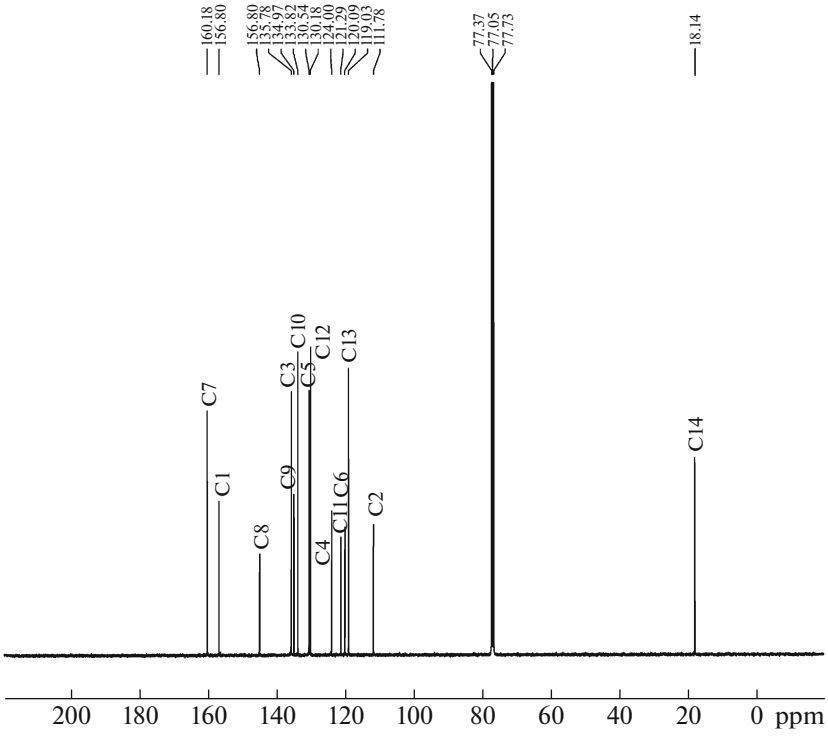

Fig. 4. The ^{13}C NMR spectrum of the compound in $CDCl_3$.

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