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STRUCTURE OF ORGANIC COMPOUNDS

(*E*)-2-[(2-Bromophenylimino)methyl]-5-methoxyphenol: X-ray and DFT-Calculated Structures[1]

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Abstract—The crystal structure of (*E*)-2-[(2-Bromophenylimino)methyl]-5-methoxyphenol is determined by using X-ray diffraction and then the molecular structure is investigated with density functional theory (DFT). X-Ray study shows that the title compound has a strong intramolecular O–H···N hydrogen bond and three dimensional crystal structure is primarily determined by C–H···π and weak van der Waals interactions. The strong O–H···N bond is an evidence of the preference for the phenol-imine tautomeric form in the solid state. Optimized molecular geometry is calculated with DFT at the B3LYP/6-31G(d,p) level. The IR spectra of compound were recorded experimentally and calculated to compare with each other. The results from both experiment and theoretical calculations are compared in this study.

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INTRODUCTION

Schiff bases are widely used as ligands in coordination chemistry and they play an important role in various fields of chemistry due to their biological activities [1, 2]. *o*-Hydroxy Schiff bases derived from the reaction of *o*-hydroxy aldehydes with aniline have been examined extensively [3–5]. Some Schiff bases derived from salicylaldehyde have attracted the interest of chemists and physicists because they show thermochromism and photochromism in the solid state by H-atom transfer from the hydroxy O atom to the N atom [6]. It has been proposed that molecules showing thermochromism are planar, while those showing photochromism are non-planar [7].

In general, *o*-Hydroxy Schiff bases exhibit two possible tautomeric forms, the phenol-imine (or benzenoid) and keto–amine (or quinoid) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are possible: O–H···N in benzenoid and N–H···O in quinoid tautomers can be seen in Figs. 1a and 1b, respectively. *o*-Hydroxy Schiff bases have been previously observed in the keto form [8], in the enol form [9] or in enol/keto mixtures [10, 11]. Related to this phenomenon, we present here the crystal and molecular structure of title compound.

[1] The article is published in the original.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

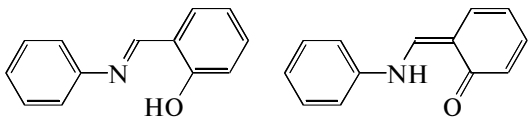
Synthesis

The compound (*E*)-2-[(2-Bromophenylimino) methyl]-5-methoxyphenol was prepared by reflux a mixture of a solution containing 4-methoxysalicylaldehyde (0.5 g 3.3 mmol) in 20 ml ethanol and a solution containing 2-bromoaniline (0.57 g 3.3 mmol) in 20 ml ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-[(2-bromophenylimino)methyl]-5-methoxyphenol suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield % 82; m.p. 367–368 K).

The IR spectra of compound were recorded on KBr disc with a Brucker 2000 FT-infrared spectrometer.

X-Ray Diffraction Analysis

A suitable sample of size 0.41 × 0.40 × 0.40 mm^3 was selected for the single crystal X-ray study. The crystal data, data collection conditions and parameters of refinement process are listed in Table 1. All non-hydrogen atom parameters were refined anisotro-



(a) (b)

Fig. 1. Phenol-imine (a) and keto-amine (b) tautomers of *o*-hydroxy Schiff bases.

Table 1. Crystal data, data collection and refinement details

Chemical Formula	$C_{14}H_{12}BrNO_2$
Crystal System, Space group, Z	Monoclinic, $C2/c$, 8
a, Å	22.5424(19)
b, Å	7.4415(5)
c, Å	16.4950(15)
β, deg	113.128(6)
V, Å^3	2544.6(4)
D_x, Mg m^{-3}	1.598
Radiation, λ, Å	MoK_α, 0.71073
μ, mm^{-1}	3.223
T, K	293
T_{min}, T_{max}	0.273, 0.403
F(000)	1232
Diffractometer	STOE IPDS II
Scanning mode	ω
Scan range	$-27 < h < 27$, $-9 < k < 9$, $-20 < l < 20$
θ_{min}, θ_{max}, deg	1.96, 26.00
Number of measured/independent reflections, R_{int}	17667/2501, 0.054
Number of reflections with 2σ(I)	1857
Number of refined parameters	168
S	0.99
$R[F^2 > 2\sigma(F^2)]$	0.036
$wR(F^2)$	0.081
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.29, −0.38
Programs	X-AREA [12], X-RED [12], SHELX97 [13]

pically and all H atoms except for H1 were located in their idealized positions and refined using a riding model with C–H distances in the range 0.93–0.96 Å, U_{iso}(H) values in the range 1.2U_{eq}(C) or 1.5U_{eq}(C) (for methyl group). H1 atom was localized from difference map and refined isotropically.

CCDC 727235 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.

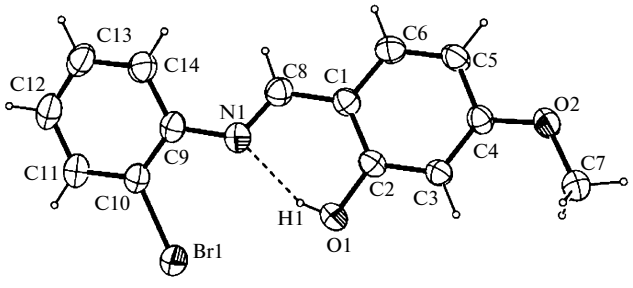


Fig. 2. An ORTEP-3 view of the title compound with the atomic numbering scheme. Dashed line shows intramolecular hydrogen bond. Displacement ellipsoids are shown at the 30% probability level.

Computational Procedure

The geometry optimization of the molecule leading to energy minima was achieved by using B3LYP hybrid exchange-correlation functional with 6-31G(d,p) basis set [14, 15]. The calculation was started from the crystallographically achieved parameters of molecule which are listed in Table 2 and carried out using GAUSSIAN03W package [16]. The optimized molecular geometry, total molecular energy, dipole moment, Mulliken charges were obtained from the computational process.

RESULTS AND DISCUSSION

An ORTEP-3 plot [17] with the atom-numbering scheme of the title compound is shown in Fig. 2. It is seen that the structure reported here adopts an phenol-imine form, because its N1=C8, O1–C2 bond distances 1.278(4) and 1.349(3) Å are in a good agreement with observed for N-(2,5-methylphenyl)salicylaldimine (1.267(2), 1.346(3) Å) and N-(2-methyl-5-chlorophenyl)salicylaldimine (1.281(3), 1.354(3) Å) [18, 19] which are phenol-imine tautomers. The same bond distances can be compared with the corresponding distances in 3-hydroxy-6-[(4-hydroxyphenylamino)methylene]cyclohexa-2,4-dienone and 2-hydroxy-6-[(4-hydroxyphenylamino)methylene] cyclohexa-2,4-dienone (1.417(2), 1.356(2) Å and 1.416(4), 1.381(3) Å) [20] which are keto-amine tautomers. In phenol-imine tautomeric form, both rings of title compound must be aromatic. In order to make an another verification for phenol-imine form and investigate the aromaticity of rings HOMA (harmonic oscillator model of aromaticity) indices were calculated [21, 22]. HOMA index is equal to 1 for aromatic systems and 0 for non-aromatics. The indices were calculated as 0.970 and 0.940 for bromo-attached ring and the other, respectively.

The dihedral angle between two aromatic ring of molecule is 23.75(12)°. Against this background we can say that the compound is non-planar and displays photochromic features. As is a common feature of *o*-hydroxysalicylidene systems, title compound displays a strong intramolecular hydrogen bond between atoms O1 and N1 [23, 24]. The crystal structure is sta-

Table 2. Fractional atomic coordinates and U_{eq}/U^*_{iso}, Å^2

Atom	*x*	*y*	*z*	U_{eq}/U^*_{iso}
C1	0.56640(13)	0.5549(4)	0.64577(18)	0.0545(7)
C2	0.54274(12)	0.7079(4)	0.59359(18)	0.0518(7)
C3	0.58348(12)	0.8446(4)	0.59170(18)	0.0529(7)
C4	0.64900(13)	0.8289(4)	0.64129(18)	0.0540(7)
C5	0.67409(14)	0.6777(4)	0.6921(2)	0.0619(8)
C6	0.63346(15)	0.5446(4)	0.6944(2)	0.0637(8)
C7	0.67081(16)	1.1131(5)	0.5929(2)	0.0748(9)
C8	0.52496(15)	0.4141(4)	0.6519(2)	0.0595(7)
C9	0.42380(14)	0.2815(4)	0.61764(18)	0.0552(7)
C10	0.35968(14)	0.3211(4)	0.5988(2)	0.0562(7)
C11	0.31869(17)	0.2000(4)	0.6127(2)	0.0675(8)
C12	0.34141(19)	0.0319(5)	0.6445(2)	0.0771(10)
C13	0.40356(19)	–0.0149(4)	0.6598(2)	0.0773(10)
C14	0.44466(17)	0.1080(4)	0.6457(2)	0.0688(9)
N1	0.46400(12)	0.4174(3)	0.60762(16)	0.0576(6)
O1	0.47920(10)	0.7289(3)	0.54450(16)	0.0667(6)
O2	0.69319(9)	0.9558(3)	0.64479(15)	0.0699(6)
Br1	0.327550(17)	0.55145(5)	0.55519(3)	0.07851(18)
H1	0.4644(18)	0.646(5)	0.556(2)	0.076(12)*

bilized by weak van der Waals and C–H···π interactions in three dimensions (Fig. 3). Geometrical parameters of the intramolecular H-bonds and intermolecular C–H···π interactions are listed in Table 3.

In DFT/B3LYP calculations, total energy of optimized geometry and dipole moment of molecule are obtained as –3317.63 a.u. and 2.1995 debye, respectively. According to calculated results for Mulliken atomic charge analysis, atoms N1, O1 and O2 have larger negative charges relative to other atoms as expected. Charges are calculated as –0.609, –0.568 and –0.513e, respectively.

Comparative results obtained from the X-ray crystallographic and computational studies of bond distances, angles and torsion angles are presented in Table 4. The experimental and computational IR spectra of compound were compared in Table 5. It is well known that the DFT, and similar calculations underestimate interactions like inter- and intramolecular hydrogen bonds and handle molecules in gaseous phase (in vacuo). That's why, somewhat differences were observed between X-ray experimental study and DFT/B3LYP calculation results of bond distance, angle and torsion angle values. The DFT-based IR results also show significant differences from experimental values for C=N, O–H and C–O stretching due to inter-

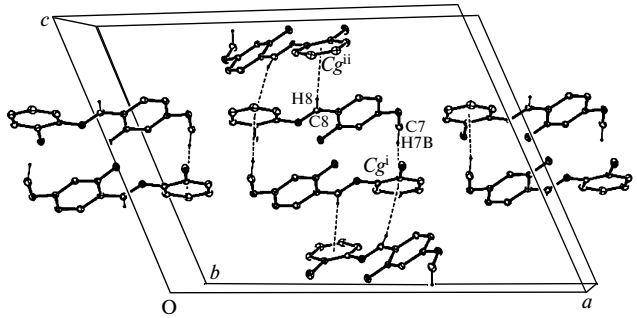


Fig. 3. A packing diagram of the title compound. Dashed lines indicate the C–H···π bonds. For clarity, only H, atoms involved in hydrogen bonding were included.

Table 3. Hydrogen bonding geometry, (Å, deg)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	∠*D*–H···*A*
O1–H1···N1	0.76(4)	1.90(4)	2.61(3)	156(4)
C7–H7B···*Cg*^{i}	0.96	3.02	3.93(3)	157.39
C8–H8···*Cg*^{ii}	0.93	3.04	3.89(3)	152.43

Note: Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, 3/2-z$. *Cg* is the centroid of C9–C14 ring.

Table 4. Selected bond lengths, angles and torsion angles, (Å, deg)

	X-Ray	DFT/B3LYP
Br1–C10	1.890(3)	1.909
C9–N1	1.410(3)	1.398
N1–C8	1.278(4)	1.296
C1–C8	1.434(4)	1.439
C2–O1	1.349(3)	1.336
C4–O2	1.358(3)	1.357
Br1–C10–C9	119.2(2)	119.58
N1–C8–C1	122.0(3)	122.03
C10–C9–N1–C8	154.3(3)	148.16
C9–N1–C8–C1	−177.1(3)	−177.26
N1–C8–C1–C6	−178.8(3)	−179.22

Table 5. The experimental and the calculated frequencies of IR spectra, cm^{-1}

Assignments	Experimental	DFT/B3LYP
C=N str.	1611	1674
C–Br str.	1027	1042
N=C–H bend. (imino)	1436	1407
C–O str. (aliphatic)	1110	1064
C–C srt. (aromatic)	1465	1476
C–C srt. (aromatic)	1559	1559
O–H bend.	1341	1390
O–H str.	2000–3000	3164
C–O str. (aromatic)	1208	1339
C–O str. (aromatic)	1171	1246

Note: Str.: stretching, bend.: bending.

molecular hydrogen bond between N and O. While C=N, stretching is shifted to lower frequency, O–H stretching is widen to 2000–3000 cm^{-1} range.

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