

Synthesis, Crystal Structure and Spectroscopic Studies of 2-*{(E)-[2-Hydroxyphenyl]imino}methyl* Phenol Schiff Base Molecule

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Abstract A new Schiff-base complex 2-*{(E)-[2-hydroxyphenyl]imino}methyl*phenol has been synthesized and characterized by elemental analyses, UV–VIS and IR spectroscopy and single crystal X-ray determination. The structure comprises two independent and similar molecules. The two independent molecules in the asymmetric unit are hydrogen bonded and have different conformations. In each molecule, $C_{13}H_{11}NO_2$, adopt an E configuration about the azomethine C–N double bond. The complex crystallized in the triclinic space group P-1. Two benzene rings and azomethine group are practically coplanar, as a result of intramolecular hydrogen bonds involving the hydroxy O atom and azomethine N atom. Also hydroxy group of the molecule is the presence intermolecular O–H...O hydrogen bonds with the hydroxy group of the other molecule.

Keywords Crystal structure · Schiff base · Hydroxypheny · Phenol

Introduction

Schiff base complex have been playing an important role in the development of coordination chemistry related to catalysis and enzymatic reactions [1–5], magnetism and molecular architectures [6, 7]. In particular salicylaldehydes are useful for the synthesis of transition metal complexes. Schiff base ligands and their metal complexes have been extensively studied over past few decades. Some Schiff bases are used as ion-selective electrode [8]. Some complexes containing nitrogen and oxygen donor atoms in the complexes are effective as stereospecific catalysts for oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry [9–12]. It is known that Schiff bases containing electroactive imine group in non-aqueous media have two reduction peaks corresponding to a one-electron transfer in a cyclic voltammogram and the electrode reaction is an EC mechanism [13]. The reduction behavior of some Schiff bases was also studied on the glassy carbon electrodes modified by the electrochemical reduction of diazonium salts and the reduction behaviors of these molecules was evaluated in connection with the role of the electron donor or acceptor groups on the phenyl ring of the diazonium salts [14, 15]. In addition, some Schiff base molecules were also studied as electrochemical and quantum chemical the effect on the corrosion of steel [16]. Aromatic Schiff bases containing a hydroxyl group in the *ortho* position may have two tautomeric forms, namely phenol-imine (O–H...N) and keto-amine (O...H–N) structures [17]. Various studies were carried out with these systems in order to establish the existence of intramolecular hydrogen bonding, stabilizing one of the tautomeric forms [18–20].

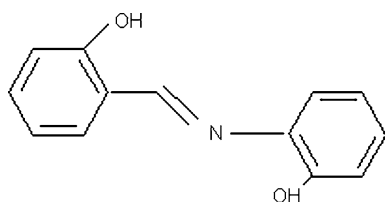
In the present study, a new Schiff-base complex 2-*{(E)-[2-hydroxyphenyl]imino}methyl*phenol has been

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Scheme 1 Structure of 2-((E)-[2-hydroxyphenyl]imino)methyl}phenol Schiff-base

synthesized and its structure was determined using the X-ray diffraction method and characterized with spectroscopic techniques. The structure of Schiff base molecule is given in [Scheme 1](#).

Experimental

General Procedures and Materials

Salicylaldehyde and 2-aminophenol were purchased from Fluka and used without further purification. Ethanol and chloroform were purchased from Carlo Erba. All other chemical substances used were reagent-grade commercial products. IR spectrum was recorded on a MATTSON 1000 FT-IR spectrophotometer with range 4,000–400 cm^{-1} using KBr pellets. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-160A spectrophotometer using chloroform as the solvent. Elemental analyses for (C, H, N) were performed using a LECO CHNS 932 elemental analyzer.

Synthesis of 2-((E)-[2-Hydroxyphenyl]imino)methyl}Phenol

The title complex, 2-((E)-[2-hydroxyphenyl]imino)methyl}phenol, was synthesized by reacting an equimolar mixture of salicylaldehyde (0.61 g, 5 mmol) and 2-aminophenol (0.55 g, 5 mmol) in boiling ethanol (100 mL). Boiling was continued for several minutes and the mixture was left aside overnight. The precipitate formed was filtered and the residue was dissolved in CHCl_3 -EtOH (3:1) and set aside for crystallization. Analysis calculated for $\text{C}_{13}\text{H}_{11}\text{NO}_2$ (%): C, 73.25; H, 5.22; N, 6.47. Found: C, 73.19; H, 5.16; N, 6.56. Yield: 0.75 g, (70%) and m.p. > 186 °C. Color: Brown. UV-VIS (λ_{max} , nm, CH_2Cl_2): 383, 258. FT-IR (KBr, cm^{-1}): 1628 $\nu(\text{CH}-\text{N})$, 3062 $\nu(\text{C}-\text{H})$, 1530 $\nu(\text{C}-\text{C})$, 1310 $\nu(\text{C}-\text{O})$.

X-ray Structure Determinations of 2-((E)-[2-Hydroxyphenyl]imino)methyl}Phenol

The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in

[Table 1](#). Diffraction measurements were made at room temperature on a Stoe IPDS II CCD X-ray diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation using $\omega/2\theta$ scan mode [21]. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the $1.76 \leq \theta \leq 26.50$ range. The structure was solved by the direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [22, 23]. The empirical absorption corrections were applied by the multi-scan method via X-RED software. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in their idealized positions and refined isotropically. ORTEP drawing [24] of the molecule with 50% probability displacement thermal ellipsoids and atom-labeling scheme are shown in [Fig. 1](#).

Table 1 Crystal data and structure refinement details for complex

CCDC no.	694516
Empirical formula	$\text{C}_{13}\text{H}_{11}\text{NO}_2$
Formula weight	213.23
Temperature (K)	293(2)
Radiation (λ , Å)	$\text{MoK}\alpha$ (0.71073)
Crystal system, space group	Triclinic, P-1
Unit cell dimensions (Å, °)	
<i>a</i>	9.0479(7)
<i>b</i>	10.1564(8)
<i>c</i>	12.3659(10)
α	110.323(6)
β	89.940(6)
γ	102.996(6)
Volume (Å ³)	1034.62(14)
<i>Z</i>	4
Calculated density (Mg m^{-3})	1.369
Absorption coefficient (mm^{-1})	0.093
$F(000)$	448
Crystal size (mm)	0.480 × 0.380 × 0.220
θ Range for data collection (°)	1.76–27.56
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	4288
Independent reflections	3227 $\{R_{\text{int}} = 0.0450\}$
Data/parameters	3227/293
Final <i>R</i> indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0493$, $wR_2 = 0.1416$
Goodness of fit on F^2	1.038
Largest difference peak and hole (e Å^{-3})	0.574 and -0.353

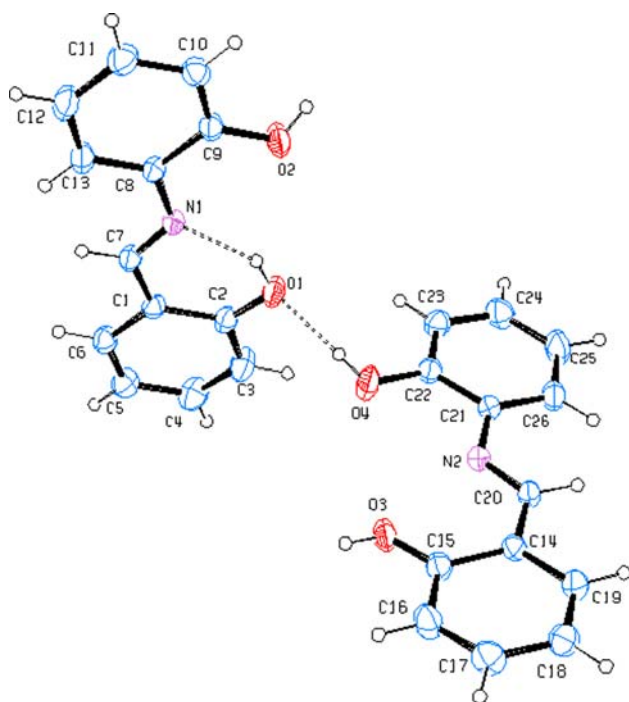


Fig. 1 The molecular structure and atomic labeling scheme of the compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by *dashed lines*

Results and Discussion

UV–VIS and IR Spectra of 2-((E)-[2-Hydroxyphenyl]imino)methyl Phenol

The UV–VIS spectra of Schiff base complex have been obtained in 10^{-2} M in chloroform at room temperature. This molecule exhibit the absorption peaks due to the localized π – π^* transition at 258 nm. The shoulder peak in 383 nm is tentatively attributed to the n – π^* transition of imino group. A strong absorption band at $1,628\text{ cm}^{-1}$ in the IR spectra of the complex is assigned to azomethine group, $\nu(\text{CH–N})$ mode [25]. The weak band of the aromatic $\nu(\text{C–H})$ stretching frequency of ligand was observed in

$3,062\text{ cm}^{-1}$. Furthermore, the $\nu(\text{C–C})$ and $\nu(\text{C–O})$ stretching frequencies were observed in $1,530\text{ cm}^{-1}$ and $1,310\text{ cm}^{-1}$, respectively.

Description of the Crystal Structure of 2-((E)-[2-Hydroxyphenyl]imino)methyl Phenol

The structure of 2-((E)-[2-hydroxyphenyl]imino)methyl phenol, crystallizes into a triclinic lattice with space group P-1. An ORTEP [24] view of the asymmetric unit is shown in Fig. 1 and selected bond distances and angles are presented in Table 2. The asymmetric unit contains two independent Schiff base molecules. The two independent molecules are almost identical with one another. In each molecule, the two benzene rings and azomethine group are

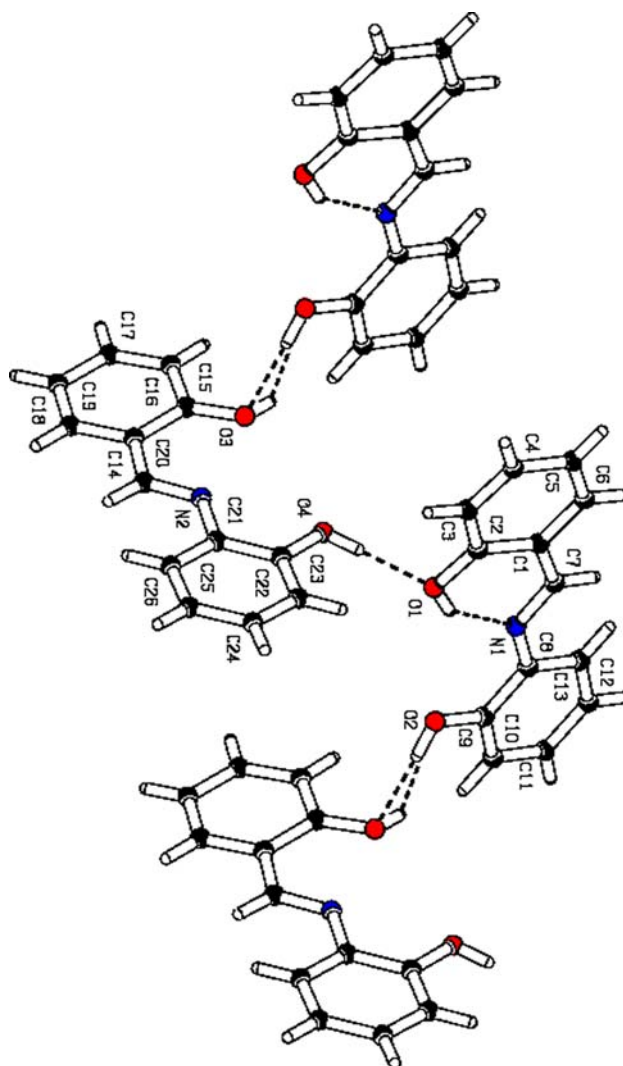


Fig. 2 The molecular structure of compound, showing the intra- and intermolecular hydrogen bonding. Intra-intermolecular O–H...N and O–H...O hydrogen bonds are shown as *dashed lines*

Table 2 Selected bond distances (Å) and angles (°) for complex

C7–N1	1.301(2)	C20–N2	1.307(2)
C9–O2	1.356(2)	C22–O4	1.346(2)
C2–O1	1.294(2)	C15–O3	1.298(2)
C8–N1	1.416(2)	C21–N2	1.414(2)
C9–O2	1.356(2)	C22–O4	1.346(2)
C7–N1–C8	126.95(14)	C20–N2–C21	126.82(14)
N1–C7–C1	123.27(15)	N2–C20–C14	123.12(15)
O1–C2–C1	121.66(16)	O3–C15–C14	120.84(15)
O2–C9–C8	117.23(16)	O4–C22–C21	117.67(15)

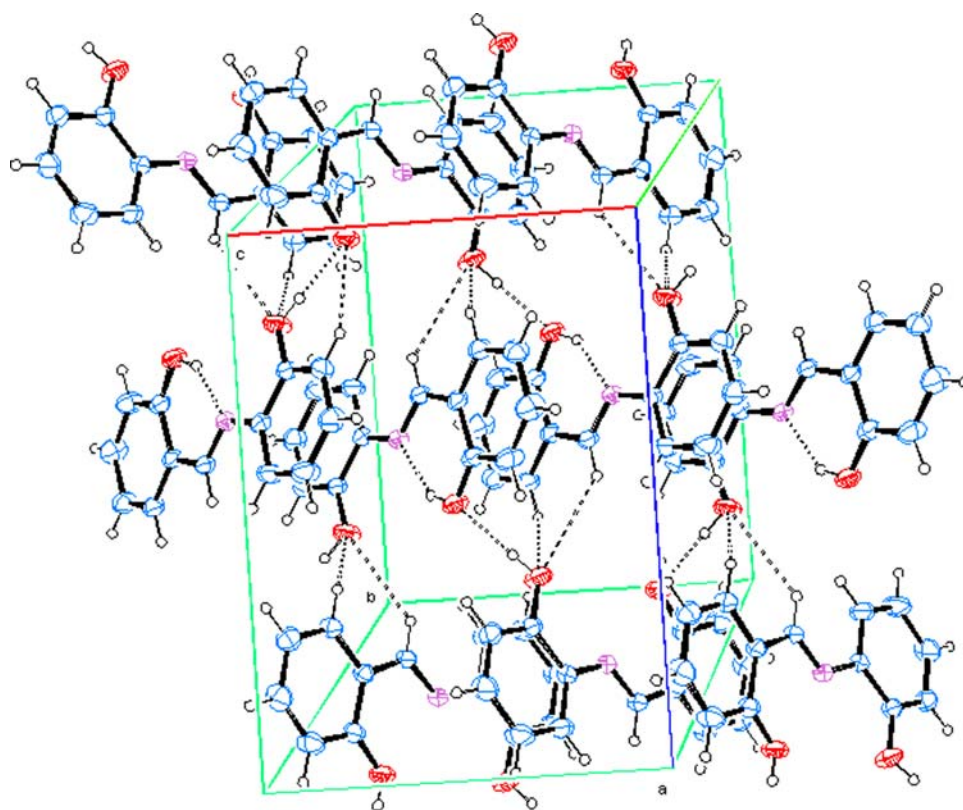


Fig. 3 The crystal packing of compound viewed along the *a* axis. Intra-intermolecular O–H...N and OH...O hydrogen bonds are shown as dashed lines

practically coplanar. The both molecules adopts an (E)-configuration about the C7–N1 and C20–N2 bonds with the azomethine nitrogen atoms. The C7–N1 and C20–N2 bond distances [1.301(2), 1.307(2) Å] are appreciably close to that of a C–N double bond (1.28 Å) [26–28]. The dihedral angle between of each molecule is 80.84(11)°. All the bond distances in the molecule are within normal ranges comparable to those of the similar compounds [26–28]. The both independent molecule is essentially coplanar. The two independent molecules in the asymmetric unit are hydrogen bonded and have different conformation. In the structure, the intramolecular hydrogen bonds involving the hydroxy O atom and azomethine N atom. Also hydroxy group of the molecule is the presence intermolecular

O–H...O hydrogen bonds with the hydroxy group of the other molecule (Fig. 2). The bond distances, bond angles and hydrogen bonding are comparable with the literature [29]. As shown in Fig. 2, interesting feature of this structure is the presence of one intra-molecular and one intermolecular O–H...N and O–H...O hydrogen bonds which stabilise this conformation, respectively, [O(1)–H(1)...N(1)] and [O(4)–H(4)...O(1)] in hydroxy group of molecule. But other hydroxy group of the molecule is the presence only intermolecular O–H...O hydrogen bonds which stabilise [O(2)–H(2)...O(3)] and [O(3)–H(3)...O(2)] (Fig. 3). Intra-intermolecular hydrogen bond distances and bond angles are listed in Table 3.

Table 3 Intra-intermolecular hydrogen bond distances and bond angles

D–H...A	d(D–H)(Å)	d(H...A)(Å)	d(D...A)(Å)	D–H...A (°)
O2–H2...O3 ^a	0.82	1.76	2.5794(18)	175
O3–H3...O2 ^b	0.82	2.22	2.5794(19)	107
O4–H4...O1	0.82	1.77	2.5837(19)	172
O1–H1...N1	0.82	1.87	2.599(2)	148

Symmetry codes: ^a $-1 + x, y, z$; ^b $1 + x, y, z$

Supplementary Material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 694516. Copies of this 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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