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X-ray Structure Analysis Online

Crystal Structure of (*E*)-4-Bromo-2-[(4-hydroxyphenyl)iminomethyl]-phenylen-1-olate

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The title compound, (*E*)-4-bromo-2-[(4-hydroxyphenyl)iminomethyl]phenylen-1-olate, $C_{13}H_{10}BrNO_2$, is in a zwitterionic form with a strong intramolecular N^+–H···O^- hydrogen bond. The title compound crystallizes in the monoclinic space group $P2_1/c$ with the following unit-cell parameters: a = 12.6746(11)Å, b = 12.8195(15)Å, c = 7.1576(7)Å, β = 94.993(7)° and V = 1158.6(2)Å^3. The crystal structure of this compound was solved by direct methods and refined to a final R = +0.0362 for 2285 reflections with $I > 2\sigma(I)$.

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Schiff-base compounds are often used as ligands in coordination chemistry because of their biological activities, and they play an important role in various fields of chemistry and biochemistry.[1] Two characteristic properties of Schiff bases are photochromism and thermochromism, and these properties are caused by proton transfer from the hydroxyl O atom to the imine N atom. In general, Schiff bases display two possible tautomeric forms, the phenol-imine (or benzenoid) and the *keto*-amine (or quinoid) forms. Another form of Schiff-base compounds is their zwitterionic form, which is rarely seen in the solid state.[2] Zwitterions have an ionic intra-molecular hydrogen bond (N^+–H···O^-), and their N^+–H bond lengths are longer than the standard inter-atomic separations observed in neutral N–H bonds (0.87 Å). The other ionic bonds, C–O^-, are not a key indicator as distinctive as the N^+–H bond, because NH forms of Schiff bases in solid state can be regarded as a resonance hybrid of two canonical structures, the quinoidal and zwitterionic forms.[3] We report here on the crystal structure of the title compound, (*E*)-4-bromo-2-[(4-hydroxyphenyl)iminomethyl]phenylen-1-olate, **1** (Fig. 1).

The compound (*E*)-4-bromo-2-[(4-hydroxyphenyl)iminomethyl]phenylen-1-olate was prepared by refluxing a mixture of a solution containing 5-bromosalicylaldehyde (0.05 g 0.25 mmol) in 20 ml of ethanol and a solution containing 4-hydroxyaniline (0.027 g 0.25 mmol) in 20 ml of ethanol. The reaction mixture was stirred for 1 h under reflux. Crystals of (*E*)-4-bromo-2-[(4-hydroxyphenyl)iminomethyl]phenylen-1-olate suitable for X-ray analysis were obtained from ethanol by slow evaporation (yield % 74; m.p. 508 – 509 K).

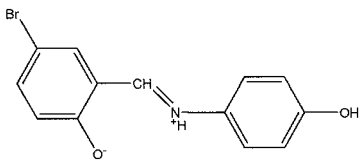


Fig. 1 Schematic diagram of the title compound..

The structure was solved by direct methods using the program SHELXS-97; the refinement and all other calculations were carried out using SHELXL-97.[6] All H atoms (except for H3) were positioned geometrically and treated using a riding model, fixing the aromatic C–H distances at 0.93 Å and the O–H distances at 0.82 Å. The position of the H3 atom was obtained from a difference map of the electron density in the unit-cell and was refined freely. The data-collection conditions and parameters of the refinement process are listed in Table 1. The atomic coordinates for non-hydrogen atoms are listed in Table 2,

Table 1 Crystal and experimental data

Formula: $C_{13}H_{10}BrNO_2$	
Formula weight: 292.13	
Crystal system: monoclinic	
Space group: $P2_1/c$	Z = 4
a = 12.6746(11)Å	
b = 12.8195(5)Å	β = 94.993(7)°
c = 7.1576(7)Å	
V = 1158.6(2)Å^3	
Density = 1.6747(3) g cm^{-1}	
T = 296(2)K	
Prism, brown	
No. of reflections used = 8533	
$2\theta_{max}$ = 52.00° Mo K_α	
R = 0.0362	
$(\Delta/\sigma)_{max}$ = 0.0000	
$(\Delta\rho)_{max}$ = 0.186 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.270 eÅ^{-3}	
Measurement: STOE IPDS II	
Program system: STOE X-RED	
Structure determination: direct methods	
Refinement: full matrix	
CCDC number: 677062	

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Table 2 Atomic coordinates and temperature factors

Atom	*x*	*y*	*z*	U_{eq}
C1	0.1681(2)	0.2985(3)	0.4613(5)	0.0433(9)
C2	0.0748(2)	0.3514(3)	0.4143(5)	0.0490(10)
C3	-0.0182(3)	0.2993(3)	0.3696(5)	0.0489(9)
C4	-0.0216(3)	0.1910(3)	0.3693(5)	0.0538(10)
C5	0.0689(3)	0.1352(3)	0.4125(5)	0.0565(10)
C6	0.1663(3)	0.1858(3)	0.4582(5)	0.0447(10)
C7	0.2643(3)	0.3496(3)	0.5138(5)	0.0494(10)
C8	0.4511(3)	0.3451(3)	0.6173(5)	0.0448(10)
C9	0.4599(3)	0.4378(3)	0.7148(5)	0.0506(10)
C10	0.5583(3)	0.4765(3)	0.7773(5)	0.0498(9)
C11	0.6485(3)	0.4224(3)	0.7439(5)	0.0450(10)
C12	0.6404(3)	0.3299(3)	0.6446(5)	0.0513(11)
C13	0.5416(3)	0.2911(3)	0.5839(5)	0.0526(10)
H3	0.339(3)	0.214(4)	0.536(6)	0.126(18)
N1	0.3518(2)	0.2999(3)	0.5536(4)	0.0481(8)
O1	0.74786(17)	0.45576(19)	0.8026(3)	0.0648(8)
O2	0.25393(17)	0.1305(2)	0.4968(3)	0.0603(7)
Br1	-0.14483(3)	0.37521(4)	0.30673(7)	0.07466(19)

Table 3 Selected bond distances (Å) and angles (°)

C7-C1	1.422(4)	C11-O1	1.362(3)
C7-N1	1.289(4)	C6-O2	1.326(4)
C8-N1	1.424(4)	C3-Br1	1.898(3)
Bond angles			
C2-C3-Br1	119.9(3)	C13-C8-N1	117.8(3)
C4-C3-Br1	119.1(2)	C9-C8-N1	122.9(3)
O2-C6-C5	120.2(3)	O1-C11-C10	123.1(3)
O2-C6-C1	121.2(3)	O1-C11-C12	117.0(3)
N1-C7-C1	121.4(3)	C7-N1-C8	126.1(3)

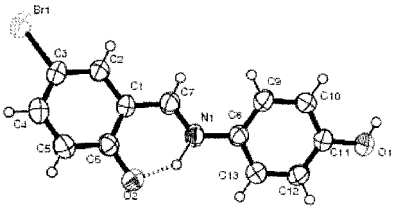


Fig. 2 Molecular structure of (I), showing the atom-numbering scheme.

and selected inter-atomic parameters are given in Table 3.

The molecular structure is shown in Fig. 2. The molecule is in a zwitterionic form, because the N^+–H bond lengths of zwitterions are longer than the standard inter-atomic separations observed in neutral N–H bonds (0.87 Å). There is a strong N^+–H···O type intra-molecular hydrogen bond in the title compound, and the N^+–H bond distance [1.12(5)Å] is in agreement with a similar zwitterion described in the literature [1.11(3)Å]. Although the C11–O1 bond length [1.362(3)Å] is as expected, the C6–O2 bond length [1.326(4)Å] is shorter than the expected value of a C–O single bond, and this bond that verifies the zwitterionic form, is comparable with a similar zwitterion mentioned in the literature [1.323 Å]. In addition to this, the C1–C7, C7–N1 and N1–C8 bond lengths display the zwitterionic character of the title compound (Table 3), and these distances are similar to other reported values [1.430(3), 1.285(3) and 1.457(3)Å, respectively].[5] There are also intermolecular O1–H1···O2 and C4–H4···O1 hydrogen bonds in the structure (Table 4). The molecule is not planar; the dihedral angle between the two benzene rings is 30.85(0.10)°. The ring involving the N–H···O hydrogen bond is almost coplanar with an adjacent ring, with an N1–C7–C1–C6 torsion angle of 2.2(5)°.

Table 4 Hydrogen-bond geometry (Å)

D-H...A	D-H	H...A	D...A	D-H...A
N1-H3...O2	1.12(5)	1.53(5)	2.517(4)	144(3)
O1-H1...O2^{i}	0.82	1.85	2.663(3)	174
C4-H4...O1^{ii}	0.93	2.55	3.473(4)	171

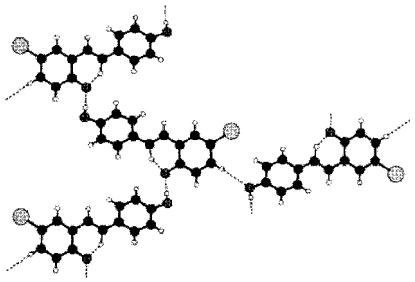


Fig. 3 Packing diagram. The dashed lines indicate hydrogen bonds.

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