



Synthesis and Crystal Structure of 1-(4-{{(E)-3,5-dibromo-2-hydroxybenzylidene}amino}phenyl)ethanone Oxime

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The title compound, 1-(4-{{(E)-3,5-dibromo-2-hydroxybenzylidene}amino}phenyl)ethanone oxime, was synthesized by the reaction of 3,5-dibromosalicylaldehyde with 4-amino-phenylethanone oxime in ethanol. The molecule crystallizes in the triclinic system, space group $P2_1/c$, with four crystallographically independent molecules in the unit cell. The two benzene rings form a dihedral angle of 21.63° . In the crystal structure, there are a strong intramolecular O2-H2...N2 hydrogen bond between the hydroxyl (O2-H2) group and the Schiff base nitrogen (N2) atom, with the distance between N2 and O2 is $2.580(4)$ Å. Moreover, a dimer is formed with another adjacent molecule by two pairs of intermolecular O1-H1...N1 hydrogen bonds.

Key Words: Oxime-type compound, Synthesis, Crystal structure.

INTRODUCTION

Schiff base compounds have been playing an important role in the development of coordination chemistry^{1,2}. During the past several decades, a large number of Schiff base complexes have been studied extensively for their facile synthesis and easily tunable steric position and application³. Many Schiff base complexes have been structurally characterized⁴, but only a relatively small number of oxime-type compounds have been characterized⁵⁻⁷. Here, we report the synthesis and crystal structure of a new oxime-type compound 1-(4-{{(E)-3,5-dibromo-2-hydroxybenzylidene}amino}phenyl) ethanone oxime.

EXPERIMENTAL

3,5-Dibromosalicylaldehyde was purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra in the range $400-4000$ cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. X-ray single crystal structure was determined on a Bruker Smart APEX CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taikhe Instrument Limited Company and the thermometer was uncorrected.

1-(4-{{(E)-3,5-dibromo-2-hydroxybenzylidene}amino}phenyl)ethanone oxime: 4-Aminophenylethanone oxime was

synthesized according to an analogous method reported earlier^{8,9}. To an ethanolic solution of 3,5-dibromosalicylaldehyde (560.2 mg, 2 mmol) was added an ethanolic solution of 4-aminophenylethanone oxime (300.6 mg, 2 mmol). The mixture solution was stirred at 328 K for 5 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was dried under vacuum and obtained orange red microcrystal. Yield, 77.4%. m.p. 491-492 K. Anal. calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{Br}_2$ (%): C, 43.72; H, 2.94; N, 6.80. Found (%): C, 43.98; H, 3.06; N, 6.63. IR: $\nu(\text{C}=\text{N})$, 1612 cm^{-1} and $\nu(\text{O}-\text{H})$, 3416 cm^{-1} . Orange-red block-like single crystals suitable for X-ray diffraction studies were obtained after about 2 weeks by slow evaporation from an ethanol/acetone solution of 1-(4-{{(E)-3,5-dibromo-2-hydroxybenzylidene}amino}phenyl)ethanone oxime.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.45 mm \times 0.40 mm \times 0.33 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 880448.

TABLE-1
CRYSTAL DATA AND REFINEMENT PARAMETERS
FOR THE TITLE COMPOUND

Empirical formula	C ₁₅ H ₁₂ N ₂ O ₂ Br ₂
Formula weight	412.09
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Cell dimensions	a = 12.2181(11) Å, b = 15.0209(14) Å, c = 8.6640(7) Å β = 108.232(1)
Volume	1510.3(2) Å ³
Z	4
Density (calculated)	1.812 mg/m ³
Absorption coefficient	5.372 mm ⁻¹
F(000)	808
Index ranges	-14 ≤ h ≤ 6, -17 ≤ k ≤ 17, -9 ≤ l ≤ 10
Reflections collected	7517 / 2651 [R(int) = 0.0751]
Independent reflections	1402
Data/restraints/parameters	2651/0/191
Goodness of fit indicator	1.011
R [I > 2σ(I)]	R ₁ = 0.0514, wR ₂ = 0.1032
Largest diff. peak and hole	0.631 and -0.559 e. Å

RESULTS AND DISCUSSION

X-ray crystallographic analysis revealed the crystal structure of the title compound (Fig. 1). Selected bond distances and angles are listed in Table-2. The crystal structure of the title compound is built up by only the C₁₅H₁₂Br₂N₂O₂ molecules and all bond lengths and angles are in normal ranges. The molecule crystallizes in the triclinic system, space group P2₁/c, with four crystallographically independent molecules in the unit cell. The two benzene rings form a dihedral angle of 21.63°.

In the crystal structure, there is a strong intramolecular O2-H2...N2 hydrogen bond between the hydroxyl (O2-H2) group and the Schiff base nitrogen (N2) atom, with the distance between N2 and O2 is 2.580(4) Å. Moreover, a dimer is formed with another adjacent molecule by two pairs of intermolecular O1-H1...N1 hydrogen bonds (Table-3, Fig. 2)¹⁰⁻¹².

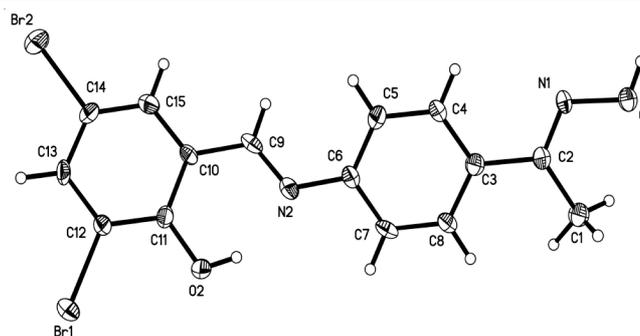


Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

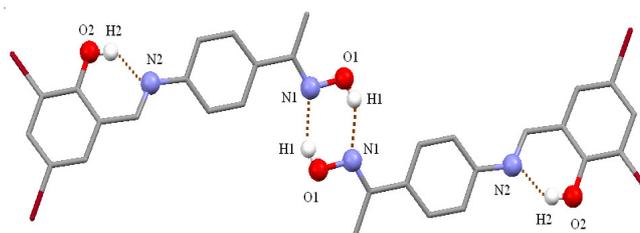


Fig. 2. Dimer formed by the title compounds showing the intramolecular and intermolecular O-H...N hydrogen bonds (dashed lines). For clarity, the H atoms not involved in the interactions have been omitted

TABLE-3
INTRAMOLECULAR AND INTERMOLECULAR O-H...N
HYDROGEN-BONDING DATA [Å, °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O1-H1...N1	0.82	2.04	2.769(3)	148
O2-H2...N2	0.82	1.86	2.580(4)	147

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TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
Br(1)-C(12)	1.873(6)	C(2)-C(3)	1.490(9)	C(10)-C(15)	1.400(8)
Br(2)-C(14)	1.911(6)	C(3)-C(8)	1.371(9)	C(10)-C(11)	1.414(8)
N(1)-C(2)	1.274(8)	C(3)-C(4)	1.394(8)	C(11)-C(12)	1.386(8)
N(1)-O(1)	1.387(6)	C(4)-C(5)	1.367(8)	C(12)-C(13)	1.398(8)
N(2)-C(9)	1.288(7)	C(5)-C(6)	1.387(8)	C(13)-C(14)	1.372(9)
N(2)-C(6)	1.411(7)	C(6)-C(7)	1.372(8)	C(14)-C(15)	1.344(9)
O(2)-C(11)	1.349(7)	C(7)-C(8)	1.374(8)		
C(1)-C(2)	1.490(9)	C(9)-C(10)	1.448(8)		
Bond	Angles	Bond	Angles	Bond	Angles
C(2)-N(1)-O(1)	113.0(5)	C(7)-C(6)-C(5)	118.1(6)	O(2)-C(11)-C(10)	121.5(6)
C(9)-N(2)-C(6)	121.9(6)	C(7)-C(6)-N(2)	117.0(6)	C(12)-C(11)-C(10)	119.0(6)
N(1)-C(2)-C(3)	115.9(6)	C(5)-C(6)-N(2)	124.8(6)	C(11)-C(12)-C(13)	121.3(6)
N(1)-C(2)-C(1)	123.7(6)	C(6)-C(7)-C(8)	120.7(6)	C(11)-C(12)-Br(1)	119.2(5)
C(3)-C(2)-C(1)	120.4(6)	C(3)-C(8)-C(7)	122.2(6)	C(13)-C(12)-Br(1)	119.3(5)
C(8)-C(3)-C(4)	116.5(6)	N(2)-C(9)-C(10)	120.8(6)	C(14)-C(13)-C(12)	118.2(6)
C(8)-C(3)-C(2)	121.7(6)	C(15)-C(10)-C(11)	118.2(6)	C(15)-C(13)-C(13)	122.0(6)
C(4)-C(3)-C(2)	121.8(6)	C(15)-C(10)-C(9)	120.5(6)	C(15)-C(14)-Br(2)	119.7(5)
C(5)-C(4)-C(3)	121.5(6)	C(11)-C(10)-C(9)	121.2(6)	C(13)-C(14)-Br(2)	118.2(5)
C(4)-C(5)-C(6)	121.0(6)	O(2)-C(11)-C(12)	119.5(6)	C(14)-C(15)-C(10)	121.3(6)

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