

Synthesis and Crystal Structure of 2-[(3-Bromo-phenylimino)methyl]phenol

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A new Schiff base 2-[(3-bromo-phenylimino)methyl]phenol, derived from condensation of salicylaldehyde with *m*-bromoaniline, has been prepared and characterized by single crystal X-ray diffraction. Schiff base is in the monoclinic system, space group $P2_1$ with $a = 3.928(14)$ Å, $b = 10.590(4)$ Å, $c = 13.212(5)$ Å, $\beta = 97.360(4)^\circ$, $M_r = 276.13$, $V = 545.1(3)$ Å³, $D_c = 1.682$ g/cm³, $Z = 2$, $\mu = 3.745$ mm⁻¹, $F_{(000)} = 276$, $R = 0.0326$, $wR = 0.0455$. The schiff base is stabilized by intermolecular C-H...O and π ... π interaction and further linked into a 2D layer structure.

Key Words: Salicylaldehyde, Schiff base, Synthesis, Crystal structure.

INTRODUCTION

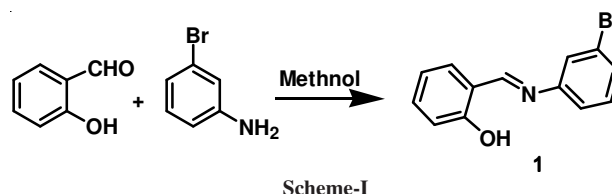
Hydrogen bondings and π ... π stacking interactions are important research content in supramolecular chemistry and crystal engineering^{1,2}. They play an important role in self-assembly^{3,4}, molecular recognition^{5,6} and the stability of inclusion complexes⁷⁻⁹ as an auxiliary stabilizing short contact. Numerous experiments have been performed and several reviews have been documented for C-H...O interactions¹⁰ and π ... π stacking interactions^{11,12}. Some Schiff bases can form C-H...O interactions and π ... π stacking because they possess hydroxyl groups and aromatic rings, which play an important role for formation, stabilization and packing of the complex crystal. On the other hand, Schiff bases in general have been reported as organic chelating ligands in the synthesis of metal complexes due to their hard donor-atom frameworks, stability and easy modification¹³. Metal complexes with Schiff base ligands have played an important role in the development of coordination chemistry due to their preparative accessibility, structural variety and many functional properties. Based on the extensive application and flexibility of these interactions in supramolecular network building¹⁴ and the discovery of application prospect of Schiff base in catalysis¹⁵, photoelectric and LED¹⁶ and biological activities^{17,18}. We report herein the synthesis and characterization of a new Schiff base obtained from salicylaldehyde and *o*-bromoaniline. The structure of compound had been established accurately from the single crystal X-ray diffraction study. The results showed that the compound is stabilized by intermolecular O-H...N and intramolecular C-H...O hydrogen bonds and π ... π interactions and

further linked into a 2D layer structure. These interactions play a very important role in the formation, stability and crystallization of compound.

EXPERIMENTAL

Crystal structure was determined on a Bruker APEX II CCD area diffractometer. Salicylaldehyde and *m*-bromoaniline were purchased from J & K Chemical Ltd. All other chemicals were commercial products and used without further purification.

Synthesis of 2-[(3-bromo-phenylimino)methyl]phenol: 2-[(3-Bromo-phenylimino)methyl]phenol has been synthesized by dissolving 5 mmol of salicylaldehyde and an equimolar quantity of *m*-bromoaniline in 50 mL of methanol. The reaction mixture was heated to 50 °C for 1 h and then cooled to room temperature followed by concentrating the resulting mixture to a yellow solid product. The yield was 1.20 g (87 %) (**Scheme-I**). Yellow block single crystals suitable for single crystal X-ray diffraction were grown in methanol by slow evaporation.



X-Ray crystal structure determination: A yellow block crystal with dimensions of 0.54 mm × 0.58 mm × 0.09 mm

was selected for measurement. Diffraction data of compound were collected at 153(2) K on a Bruker APEX II CCD area diffractometer equipped with a graphite-monochromatic MoK α radiation ($\lambda = 0.71073$ Å). A total of 4683 reflections were collected in the range of $2.5 \leq \theta \leq 29.1^\circ$ by using an φ - ω multi-scan mode, of which 2605 were unique with $R_{\text{int}} = 0.030$ and 2033 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELX-97 program package¹⁹. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were fixed at their ideal positions. The final $R = 0.0326$, $wR = 0.0455$ ($w = 1/[\sigma^2(F_o^2) + (0.0013P)^2 + -0.1P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 0.98$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.74$ and $(\Delta\rho)_{\text{min}} = -0.56$ e/Å³. The crystal data, experimental details, refinement results and details of structure determinations are shown in Table-1. Selected bond lengths and bond angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT FOR THE COMPOUND

Parameter	Compound
Empirical formula	C ₁₃ H ₁₀ NOBr
Formula weight	276.13
Crystal size (mm)	0.54 × 0.28 × 0.09
Crystal system, space group	monoclinic, P2 ₁
a, b, c (Å)	3.9280(14), 10.59(4), 13.212(5)
α, β, γ (°)	$\beta = 97.360(4)$
V (Å ³)	5451(3)
D _c (g cm ⁻³) Z	1.682, 2
μ (mm ⁻¹)	3.745
F ₍₀₀₀₎	276
Index ranges (H, k, l)	$-5 \leq h \leq 5, -14 \leq k \leq 13, -16 \leq l \leq 17$
θ range (°)	2.47–29.12
Reflections collected/unique	4683–2605
R, wR [$I \geq 2\sigma(I)$]	0.0326, 0.0455
R, wR [all data]	0.0435, 0.0472
GOF on F ²	0.978
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ (e Å ⁻³)	0.740, -0.561
Final weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0013P)^2 - 0.1P]$, where $P = (F_o^2 + 2F_c^2)/3$.	

RESULTS AND DISCUSSION

The Schiff base was prepared in excellent yields (87 %) in absolute methanol. The compound is yellow solids and stable in air at room temperature and also soluble in common polar organic solvents, such as DMSO, methanol and ethanol.

The compound is build up only by Schiff base molecules, within which all bond lengths and bond angles of ligand are in normal ranges. Its crystal structure with the atomic numbering scheme is presented in Fig. 1. The result shows that the

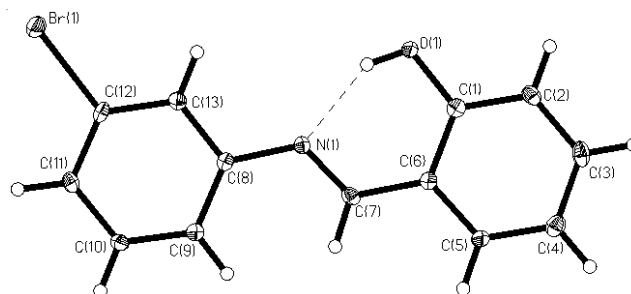


Fig. 1. Molecular structure of the compound displacement ellipsoids are drawn at the 30 % probability level

whole molecule assigns to be E configuration with respect to the azomethine -CH=N- bond on the basis of the crystal data with the C(7)=N(1) distance is 1.285(4) Å. The whole molecule is nearly coplanar with the dihedral angle of two phenyl rings (ring A, C(1)-C(6) and ring B, C(8)-C(13)) of 6.24° , which is interpreted by conjugation effect and the stabilization of ring from intramolecular hydrogen bond.

In the crystal structure of the Schiff base, there is a "soft" intermolecular interaction C-H...O hydrogen bonds and π - π stacking interaction in the lattice structure. Discrete monomeric molecules are held together by intermolecular hydrogen bond C(7)-H(7)...O(1), atom C7 acted as hydrogenbond donor, via H7, to O1 at the symmetry position ($-x + 2, 1/2 + y, -z + 1$), thus hydrogen bond C7 H7...O1 is formed. The C7-H7...O1 hydrogen bond existed with bond lengths being 2.773 Å and bond angle being 109.8° . Combination of the hydrogen bonds link the molecules to form a 1D zig-zag chain along c-axis (Fig. 2).

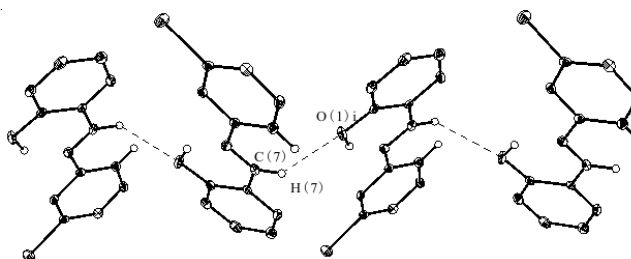


Fig. 2. A one-dimensional zig-zag chain of 1 along b-axis (C-H...O hydrogen bond was showed as dashed lines, hydrogen atoms were omitted for clarity. $-x + 2, 1/2 + y, -z + 1$)

Another, the Schiff base skeletons are stacked into column through π - π interaction. A π - π interaction dimer is formed between the adjacent Schiff bases with an parallel manner, of which the dihedral angles being 0.00° , the intercentroid distances of two rings A and two rings B in two neighboring molecules are 3.928 and 3.928 Å, respectively. The corresponding

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

Bonds	d	Bonds	d	Bonds	d
Br(1)-C(12)	1.908(3)	O(1)-C(1)	1.360(4)	O(1)-H(10)	0.8355
N(1)-C(7)	1.285(4)	N(1)-C(8)	1.422(4)	C(6)-C(7)	1.380(4)
C(1)-C(6)	1.414(4)	C(8)-C(9)	1.394(4)	C(7)-H(7)	0.9500
Angle	ω	Angle	ω	Angle	ω
C(1)O(1)H(10)	107.7	C(7)N(1)C(8)	121.5(3)	O(1)-C(1)-C(2)	118.6(3)
C(1)C(6)C(7)	122.1(3)	N(1)C(7)C(6)	122.6(3)	C(11)C(12)Br(1)	119.4(3)

perpendicular distances of them are 3.4685 Å and 3.3984 Å, respectively. All the intercentroid and interplanar distances are comparable to the reported contact calculated²⁰. Combination of these aromatic π - π stacking interactions generates a column along *b*-axis.

Combination of the C(7)-H(7)···O(1) and the aromatic π ··· π stacking interactions linked **1** to generate a 2D network structure (Fig. 3). These interactions also mutually strengthen and solidify the molecule.

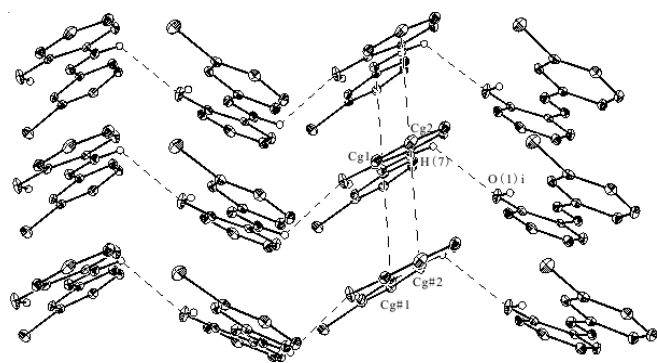


Fig. 3. 2D packing diagram of the title compound, the π ··· π stacking interactions and C-H···O hydrogen bonds were showed as dashed lines. (For clarity, some H atoms have been omitted. Symmetry code: (#): $x-1, y, z$; (i): $-x+2, 1/2+y, -z+1$. Cg is the center of ring A or ring B)

Conclusion

A new Schiff base prepared by the condensation of salicylaldehyde with *m*-bromoaniline. The structure had been established accurately from the single crystal X-ray diffraction study. The results showed that the compound is stabilized by intermolecular O-H···N and intramolecular C-H···O hydrogen bonds and π ··· π interactions and further linked into a 2D layer structure. These interactions play a very important role in the formation, stability and crystallization of compound.

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