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Spectroscopic studies and structure determination of Schiff base derived from 5-bromosalicylaldehyde and 4-aminobenzoic acid

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ABSTRACT

The Schiff base have been characterized by IR, ^{1}H-NMR spectroscopy, ESI mass spectrometry and elemental analysis. The 4-(5-bromo-2-hydroxybenzylideneamino) benzoic acid was structurally characterized (monoclinic space group $P2_1/c$, unit cell dimensions a = 2857.63(8) pm, b = 686.90(2) pm, c = 612.35(2) pm, β= 94.411(3)°). It forms dimers in the solid state which are connected by intermolecular hydrogen bonds between the COOH groups.

Keywords: Schiff base, spectroscopic studies, x-ray diffraction, hydrogen bonds.

INTRODUCTION

Schiff bases are widely employed in synthetic organic and inorganic chemistry. They were reported to show diverse biological activity[1-5] and have many applications as ligands in coordination chemistry of transition metals[6-9].

The Schiff base shown in this paper have been synthesized by Brewster and Millam[10] who studied phototropic and thermotropic anils from 5-Bromosalicylaldehyde. Schiff bases very similar to this compound have shown microbiological[11] activity and antifungal properties[12].

Our work is based in the structure determination of this compound with spectroscopic methods and single crystal x-ray diffraction data. The x-ray diffraction from single crystal has shown the forming of intramolecular and intermolecular hydrogen bonds in solid state and the existing of this compound in dimer forms.

MATERIAL AND METHODS

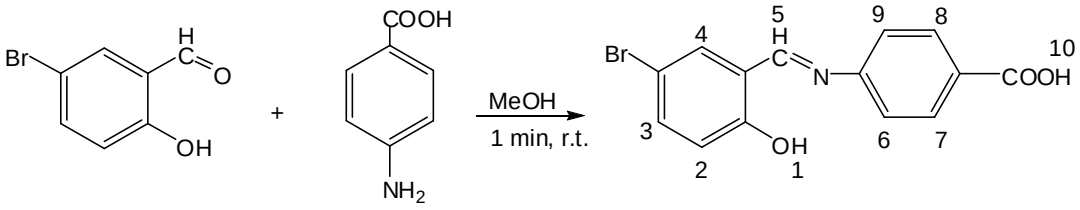
Instruments

The infrared spectra were determined on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets. The ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer. The mass spectra were measured on an FT-ICR-MS Bruker-Daltonics ESI spectrometer (APEX II, 7 Tesla). Elemental analyses were performed on a VARIO EL microanalyzer (Heraeus). The crystallographic data were collected on an Xcalibur-S diffractometer (Oxford Diffraction).

Preparation of Schiff base

The Schiff base where prepared by scheme 1.

Scheme 1.



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Synthesis of 4-(5-bromo-2-hydroxybenzylideneamino)benzoic acid (**1**)

A methanolic solution of 5-bromo salicylaldehyde (5 mmol in 25 mL) was added to a methanolic solution of 4-aminobenzoic acid (5 mmol in 15 mL) at room temperature. In 1 min. a yellow precipitate of the Schiff base was formed, which was isolated by filtration and washed with acetone and diethyl ether. Single crystals were obtained by recrystallization from 1,4-dioxane. Yield 85%. IR (KBr): 3443, 1700, 1683, 1618, 1599, 1561, 1431, 1277, 1172 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 6.56 (d), 6.99 (d) 7.49 (d) 7.62 (d), 7.72 (d), 7.91 (s) 8.01 (d), 8.96 (s), 10.22 (s), 12.65 (s) ppm; ESI-MS *m/z* 319.8 (M$^-$); Anal. Calc. for $C_{14}H_{10}BrNO_3$: C, 52.52; H, 3.15; N, 4.38. Found: C, 52.53; H, 3.22; N, 4.23.

RESULTS AND DISCUSSION

In the ^{1}H NMR spectra, the aromatic protons (7H, H-2,3,4,6,7,8,9 in compound **1** are observed in the range of 6.56 to 8.01 ppm. The azomethine proton (1H, N=CH) is observed at 8.96 ppm, the phenolic proton H-1 at 10.22 ppm, and the carboxylic proton (H-10) appears as a broad signal at 12.65 ppm, wich can be explained with the forming of intermolecular hydrogen bonds between the carboxylic acid groups of two molecules (Fig. 2). The compound exhibit the expected multiplicities.

4-(5-bromo-2-hydroxybenzylideneamino) benzoic acid was obtained as single crystals from 1,4-dioxane and the molecular structure could be determined by X-ray diffraction (Table 1, Fig. 1). Selected bond lengths and bond angles are given in Table 2. In the solid state, the molecule forms hydrogen-bridged dimers as expected for carboxylic acids[13] (Fig. 2, Table 3). Besides this intermolecular interaction, an intramolecular hydrogen donor-acceptor bond between N(1) and H(1O1) is observed. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement.

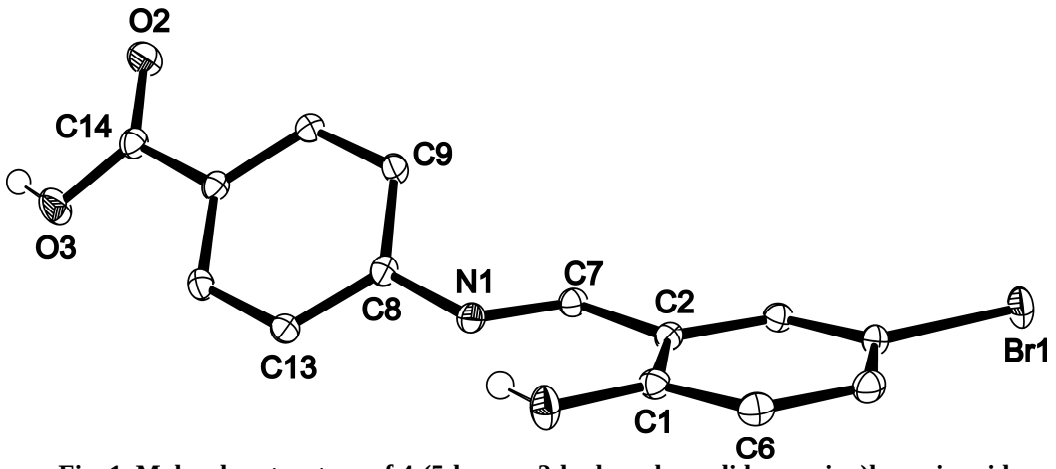

Fig. 1. Molecular structure of 4-(5-bromo-2-hydroxybenzylideneamino)benzoic acid

Crystal structure determination

X-ray data were collected on Xcalibur-S diffractometer (Oxford Diffraction) using Mo-K□ radiation (□ = 71.073 pm) and □-scan rotation. Data reduction was performed with the CrysAlis Pro[14] including the program SCALE3 ABSPACK[15] for empirical absorption correction. The structure was solved by direct methods[16] and the refinement of all non-hydrogen atoms was performed with SHELX97[17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. A difference-density Fourier map was used to locate all hydrogen atoms in the final stage of the structure refinement. Structure figures were generated with ORTEP[18] and DIAMOND-3[19].

Table 1. Crystal data and structure refinement

Empirical formula	$C_{14}H_{10}BrNO_3$	
Formula weight	320.14	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 2857.63(8) pm	α = 90°
	b = 686.90(2) pm	β = 94.411(3)°
	c = 612.35(2) pm	γ = 90°
Volume	1.19843(6) nm^3	
Z	4	
Density (calculated)	1.774 Mg/m^3	
Absorption coefficient	3.433 mm^{-1}	
F(000)	640	
Crystal size	0.4 x 0.4 x 0.05 mm^3	
Theta range for data collection	2.86 to 30.51°.	
Index ranges	-40<=h<=40, -9<=k<=9, -8<=l<=8	
Reflections collected	20685	
Independent reflections	3658 [R(int) = 0.0308]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.47046	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3658 / 0 / 212	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0625	
R indices (all data)	R1 = 0.0309, wR2 = 0.0643	

Largest diff. peak and hole 0.438 and -0.355 e.Å^{-3}

Table 2. Selected bond lengths (pm) and angles (°)

Br(1)-C(4)	189.5(1)
O(1)-C(1)	134.9(2)
O(1)-H(1O1)	76(3)
O(2)-C(14)	123.0(2)
O(3)-C(14)	130.6(2)
O(3)-H(1O3)	80(3)
N(1)-C(7)	128.5(2)
N(1)-C(8)	141.8(2)
C(1)-C(6)	139.5(2)
C(1)-C(2)	141.3(2)
C(2)-C(3)	139.9(2)
C(2)-C(7)	145.3(2)
C(3)-C(4)	137.4(2)
C(3)-H(3)	95(2)
C(4)-C(5)	139.7(2)
C(5)-C(6)	138.2(2)
C(5)-H(5)	98(2)
C(6)-H(6)	92(2)
C(7)-H(7)	92(2)
C(8)-C(13)	138.9(2)
C(8)-C(9)	140.1(2)
C(9)-C(10)	139.1(2)
C(9)-H(9)	90(2)
C(10)-C(11)	139.0(2)
C(10)-H(10)	97(2)
C(11)-C(12)	139.4(2)
C(11)-C(14)	148.7(2)
C(12)-C(13)	139.2(2)
C(12)-H(12)	90(2)
C(13)-H(13)	95(2)
C(1)-O(1)-H(1O1)	108(2)
C(14)-O(3)-H(1O3)	110(2)
C(7)-N(1)-C(8)	120.4(1)
O(1)-C(1)-C(6)	118.5(1)
O(1)-C(1)-C(2)	121.7(2)
C(6)-C(1)-C(2)	119.8(1)
C(3)-C(2)-C(1)	119.1(1)
C(3)-C(2)-C(7)	119.6(1)
C(1)-C(2)-C(7)	121.1(1)
C(4)-C(3)-C(2)	120.1(1)
C(4)-C(3)-H(3)	123(1)
C(2)-C(3)-H(3)	117(1)
C(3)-C(4)-C(5)	121.1(1)
C(3)-C(4)-Br(1)	119.7(1)
C(5)-C(4)-Br(1)	119.2(1)
C(6)-C(5)-C(4)	119.5(1)

C(6)-C(5)-H(5)	122(1)
C(4)-C(5)-H(5)	119(1)
C(5)-C(6)-C(1)	120.4 (1)
C(5)-C(6)-H(6)	121(1)
C(1)-C(6)-H(6)	119(1)
N(1)-C(7)-C(2)	121.1(1)
N(1)-C(7)-H(7)	121(1)
C(2)-C(7)-H(7)	119(1)
C(13)-C(8)-C(9)	120.3(1)
C(13)-C(8)-N(1)	118.0(1)
C(9)-C(8)-N(1)	121.6(1)
C(10)-C(9)-C(8)	119.4(1)
C(10)-C(9)-H(9)	122(1)
C(8)-C(9)-H(9)	119(1)
C(11)-C(10)-C(9)	120.2(1)
C(11)-C(10)-H(10)	120(1)
C(9)-C(10)-H(10)	120(1)
C(10)-C(11)-C(12)	120.2(1)
C(10)-C(11)-C(14)	118.7(1)
C(12)-C(11)-C(14)	121.3(3)
C(13)-C(12)-C(11)	119.1(3)
C(13)-C(12)-H(12)	122(2)
C(11)-C(12)-H(12)	118(1)
C(8)-C(13)-C(12)	120.0(1)
C(8)-C(13)-H(13)	118(1)
C(12)-C(13)-H(13)	122(1)
O(2)-C(14)-O(3)	124.1(1)
O(2)-C(14)-C(11)	121.5(1)
O(3)-C(14)-C(11)	114.4(1

Table 3. Hydrogen donor-acceptor bonds (pm and °).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O1)...N(1)	76(3)	191(3)	259.2(2)	150(3)
O(3)-H(1O3)...O(2)’	80(3)	183(3)	263.0(2)	178(3)

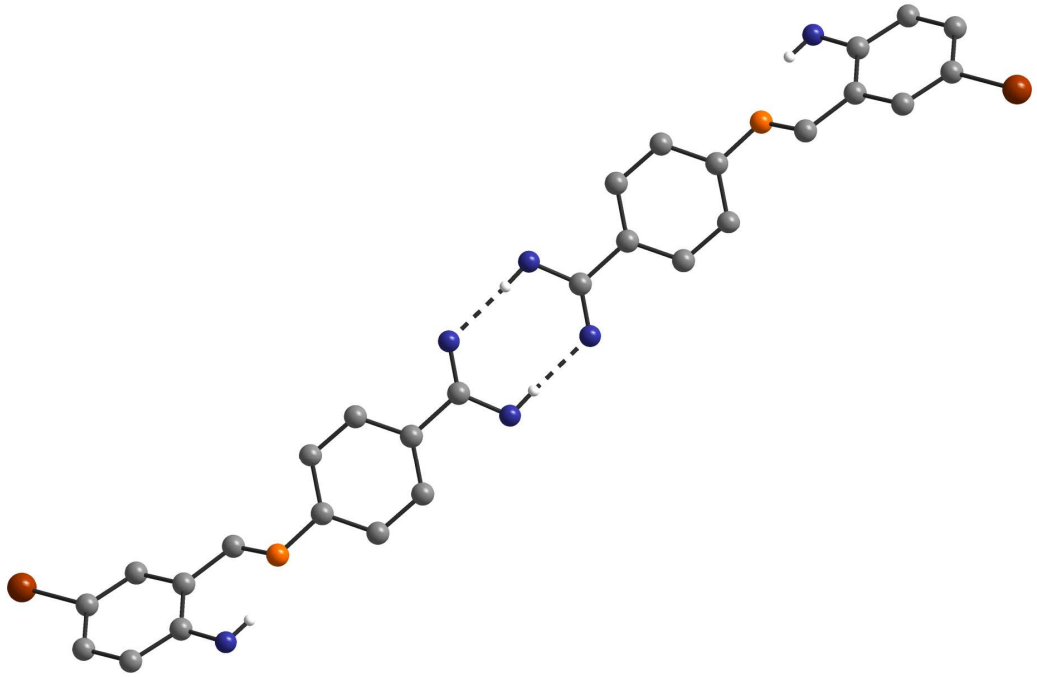

Fig. 2. Hydrogen-bridged dimers of 4-(5-bromo-2-hydroxybenzylideneamino)benzoic acid

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REFERENCES

[1] A. H. El-masry, H. H. Fahmy, S. H. Ali Abdelwahed, *Molecules*, **2000**, 5, 1429.
[2] E. M. Hodnett, W. J. Dunn, *J. Med. Chem.*, **1970,** 13, 768.
[3] S. Holla, S. Rao, K. Sarojini, M. Akberali, S. Kumari, *Eur. J. Med. Chem.*, **2006,** 41, 657.
[4] A. Jarrahpour, D. Khalili, E. De Clercq, C. Salmi, M. Brunel, *Molecules*, **2007**, 12, 1720.
[5] M. Hania, *E-Journal of Chemistry*, **2009**, 6, 629.
[6] C. Spinu, M. Pleniceanu, C. Tigae, *Turk. J. Chem.*, **2008**, 32, 487.
[7] H. Temel, H. Hosgoren, *Transition Met. Chem.*, **2002**, 27, 609.
[8] H. Temel, S. Ilhan, M. Sekerci, R. Ziyadanogullari, *Spectrosc. Letters*, **2002**, 35, 219.
[9] H. Temel, M. Sekerci, *Synth. React. Inorg. Met.-Org. Chem.*, **2001**, 31, 849.
[10] C. M. Brewster, L. H. Millam, *J. Am. Chem. Soc.* **1933**, 55, 763.
[11] J. Parekh, P. Inamdhar, R. Nair, S. Baluja, S. Chanda, *J. Serb. Chem. Soc.* **2005**, 70, 1155.
[12] D.B. Reisner and P.M. Borick, *J. Am. Pharmaceut. Assoc.*, **1955**, 44, 148.
[13] I. Wolfs, H. O. Desseyn, *Spectrochim. Acta (A)*, **1996**, 52, 1521.
[14] CrysAlis Pro: Data collection and data reduction software package, Varian, Inc. SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics.
[15] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.*, **1993**, 26, 343.
[16] G. M. Sheldrick, SHELXS97 and SHELXL97, Programs for Crystal Structure Analysis, University of Göttingen, Germany, **1997**.
[17] L. J. Farrugia, *J. Appl. Cryst.*, **1997**, 30, 565.
[18] K. Brandenburg, DIAMOND 3, Crystal Impact GbR, Bonn, Germany, **2006**.