

Synthesis, Characterization and Crystal Structures of *N,N'*-bis(5-Fluoro-2-hydroxybenzylidene)-ethylenediamine and 4,4'-Difluoro-2,2'-[(hydrazine-1,2-diylidene)bis(methanylylidene)]diphenol

WEI-MING ZHANG^{1,*}, SHAO-SONG QIAN² and ZHONGLU YOU³

¹Nanjing Institute for the Comprehensive Utilization of Wild Plant, Nanjing 210042, P.R. China

²School of Life Sciences, Shandong University of Technology, Zibo 255049, P.R. China

³Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P.R. China

*Corresponding author: E-mail: youzhonglu@126.com

Received: 13 May 2014;

Accepted: 5 September 2014;

Published online: 6 November 2014;

AJC-16247

Two new *bis*-Schiff base compounds, *N,N'*-bis(5-fluoro-2-hydroxybenzylidene)-ethylenediamine (**1**) and 4,4'-difluoro-2,2'-[(hydrazine-1,2-diylidene)bis(methanylylidene)]diphenol (**2**), were prepared and structurally characterized by elemental analysis, IR, ¹H NMR and UV-visible spectra and single crystal X-ray determination. Compound **1** crystallizes as monoclinic space group P2₁/n, with unit cell dimensions a = 7.227(2) Å, b = 10.970(3) Å, c = 9.973(2) Å, β = 104.913(2)°, V = 695.1(3) Å³, Z = 2, R₁ = 0.0893 and wR₂ = 0.2724. Compound **2** crystallizes as monoclinic space group P2₁/n, with unit cell dimensions a = 8.205(1) Å, b = 6.643(1) Å, c = 11.816(2) Å, β = 105.848(3)°, V = 619.6(1) Å³, Z = 2, R₁ = 0.0424 and wR₂ = 0.0879. Crystal of the compounds are stabilized by hydrogen bonds and π···π interactions.

Keywords: Schiff base, Crystal structure, Hydrogen bonding, π···π interaction.

INTRODUCTION

Schiff bases are a kind of important compounds bearing the typical -N=CH- groups, which can easily be prepared by the condensation reactions of carbonyl-containing compounds with primary amines. The compounds have attracted considerable attention for their wide range of biological activities, such as antibacterial^{1,2}, antitumor^{3,4} and cytotoxic^{5,6}. In addition, *bis*-Schiff bases have been widely used as polydentate ligands in coordination chemistry⁷⁻¹¹. Salicylaldehyde is a common material for the preparation of Schiff bases. However, Schiff bases derived from 5-fluorosalicylaldehyde have seldom been reported. In the present paper, two new *bis*-Schiff bases, *N,N'*-bis(5-fluoro-2-hydroxybenzylidene)ethylenediamine (**1**) and 4,4'-difluoro-2,2'-[(hydrazine-1,2-diylidene)bis(methanylylidene)]diphenol (**2**), are presented.

EXPERIMENTAL

Starting materials, reagents and solvents with AR grade were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the 4000-400 cm⁻¹ region. UV-visible spectra were recorded on a Lambda 900 spectrometer with methanol as solvent. ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer.

Synthesis of *N,N'*-bis(5-fluoro-2-hydroxybenzylidene)ethylenediamine (1**):** 5-Fluorosalicylaldehyde (2 mmol, 0.28 g) and ethane-1,2-diamine (1 mmol, 0.06 g) were mixed in methanol and stirred at room temperature for 1 h. The solvent was evaporated to obtain yellow crystalline product of compound **1**, which was washed with methanol and dried in air. Yield: 91 %. Single crystals of compound **1** suitable for X-ray diffraction were obtained by recrystallization of the product in methanol. Anal. Calcd. for C₁₆H₁₄N₂O₂F₂: C, 63.2; H, 4.6; N, 9.2; found: C, 63.0; H, 4.7; N, 9.3 %. IR data (KBr, ν_{max}, cm⁻¹): 1632s, 1577m, 1499s, 1401m, 1364m, 1322w, 1273s, 1226s, 1138m, 1041s, 962w, 828s, 773s, 670w, 578w, 517w, 469w. UV-visible (nm, cm mol⁻¹ L⁻¹): 241, 7200; 259, 4050; 360, 2310. ¹H NMR (DMSO-*d*₆, 300 MHz): 8.59 (s, 2H), 7.35 (q, 2H), 7.20 (m, 2H), 6.89 (q, 2H), 3.94 (t, 4H).

Synthesis of 4,4'-difluoro-2,2'-[(hydrazine-1,2-diylidene)bis(methanylylidene)]diphenol (2**):** 5-Fluorosalicylaldehyde (2 mmol, 0.28 g) and hydrazine hydrate (1 mmol, 0.05 g) were mixed in methanol and stirred at room temperature for 1 h. The solvent was evaporated to obtain yellow crystalline product of compound **2**, which was washed with methanol and dried in air. Yield: 73 %. Single crystals of compound **2** suitable for X-ray diffraction were obtained by recrystallization of the product in methanol. Anal. Calcd. for C₁₄H₁₀N₂O₂F₂: C, 60.9; H, 3.6; N, 10.1; found: C, 60.7; H, 3.6; N, 10.3 %. IR

data (KBr, ν_{\max} , cm^{-1}): 1628s, 1575m, 1545w, 1491s, 1450w, 1395m, 1338m, 1320w, 1277s, 1267m, 1226m, 1203m, 1172w, 1131w, 1037w, 982w, 878m, 767s, 717m, 678w, 635w, 523w, 477w. UV-visible (nm, $\text{cm mol}^{-1} \text{L}^{-1}$): 290, 5100; 366, 4030. $^1\text{H NMR}$ (DMSO- d_6 , 300 MHz): 8.45 (s, 2H), 7.57 (s, 2H), 7.23 (m, 2H), 6.96 (q, 2H).

Data collection, structural determination and refinement: Diffraction intensities for the compounds were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The collected data were reduced using the SAINT program¹² and multi-scan absorption corrections were performed using the SADABS program¹³. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL¹⁴. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the compounds are summarized in Table-1. Selected bond values are listed in Table-2. Hydrogen bonding information is given in Tables 3 and 4.

RESULTS AND DISCUSSION

Compounds **1** and **2** were readily synthesized by reaction of 1:1 molar ratio of 5-fluorosalicylaldehyde with ethane-1,2-diamine and hydrazine hydrate, respectively, in methanol at room temperature. Single crystals of the compounds suitable for X-ray diffraction were obtained by slow evaporation of the solutions containing the compounds in air. The compounds have been characterized by elemental analyses, IR and UV-visible

TABLE-1
CRYSTALLOGRAPHIC AND
EXPERIMENTAL DATA FOR THE COMPOUNDS

Compound	1	2
m.f.	$\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{F}_2$	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{F}_2$
m.w.	304.3	276.2
Temperature (K)	298(2)	298(2)
Crystal shape/color	Block/yellow	Block/yellow
Crystal size (mm^3)	$0.17 \times 0.13 \times 0.13$	$0.32 \times 0.30 \times 0.27$
Crystal system	Monoclinic	Monoclinic
Space group	$\text{P2}_1/\text{n}$	$\text{P2}_1/\text{n}$
a (\AA)	7.227(2)	8.205(1)
b (\AA)	10.970(3)	6.643(1)
c (\AA)	9.073(2)	11.816(2)
β ($^\circ$)	104.913(2)	105.848(3)
V (\AA^3)	695.1(3)	619.6(1)
Z	2	2
D_c (g cm^{-3})	1.454	1.481
μ ($\text{MoK}\alpha$) (mm^{-1})	0.115	0.121
F(000)	316	284
Reflections collected	6347	5729
Unique reflections	1252	1134
Observed reflections ($I \geq 2\sigma(I)$)	881	721
Parameters	101	92
Restraints	0	0
Min. and max. transmission	0.9807, 0.9852	0.9623, 0.9681
Goodness-of-fit on F^2	1.228	1.058
R_1 , wR_2 [$I \geq 2\sigma(I)$] ^a	0.0893, 0.2724	0.0424, 0.0879
R_1 , wR_2 (all data) ^a	0.1181, 0.2919	0.0836, 0.1022
Large diff. peak and hole ($\text{e}\text{\AA}^{-3}$)	0.292, -0.268	0.133, -0.164

$$^a R_1 = F_o - F_c/F_o, wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$$

TABLE-2
SELECTED BOND DISTANCES (\AA)
AND BOND ANGLES ($^\circ$) FOR THE COMPOUNDS

Compound 1			
N1-C7	1.267(6)	N1-C8	1.467(6)
C7-N1-C8	119.6(5)		
Compound 2			
N1-C7	1.277(2)	N1-N1A	1.401(3)
C7-N1-N1A	113.5(2)		
Symmetry code for A: $1 - x, -y, 2 - z$			

TABLE-3
HYDROGEN BOND DISTANCES (\AA)
AND BOND ANGLES ($^\circ$) FOR THE COMPOUNDS

D-H...A	d(D-)	d(H...A)	d(D...A)	Angle (D...A)
Compound 1				
O1-1...N1	0.82	1.86	2.587(5)	148
Compound 2				
O1-1...N1	0.82	1.89	2.616(2)	146
C7-7...O1 ⁱⁱ	0.93	2.48	3.390(3)	166
Symmetry code for ii: $1/2 + x, 1/2 - y, 1/2 + z$				

TABLE-4
PARAMETERS BETWEEN THE PLANES OF THE COMPOUNDS

Cg	Distance between ring centroids (\AA)	Dihedral angle ($^\circ$)	Perpendicular distance of Cg(I) on Cg(J) (\AA)	Perpendicular distance of Cg(J) on Cg(I) (\AA)
Compound 1				
Cg1-Cg1 ⁱⁱⁱ	4.714	0.03	3.482	3.482
Cg1-Cg1 ^{iv}	3.691	0.03	3.474	3.474
Compound 2				
Cg2-Cg2 ^v	4.908	58.72	1.428	4.685
Cg2-Cg2 ^{vi}	4.518	0.00	3.435	3.435
Symmetry codes: (iii): $-x, -y, 1 - z$; (iv): $1 - x, -y, 1 - z$; (v): $1/2 - x, 1/2 + y, 1/2 - z$; (vi): $-x, -y, 1 - z$. Cg1 is the centroid of C1-C6 benzene ring of compound 1 . Cg2 is the centroid of C1-C6 benzene ring of compound 2				

and $^1\text{H NMR}$ spectra. Structures of the compounds were further confirmed by single crystal X-ray crystallography.

Structure description of the compounds: Figs. 1 and 2 give perspective views of compounds **1** and **2** with atomic labeling systems. X-ray crystallography reveals that the compounds are similar *bis*-Schiff bases. The molecules of the compounds adopt E configuration with respect to the methyldene groups. The distances of the methyldene bonds are 1.267(6) \AA in compound **1** and 1.277(2) \AA in compound **2**, confirm them as typical double bonds. The bond lengths in both compounds are comparable to each other and are within normal values^{15,16}. The dihedral angles between the two benzene rings are 0° due to the centrosymmetric of the compounds.

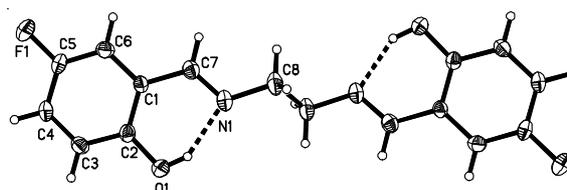


Fig. 1. A perspective view of the molecular structure of compound **1** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines. Unlabeled atoms are related to the symmetry operation $1 - x, 1 - y, 1 - z$

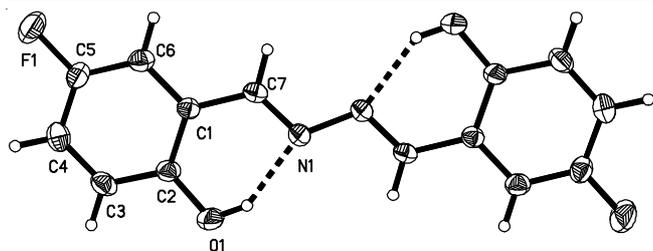


Fig. 2. A perspective view of the molecular structure of compound **2** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen bonds are shown as dashed lines. Unlabeled atoms are related to the symmetry operation $1 - x, -y, 2 - z$.

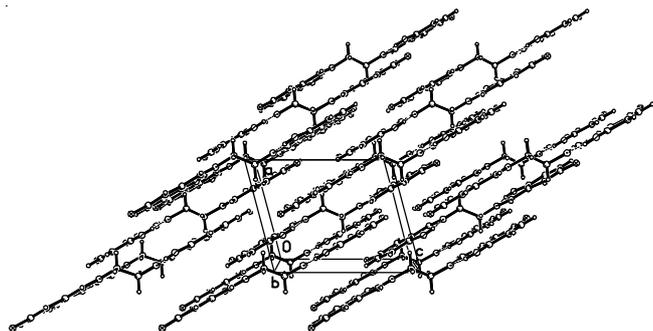


Fig. 3. Molecular packing structure of compound **1**, viewed along the b-axis direction. Hydrogen bonds are shown as dashed lines

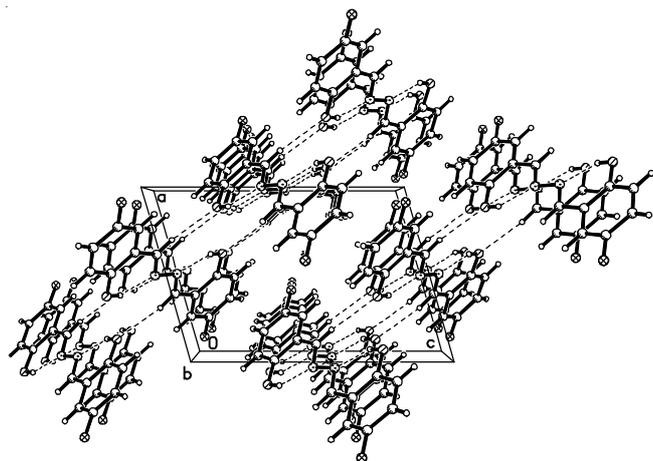


Fig. 4. Molecular packing structure of compound **2**, viewed along the b-axis direction. Hydrogen bonds are shown as dashed lines

In the crystal structure of compound **1**, molecules are stack *via* $\pi \cdots \pi$ interactions along to the a-axis (Fig. 3). In the crystal structure of compound **2**, molecules are linked through C-H \cdots O hydrogen bonds, to form chains. The molecules are further stack *via* $\pi \cdots \pi$ interactions along to the b-axis (Fig. 4).

Supplementary information

CCDC-1002202 for compound **1** and 1002203 for compound **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336033 or E-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

1. R.P. Saini, V. Kumar, A.K. Gupta and G.K. Gupta, *Med. Chem. Res.*, **23**, 690 (2014).
2. F. Zhang, Q. Wen, S.-F. Wang, B. Shahla Karim, Y.-S. Yang, J.-J. Liu, W.-M. Zhang and H.-L. Zhu, *Bioorg. Med. Chem. Lett.*, **24**, 90 (2014).
3. M.M. Kamel, H.I. Ali, M.M. Anwar, N.A. Mohamed and A.M. Soliman, *Eur. J. Med. Chem.*, **45**, 572 (2010).
4. S.J. Ren, R. Wang, K. Komatsu, P. Bonaz-Krause, Y. Zyrianov, C.E. McKenna, C. Csipke, Z.A. Tokes and E.J. Lien, *J. Med. Chem.*, **45**, 410 (2002).
5. P. Sambasiva Rao, C. Kurumurthy, B. Veeraswamy, G. Santhosh kumar, B. Narsaiah, K. Pranay Kumar, U.S.N. Murthy, S. Karnewar and S. Kotamraju, *Med. Chem. Res.*, **22**, 1747 (2013).
6. S.H. Sumra and Z.H. Chohan, *J. Enzyme Inhib. Med. Chem.*, **28**, 1291 (2013).
7. J.-Q. Ren, Q.-Z. Jiao, Y.-N. Wang, F.-Y. Xu, X.-S. Cheng and Z.-L. You, *Wuji Huaxue Xuebao*, **30**, 640 (2014).
8. J.-C. Zhang, Y.-N. Li, D. Huang, F.-Y. Xu, X.-S. Cheng and Z.-L. You, *Wuji Huaxue Xuebao*, **30**, 425 (2014).
9. X.-S. Zhou, Z.-L. You, D.-M. Xian and D.-P. Dong, *Wuji Huaxue Xuebao*, **29**, 850 (2013).
10. Z.-L. You, X.-Y. Qiu, D.-M. Xian and M. Zhang, *Inorg. Chem. Commun.*, **26**, 11 (2012).
11. Z.-L. You, D.-M. Xian and M. Zhang, *Cryst. Eng. Comm.*, **14**, 7133 (2012).
12. Bruker, SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2002).
13. G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector, University of Göttingen, Germany (1996).
14. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
15. D.J. Darensbourg and D.R. Billodeaux, *Inorg. Chem.*, **44**, 1433 (2005).
16. A. Davis, C.A. Kilner and T.P. Kee, *Inorg. Chim. Acta*, **357**, 3493 (2004).