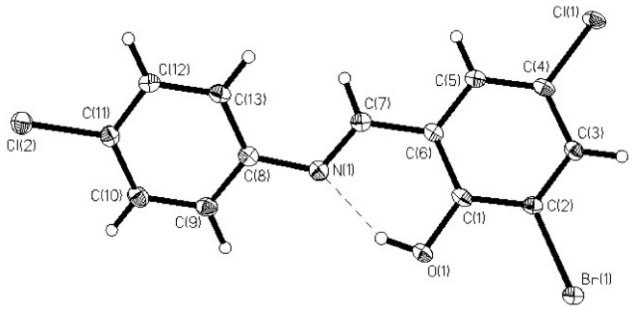
Crystal structure of 2-bromo-4-chloro-6-[(4-chlorophenylimino)methyl]phenol, $C_{13}H_8BrCl_2NO$

Xin-Li Zhang*

Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, Shaanxi, P. R. China

Received May 6, 2011, accepted and available on-line September 9, 2011; CCDC no. 1267/3565



Abstract

$C_{13}H_8BrCl_2NO$, monoclinic, $P12_1/c1$ (no. 14), a = 7.712(2) Å, b = 21.437(5) Å, c = 8.541(2) Å, β = 113.138(3)°, V = 1298.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.079, T = 153 K.

Source of material

3-Bromo-5-chlorosalicylaldehyde (23.5 mg, 0.1 mmol) was dissolved in 15 mL methanol, then the solution of 4-chloroaniline (12.8 mg, 0.1 mmol) in 15 mL methanol was added with vigorous stirring. The reaction mixture was refluxed for 1 h and cooled at room temperature, then the orange products appeared. The products were filtered off, washed with cold methanol, and finally dried to obtain the title Schiff base (yield 72.3 %). Single crystals suitable for X-ray structure determination were obtained by slowly evaporating the filtrate for about ten days at room temperature.

Experimental details

Atom H1O was refined by Fourier method. All the other H atoms were positioned geometrically with d(O—H) = 0.84 Å and d(C—H) = 0.95 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(O).

Discussion

Schiff base ligands have played an important role in the development of coordination chemistry related to catalysis and enzymatic reactions [1,2], magnetism and molecular architectures [3,4] and biological properties [5,6]. 3-Bromo-5-chlorosalicylaldehyde is an important intermediate in synthesizing pesticides and drugs, and an active aldehyde easily to react with many amines, but the Schiff base with 4-chloroaniline has not been reported so far.

The title crystal structure is built up by only the Schiff base molecules, within which all bond lengths and bond angles are in normal ranges [7]. The distance d(C7—N1) = 1.284(3) Å reveals the typical C=N Schiff base bond and d(C8—N1) = 1.418(3) Å visualizes a single bond. The molecule adopts a *trans* configuration about C=N, and the whole molecule is nearly coplanar with a dihedral angle of 32.67(1)° between the two aromatic rings. An intramolecular O–H···N hydrogen bond is observed between hydroxyl and imine group. Two discrete molecules are held together into a dimer by the intermolecular hydrogen bond C7–H7···Cl2 (–x+1,–y+1,–z+1), the dimers are linked by C10–H10···Cl2 interaction (–x+2,–y+1,–z+2) to form a chain, the $R_4^4(8)$ rings are generated by the combination of two C10–H10···Cl2 hydrogen bonds. The chains are further linked to generate a two-dimentional network structure by Br1···Br1(–x+1,–y+1,–z+1) interactions with d(Br1···Br1) = 3.837 Å. The hydrogen bonds and halogen-halogen interactions play very important roles in formation, stability and crystallization of the title compound.

Table 1. Data collection and handling.

Crystal:	orange block, size 0.42 × 0.42 × 0.46 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	35.62 cm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ/ω
$2\theta_{max}$:	58.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11391, 3471
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2756
$N(param)_{refined}$:	167
Programs:	SHELXS-97, SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.0506	0.1069	0.0884	0.029
H(5)	4*e*	0.1119	0.2928	0.0478	0.028
H(7)	4*e*	0.3515	0.3515	0.2707	0.029
H(9)	4*e*	0.6863	0.3579	0.7939	0.034
H(10)	4*e*	0.8406	0.4523	0.8994	0.035
H(12)	4*e*	0.7412	0.5078	0.4181	0.034
H(13)	4*e*	0.5817	0.4146	0.3129	0.033
H(1O)	4*e*	0.547(5)	0.235(1)	0.535(4)	0.05(1)

* e-mail: zhangxinli6008@163.com

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4*e*	0.33546(4)	0.07049(1)	0.41978(3)	0.0368(2)	0.0282(2)	0.0239(2)	0.0000(1)	0.0057(1)	0.0042(1)
Cl(1)	4*e*	–0.12118(8)	0.19969(3)	–0.15815(7)	0.0206(3)	0.0409(4)	0.0208(3)	–0.0020(3)	0.0020(2)	0.0068(2)
Cl(2)	4*e*	0.9313(1)	0.55644(3)	0.74447(8)	0.0417(4)	0.0261(3)	0.0319(3)	–0.0011(3)	0.0097(3)	–0.0041(3)
O(1)	4*e*	0.5078(2)	0.19851(9)	0.5143(2)	0.0250(9)	0.031(1)	0.0208(9)	0.0005(8)	0.0012(7)	0.0005(7)
N(1)	4*e*	0.5257(3)	0.31904(9)	0.4862(2)	0.024(1)	0.029(1)	0.024(1)	–0.0008(9)	0.0119(8)	–0.0005(8)
C(1)	4*e*	0.3610(3)	0.2001(1)	0.3614(3)	0.017(1)	0.032(1)	0.018(1)	0.001(1)	0.0068(9)	–0.0007(9)
C(2)	4*e*	0.2637(3)	0.1454(1)	0.2925(3)	0.025(1)	0.027(1)	0.020(1)	0.001(1)	0.010(1)	0.0030(9)
C(3)	4*e*	0.1150(3)	0.1447(1)	0.1343(3)	0.020(1)	0.030(1)	0.021(1)	–0.003(1)	0.0081(9)	–0.001(1)
C(4)	4*e*	0.0617(3)	0.2001(1)	0.0440(3)	0.018(1)	0.036(1)	0.018(1)	0.002(1)	0.0079(9)	0.002(1)
C(5)	4*e*	0.1517(3)	0.2552(1)	0.1104(3)	0.020(1)	0.030(1)	0.022(1)	0.003(1)	0.009(1)	0.004(1)
C(6)	4*e*	0.3014(3)	0.2560(1)	0.2695(3)	0.016(1)	0.029(1)	0.020(1)	0.0021(9)	0.0087(9)	–0.0002(9)
C(7)	4*e*	0.3921(3)	0.3149(1)	0.3378(3)	0.022(1)	0.026(1)	0.026(1)	0.004(1)	0.012(1)	0.002(1)
C(8)	4*e*	0.6153(3)	0.3774(1)	0.5423(3)	0.024(1)	0.028(1)	0.025(1)	0.002(1)	0.011(1)	–0.001(1)
C(9)	4*e*	0.6956(3)	0.3886(1)	0.7173(3)	0.027(1)	0.034(1)	0.024(1)	0.000(1)	0.012(1)	0.004(1)
C(10)	4*e*	0.7891(4)	0.4443(1)	0.7805(3)	0.031(1)	0.039(2)	0.020(1)	–0.001(1)	0.011(1)	–0.003(1)
C(11)	4*e*	0.8060(3)	0.4876(1)	0.6681(3)	0.024(1)	0.024(1)	0.028(1)	0.002(1)	0.009(1)	–0.003(1)
C(12)	4*e*	0.7290(3)	0.4773(1)	0.4939(3)	0.031(1)	0.028(1)	0.025(1)	0.001(1)	0.010(1)	0.005(1)
C(13)	4*e*	0.6344(4)	0.4221(1)	0.4321(3)	0.031(1)	0.031(1)	0.021(1)	0.001(1)	0.010(1)	0.002(1)

Acknowledgment. The author is thankful for financial support from research project of the Phytochemistry Key Laboratory of Shaanxi Province (grant no. 2010JS069)

References

1. Schuetz, S. A.; Silvernail, C. M.; Incarvito, C. D.; Rheingold, A. L.; Clark, J. L.; Day,V. W.; Belot, J. A.: Mononuclear, Five-Coordinate Lanthanide Amido and Aryloxide Complexes Bearing Tetradentate (N_2O_2) Schiff Bases. Inorg. Chem. **43** (2004) 6203-6214.
2. May, J. P.; Ting, R.; Lermer, L.; Thomas, J. M.; Roupioz, Y.; Perrin, D. M.: Covalent Schiff Base Catalysis and Turnover by a DNAzyme: A M^{2+}-Independent AP-Endonuclease Mimic. J. Am. Chem. Soc. **126** (2004) 4145-4156.
3. He, M.; Li, Q. F.; Xie, T.; Xu, G. M.; Yu, J.; Li, W.: Synthesis, Structure and Magnetic Property of a Binuclear Nickel(II) Complex. Chin. J. Struct. Chem. **29** (2010) 582-586.
4. Chen, X. H.; Liu, S. X.: Synthesis and Crystal Structure of Ni^{2+} Complex with *N*-Salicylaldehyde-*N*′-phenoxyacetylhydrazine Ligand. Chin. J. Struct. Chem. **23** (2004) 33-37.
5. Wang, N; Shi, Q . Synthesis and crystal structure of (*E*)-2-(3'-bromo-5'-chloro-salicylidene amino)-4-methyl pyridine. Chin. J. Struct. Chem. **27** (2008) 191-194.
6. Zhong, X.; Yi, J.; Sun, J.; Wei, H. L.; Liu, W. S.; Yu, K. B.: Synthesis and crystal structure of some transition metal complexes with a novel bis-Schiff base ligand and their antitumor activities. Eur. J. Med. Chem. **41** (2006) 1090-1092.
7. Zhang,X. L.: 2-Bromo-4-chloro-6-[(*E*)-*p*-tolyliminomethyl]phenol. Acta Crystallogr. **E65** (2009) o513.
8. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.