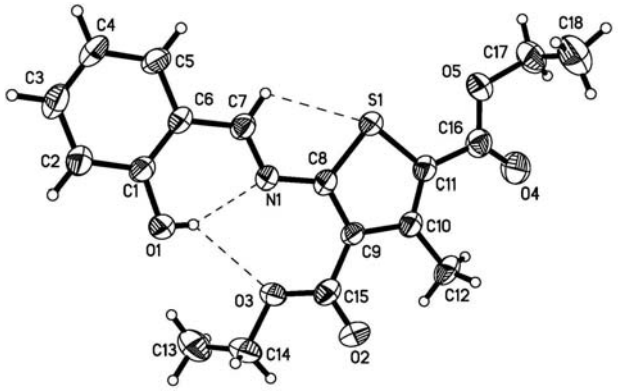
Crystal structure of diethyl (*E*)-5-(2-hydroxybenzylideneamino)-3-methylthiophene-2,4-dicarboxylate, $C_{18}H_{19}NO_5S$

Xue-Ping Zhong, Cui-Wu Lin, Wan-Xing Wei and Hong Zhou*

Guangxi University, College of Chemistry and Chemical Engineering, Guangxi 530004, P. R. China

Received November 24, 2010, accepted and available on-line January 25, 2011; CCDC no. 1267/3303



Abstract

$C_{18}H_{19}NO_5S$, triclinic, $P\bar{1}$ (no. 2), a = 9.481(7) Å, b = 9.598(7) Å, c = 9.821(7) Å, α = 101.491(9)°, β = 90.80(1)°, γ = 93.88(1)°, V = 873.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.061, $wR_{ref}(F^2)$ = 0.197, T = 293 K.

Source of material

Diethyl 2-amino-4-methylthiophene-3,5-dicarboxylate (AMD) was prepared according to [1]. AMD (2.000 g, 7.773 mmol) dissolved by ethanol (15 ml) was added with an ethanol solution (20 ml) of salicylaldehyde (4.680 g, 38.323 mmol) in a round-bottomed flask. The mixture was stirred continuously and refluxed for 4 h. The solvent was evaporated under reduced pressure and a pale yellow product was obtained. The product was redissolved in methanol, and after 10 days yellow crystals suitable for X-ray analysis were obtained.

Experimental details

H1 bound to O1 was found in the difference Fourier map and refined freely. Other H atoms were positioned geometrically with d(C—H) = 0.93 - 0.96 Å and treated as riding with U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

Schiff bases are synthesized from an aromatic or aliphatic amines and carbonyl compounds in nucleophilic addition by elimination of water to the imine [2]. They are usually used as catalysts, intermediates inorganic synthesis, and polymer stabilisers [3]. They also have been shown to exhibit interesting physico-chemical properties [4] and significant biological activity, in particular antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, and antipyretic properties [5,6]. The *o*-hydroxy Schiff base ligands and their complexes derived from the reaction of *o*-hydroxyaldehydes with amine have been extensively studied. They are of great interest for photochromic and thermochromic behaviour. The reversible H atom transfer from the hydroxyl-O atom to the imine-N atom, this intramolecular H-atom transfer often used for laser dyes, and fluorescent probes [7]. Over the past decades extensive studies have been made on the structures of transition metal complexes with *o*-hydroxy Schiff bases, however, a relatively small number of free Schiff bases have been structurally characterized [8].

In the title crystal structure, all values of the geometric parameters are normal. The sulphur contacts were clearly identified as S1—C8 and S1—C11 with bond lengths of 1.730(3) and 1.732(3) Å, respectively, which correspond to the related structures [9]. The benzene ring and thiophene ring are each almost planar. Intramolecular hydrogen bonds (d(O1···O3) = 3.293 Å, d(O1···N1) = 2.630 Å and d(C7···S) = 3.028 Å) effect this conformation. The molecules are further interlinked through intermolecular C–H···π hydrogen bonding as well as van der Waals interactions into the 3D architecture.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.18 × 0.24 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.14 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5044, 3197
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2108
$N(param)_{refined}$:	233
Programs:	SHELXS-97, SHELXL-97 [10]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.5432	0.7815	0.8143	0.062
H(3)	2*i*	0.6580	0.6189	0.9107	0.068
H(4)	2*i*	0.6089	0.3774	0.8340	0.065
H(5)	2*i*	0.4441	0.2961	0.6543	0.056
H(7)	2*i*	0.2696	0.3379	0.4886	0.049
H(12A)	2*i*	–0.1613	0.4583	0.0023	0.077
H(12B)	2*i*	–0.1253	0.6119	0.0907	0.077
H(12C)	2*i*	–0.2555	0.5181	0.1276	0.077
H(15A)	2*i*	0.3775	0.9223	0.4348	0.143
H(15B)	2*i*	0.3328	1.0696	0.4097	0.143
H(15C)	2*i*	0.3508	0.9445	0.2829	0.143
H(14A)	2*i*	0.1167	0.9569	0.3179	0.101
H(14B)	2*i*	0.1387	0.9544	0.4764	0.101
H(17A)	2*i*	–0.1415	–0.1388	0.0660	0.082
H(17B)	2*i*	–0.2178	–0.0507	–0.0281	0.082

* Correspondence author (e-mail: hongzhou123@yahoo.com.cn)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(18A)	2*i*	–0.3070	–0.0612	0.2387	0.130
H(18B)	2*i*	–0.3720	–0.1675	0.1071	0.130
H(18C)	2*i*	–0.3904	–0.0038	0.1249	0.130
H(1)	2*i*	0.310(4)	0.699(4)	0.568(3)	0.04(1)

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}
N(1)	2*i*	0.2098(3)	0.5195(3)	0.4658(2)	0.035(2)	0.038(2)	0.040(1)	0.002(1)	–0.006(1)	0.010(1)
C(1)	2*i*	0.4202(4)	0.6367(4)	0.6762(3)	0.040(2)	0.043(2)	0.041(2)	0.008(2)	–0.005(2)	0.010(1)
C(2)	2*i*	0.5219(4)	0.6844(4)	0.7823(3)	0.051(2)	0.050(2)	0.052(2)	0.007(2)	–0.014(2)	0.003(2)
C(3)	2*i*	0.5907(4)	0.5864(4)	0.8396(3)	0.049(2)	0.075(3)	0.046(2)	0.012(2)	–0.015(2)	0.008(2)
C(4)	2*i*	0.5620(4)	0.4418(4)	0.7938(4)	0.045(2)	0.070(3)	0.053(2)	0.017(2)	–0.013(2)	0.018(2)
C(5)	2*i*	0.4626(4)	0.3934(4)	0.6873(3)	0.047(2)	0.048(2)	0.049(2)	0.013(2)	–0.005(2)	0.016(2)
C(6)	2*i*	0.3892(3)	0.4914(3)	0.6283(3)	0.032(2)	0.047(2)	0.033(1)	0.005(2)	–0.002(1)	0.012(1)
C(7)	2*i*	0.2840(3)	0.4359(4)	0.5199(3)	0.041(2)	0.044(2)	0.037(2)	0.006(2)	–0.005(1)	0.008(1)
C(8)	2*i*	0.1084(3)	0.4631(3)	0.3608(3)	0.033(2)	0.042(2)	0.036(2)	0.006(1)	–0.003(1)	0.007(1)
C(9)	2*i*	0.0292(3)	0.5443(3)	0.2917(3)	0.033(2)	0.038(2)	0.041(2)	0.005(1)	–0.002(1)	0.014(1)
C(10)	2*i*	–0.0680(3)	0.4565(4)	0.1895(3)	0.033(2)	0.046(2)	0.040(2)	0.001(2)	–0.001(1)	0.015(1)
C(11)	2*i*	–0.0587(4)	0.3166(4)	0.1865(3)	0.038(2)	0.046(2)	0.041(2)	0.003(2)	–0.005(1)	0.008(1)
C(12)	2*i*	–0.1609(4)	0.5166(4)	0.0939(3)	0.043(2)	0.069(3)	0.047(2)	0.008(2)	–0.011(2)	0.022(2)
C(13)	2*i*	0.3211(5)	0.9682(5)	0.3773(6)	0.081(4)	0.049(3)	0.155(5)	–0.017(2)	–0.014(3)	0.025(3)
C(14)	2*i*	0.1731(5)	0.9201(4)	0.3841(6)	0.072(3)	0.034(2)	0.146(4)	0.002(2)	–0.016(3)	0.015(2)
C(15)	2*i*	0.0331(4)	0.7021(4)	0.3242(3)	0.047(2)	0.052(2)	0.046(2)	0.009(2)	–0.010(2)	0.015(2)
C(16)	2*i*	–0.1425(4)	0.1945(4)	0.0992(3)	0.051(2)	0.052(2)	0.043(2)	0.003(2)	–0.007(2)	0.001(2)
C(17)	2*i*	–0.1960(5)	–0.0565(4)	0.0673(4)	0.074(3)	0.045(2)	0.076(3)	–0.006(2)	–0.009(2)	–0.009(2)
C(18)	2*i*	–0.3278(5)	–0.0737(5)	0.1409(5)	0.084(4)	0.066(3)	0.099(3)	–0.015(3)	0.010(3)	–0.001(3)
O(1)	2*i*	0.3559(3)	0.7363(3)	0.6237(3)	0.069(2)	0.037(1)	0.060(2)	0.005(1)	–0.028(1)	0.006(1)
O(2)	2*i*	–0.0728(3)	0.7667(3)	0.3296(3)	0.053(2)	0.049(2)	0.102(2)	0.018(1)	–0.014(2)	0.014(1)
O(3)	2*i*	0.1613(3)	0.7647(2)	0.3515(3)	0.043(2)	0.032(1)	0.091(2)	0.002(1)	–0.007(1)	0.013(1)
O(4)	2*i*	–0.2231(3)	0.2025(3)	0.0070(3)	0.090(2)	0.066(2)	0.073(2)	–0.006(2)	–0.044(2)	0.009(1)
O(5)	2*i*	–0.1135(3)	0.0711(3)	0.1351(3)	0.062(2)	0.041(1)	0.073(2)	–0.006(1)	–0.019(1)	0.006(1)
S(1)	2*i*	0.06239(9)	0.28268(9)	0.30736(8)	0.0458(6)	0.0381(5)	0.0502(5)	0.0031(4)	–0.0149(4)	0.0094(4)

Acknowledgments. This work was supported by the National Natural Science Foundation of China (grant nos. 20962002, 20662001) and and National Undergraduates Innovating Experimentation Project (grant no. 091059314).

References

1. Shaukat, S.; Saqib, A.; Nasir, K.; Masood, P.: 3-[(*E*)-(5-Bromo-2-hydroxyphenyl)methylideneaminomethyl]cyclohexanecarboxylic acid. Acta Crystallogr. **E63** (2007) o879-o880.
2. da Silvaa, C. M.; da Silvaa, D. L.; Modolob, L. V.; Alvesa, R. B.; de Resendec, M. A.; Martinsc, C. V. B.; de Fátimaa, Â.: Schiff bases: A short review of their antimicrobial activities. J. Adv. Res. (2011) in press.
3. Malai, H. S. A. H.; Mohammad, A. A.; Aminul H. M.; Paul, V. B.; Boujemaa, M.; Keith, S. M.: Magnetic, spectroscopic and X-ray crystallographic structural studies on copper(II) complexes of tridentate NNS Schiff base ligands formed from 2-acetylpyrazine and *S*-methyl- and *S*-benzyldithiocarbazates. Inorg. Chim. Acta **362** (2009) 3648-3656.
4. Ainscough, E. W.; Brodie, A. M.; Denny, W. A.; Finlay, G. J.; Ranford, J. D.; Waters, J. M.: Nitrogen, sulfur and oxygen donor adducts with copper(II) complexes of antitumor 2-formylpyridinethiosemicarbazone analogs: Physicochemical and cytotoxic studies. J. Inorg. Biochem. **70** (1998) 175-185.
5. Akbar, A. M.; Majumder, S. M. M. H.; Butcher, R. J.; Jasinski, J. P.; Jasinski, J. M.: The preparation and characterization of bis-chelated nickel(II) complexes of the 6-methylpyridine-2-carboxaldehyde Schiff bases of S-alkyldithiocarbazates and the X-ray crystal structure of the bis{*S*-methyl-*β*-*N*-(6-methylpyrid-2-yl)-methylenedithiocarbazato}-nickel(II) complex. Polyhedron **16** (1997) 2749-2754.
6. Sahín, O.; Büyükgüngör, O.; Albayrak, C.; Odabasoglu, M.: Synthesis, Crystal Structure and Conformational Analysis of (*E*)-5-Methoxy-2-((4-methoxyphenylimino)methyl)phenol. Chin. J. Struct. Chem. **29** 359-364.
7. Samit, M.; Susanta, H.; Supriya, D.; Papu, B.; Sasankasekhar, M.: Syntheses, structures and electrochemistry of manganese(III) complexes derived from *N*,*N*'-*o*-phenylenebis(3-ethoxysalicylaldimine): Efficient catalyst for styrene epoxidation. Polyhedron **28** (2009) 2473-2479.
8. Akkurt, M.; Yalcín, S. P.; Asirib, A. M.; Büyükgüngör, O.: Diethyl 5-[(2-hydroxy-1-naphthyl)methylideneamino]-3-methylthiophene-2,4-dicarboxylate. Acta Crystallogr. **E64** (2008) o923.
9. Zhang, Q.; Jiao, Y. H.: Crystal structure of diethyl 2-amino-4-methylthiophene-3,5-dicarboxylate, $C_{11}H_{15}NO_4S$. Z. Kristallogr. NCS **225** (2010) 283-284.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.