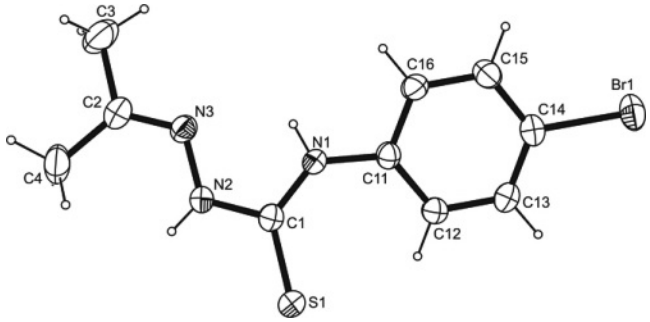
Crystal structure of 4-(4-bromophenyl)-1-(propan-2-ylidene)thiosemicarbazide, $C_{10}H_{12}BrN_3S$

Tatenda Madanhire, Abubak'r Abrahams, Eric C. Hosten and Richard Betz*

Nelson Mandela Metropolitan University, Summerstrand Campus, Department of Chemistry, University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa

Received August 17, 2014, accepted January 30, 2015, available online March 19, 2015, CCDC no. 1267/4242



Abstract

$C_{10}H_{12}BrN_3S$, monoclinic, $P2_1/n$ (no. 14), a = 8.5610(2) Å, b = 11.0120(3) Å, c = 13.2140(4) Å, β = 107.345(1)°, V = 1189.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.0249, $wR_{ref}(F^2)$ = 0.0650, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.112×0.229×0.366 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	36.04 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	57.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13943, 3076
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2672
$N(param)_{refined}$:	146
Programs:	SHELX, WinGX, MERCURY, PLATON [6–9]

Source of material

The title compound was prepared upon reacting 4-(4-bromophenyl)thiosemicarbazide with acetone. Crystals suitable for the diffraction study were obtained upon recrystallization from ethanol.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [6]), with U_{iso}(H) set to 1.5U_{eq}(C). Both nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Discussion

Schiff-base-type bidentate *N,S*-ligands have attracted some attention in coordination chemistry, specifically thionohydrazide-derived members of this class of molecules. In general, they are easily obtained upon acid-catalyzed condensation reaction of a primary amine and a ketone. If a thionohydrazine derivative is used, thioamide-type resonance significantly enhances the versatility of the ligand and allows for different modes of chelation of transition metals. In continuation of our ongoing research on the field of mixed *O,N,S* ligand systems, the title compound was synthesized and its molecular and crystal structure was determined. Structural analyses for a comparable Schiff base ligand system derived from a different ketone are apparent in the literature [1]. The title compound is the Schiff base derived upon condensation reaction of acetone and 4-(4-bromophenyl)thiosemicarbazide. The least-squares planes as defined by the non-hydrogen atoms of the phenyl group as well as the two atoms directly bonded to it on the one hand and the non-hydrogen atoms of the chain-type substituent on the other hand enclose an angle of 14.38(9)°. The C=S bond length is found at 1.6686(16) Å which is in good agreement with other thioketones whose metrical parameters have been deposited with the Cambridge Structural Database [2]. The two C(=S)–N bonds differ slightly in length with values of 1.343(2) Å and 1.366(2) Å with the shorter bond established towards the nitrogen atom bonded to the aromatic system. The N–N bond is measured at 1.3855(19) Å. In the crystal, intra- and intermolecular classical hydrogen bonds of the N–H···N type as well as the N–H···Br type are apparent next to C–H···S contacts whose range falls below the sum of van-der-Waals radii of the atoms participating in them [3] . The latter are supported by a hydrogen atom in *ortho* position to the bromine atom giving rise to centrosymmetric dimers. In terms of graph-set analysis [4, 5], the descriptor for the classical hydrogen bonds is $S(5)C^1_1(9)$ on the unary level while the C–H···S contacts necessitate a $R^2_2(14)$ descriptor on the same level. In total, the molecles are connected to strands along the crystallographic *b* axis.

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

Atom	Site	x	y	z	U_{iso}
H(71)	4*e*	0.458(3)	0.367(2)	0.362(2)	0.033(5)
H(72)	4*e*	0.385(3)	0.098(2)	0.386(2)	0.036(6)
H(3A)	4*e*	0.7452	0.2279	0.2498	0.076
H(3B)	4*e*	0.7163	0.1021	0.1863	0.076
H(3C)	4*e*	0.8474	0.1101	0.3014	0.076
H(4A)	4*e*	0.6368	–0.0531	0.3874	0.068
H(4B)	4*e*	0.6125	–0.0711	0.2634	0.068
H(4C)	4*e*	0.4594	–0.0366	0.3037	0.068
H(12)	4*e*	0.1806	0.4573	0.4956	0.036
H(13)	4*e*	0.1034	0.6607	0.5043	0.038
H(15)	4*e*	0.3805	0.7614	0.3192	0.037
H(16)	4*e*	0.4573	0.5598	0.3092	0.034

* Correspondence author (e-mail: Richard.Betz@nmmu.ac.za)

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*	0.16765(2)	0.89262(2)	0.41707(2)	0.0482(1)	0.0257(1)	0.0394(1)	0.00961(7)	0.01152(8)	0.00104(7)
S(1)	4*e*	0.16908(6)	0.22467(4)	0.44900(4)	0.0392(2)	0.0284(2)	0.0586(3)	0.0003(2)	0.0304(2)	–0.0012(2)
N(1)	4*e*	0.3810(2)	0.3703(1)	0.3882(1)	0.0281(7)	0.0241(7)	0.0359(7)	0.0002(5)	0.0169(6)	–0.0027(6)
N(2)	4*e*	0.4197(2)	0.1676(1)	0.3842(1)	0.0296(7)	0.0221(7)	0.0356(7)	0.0016(6)	0.0144(6)	–0.0012(6)
N(3)	4*e*	0.5396(2)	0.1948(1)	0.3367(1)	0.0262(7)	0.0297(7)	0.0304(7)	0.0022(6)	0.0106(6)	–0.0009(6)
C(1)	4*e*	0.3283(2)	0.2598(2)	0.4063(1)	0.0261(7)	0.0256(8)	0.0255(7)	0.0012(6)	0.0074(6)	–0.0018(6)
C(2)	4*e*	0.6112(2)	0.1065(2)	0.3062(1)	0.0273(8)	0.0368(9)	0.0282(8)	0.0044(7)	0.0066(7)	–0.0048(7)
C(3)	4*e*	0.7412(3)	0.1395(2)	0.2566(2)	0.044(1)	0.061(1)	0.057(1)	0.004(1)	0.030(1)	–0.008(1)
C(4)	4*e*	0.5771(3)	–0.0248(2)	0.3160(2)	0.051(1)	0.032(1)	0.055(1)	0.0084(9)	0.019(1)	–0.0098(9)
C(11)	4*e*	0.3246(2)	0.4883(2)	0.3991(1)	0.0239(7)	0.0233(7)	0.0258(7)	0.0004(6)	0.0060(6)	–0.0026(6)
C(12)	4*e*	0.2202(2)	0.5185(2)	0.4589(1)	0.0346(8)	0.0254(8)	0.0335(8)	–0.0009(7)	0.0161(7)	–0.0013(7)
C(13)	4*e*	0.1748(2)	0.6394(2)	0.4642(1)	0.0337(9)	0.0299(9)	0.0354(9)	0.0043(7)	0.0153(7)	–0.0034(7)
C(14)	4*e*	0.2331(2)	0.7280(2)	0.4115(1)	0.0313(8)	0.0237(8)	0.0280(8)	0.0035(6)	0.0047(6)	–0.0016(6)
C(15)	4*e*	0.3390(2)	0.6995(2)	0.3542(1)	0.0379(9)	0.0258(8)	0.0296(8)	–0.0019(7)	0.0106(7)	0.0014(6)
C(16)	4*e*	0.3843(2)	0.5798(2)	0.3484(1)	0.0302(8)	0.0282(8)	0.0297(8)	–0.0018(6)	0.0137(7)	–0.0031(6)

Acknowledgments. The authors thank Mrs Brenda Holtman for helpful discussions.

References

1. Lukmantara, A. Y.; Kalinowski, D. S.; Kumar, N.; Richardson, D. R.: Structure-activity studies of 4-phenyl-substituted 2'-benzoylpyridine thiosemicarbazones with potent and selective anti-tumour activity. Org. Biomol. Chem. **11** (2013) 6414–6425.
2. Allen, F. H.: The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. **B58** (2002) 380–388.
3. Bondi, A.: van der Waals Volumes and Radii. J. Phys. Chem. **68** (1964) 441–451.
4. Bernstein, J.; Davis, R. E.; Shimoni, L.; Chang, N.-L.: Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals. Angew. Chem. Int. Ed. Engl. **34** (1995) 1555–1573.
5. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. **B46** (1990) 256–262.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
7. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
8. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.: Mercury CSD 2.0 - new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466–470.
9. Spek, A. L.: Structure validation in chemical crystallography. Acta Crystallogr. **D65** (2009) 148–155.