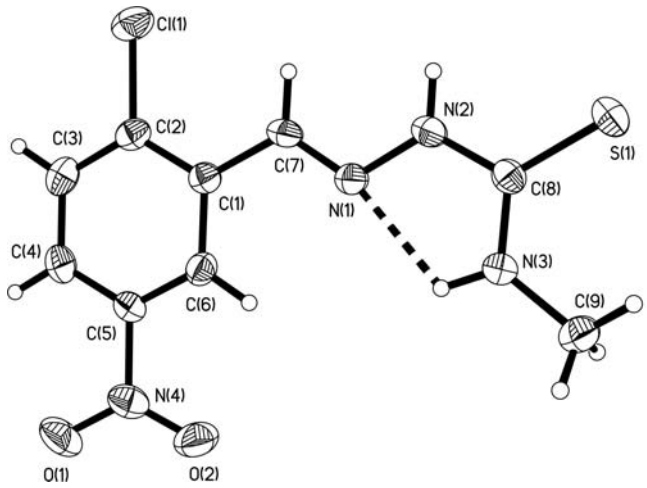
Crystal structure of 2-chloro-5-nitrobenzaldehyde 4-methylthiosemicarbazone, $C_9H_9ClN_4O_2S$

Rongchun Li*

Dezhou University, Department of Chemistry, Dezhou 253023, P. R. China

Received November 28, 2010, accepted and available on-line February 9, 2011; CCDC no. 1267/3311



Abstract

$C_9H_9ClN_4O_2S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.239(1) Å, b = 14.504(3) Å, c = 15.510(4) Å, V = 1178.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.052, $wR_{ref}(F^2)$ = 0.104, T = 298 K.

Source of material

The compound was prepared by the Schiff-base condensation of equimolar quantities of 2-chloro-5-nitrobenzaldehyde (0.185 g, 1 mmol) with 4-methylthiosemicarbazone (0.105 g, 1 mmol) in methanol. The excess methanol was removed by distillation. Colorless block-shaped single crystals were obatined by slow evaporation of an ethanol solution of the product in air.

Experimental details

The amino H atoms were located in a difference Fourier map and refined with d(N—H) = 0.90(1) Å and U_{iso}(H) = 0.080 Å^2. The remaining H atoms were positioned geometrically with d(C—H) = 0.93 - 0.96 Å and refined using a riding model with U_{iso}(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(C9). The Flack parameter value x = –0.18(11) confirms the determined absolute structure.

Discussion

Thiosemicarbazone and its derivatives are important materials for the preparation of Schiff bases [1-4]. Such compounds exibit interesting biological properties [5]. We reported recently the crystal structure of one of the thiosemicarbazone derivtives [6]. The title molecule possesses an *E* configuration around the C7=N1 bond. The bond lengths are in the normal ranges [7], and are comparable to those observed in similar compounds [8-10]. Through the intramolecular hydrogen bond N3–H···N1, a five-membered ring is formed. In the crystal structure, molecules are linked through intermolecular N–H···S and N–H···O hydrogen bonds, to form two-dimensional layers parallel to the (001) plane.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.22 × 0.23 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.96 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, ω
$2\theta_{max}$:	53.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6412, 2549
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1371
$N(param)_{refined}$:	160
Programs:	SHELXS-97, SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(3A)	4*a*	–0.2405	0.5634	0.2295	0.067
H(4)	4*a*	–0.1205	0.7146	0.1948	0.064
H(6)	4*a*	0.4376	0.6182	0.0451	0.054
H(7)	4*a*	0.3266	0.3775	0.0719	0.052
H(9A)	4*a*	1.2743	0.5279	–0.1224	0.086
H(9B)	4*a*	1.0775	0.5628	–0.1912	0.086
H(9C)	4*a*	1.1784	0.4611	–0.1949	0.086
H(2)	4*a*	0.645(8)	0.324(1)	–0.008(2)	0.080
H(3)	4*a*	0.813(6)	0.522(2)	–0.078(2)	0.080

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}
Cl(1)	4*a*	–0.0722(2)	0.39130(7)	0.18104(7)	0.0673(9)	0.0619(7)	0.0681(8)	–0.0148(7)	0.0052(7)	0.0175(6)
N(1)	4*a*	0.5515(7)	0.4558(2)	0.0079(2)	0.048(2)	0.038(2)	0.046(2)	–0.002(2)	0.006(2)	–0.001(2)
N(2)	4*a*	0.6770(7)	0.3814(2)	–0.0256(2)	0.059(3)	0.034(2)	0.056(2)	0.001(2)	0.010(2)	0.001(2)
N(3)	4*a*	0.9218(7)	0.4815(2)	–0.1022(2)	0.049(2)	0.036(2)	0.060(2)	0.000(2)	0.007(2)	0.003(2)

* e-mail: rongchunli01@126.com

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(4)	4*a*	0.2490(9)	0.7716(2)	0.0974(2)	0.078(3)	0.043(2)	0.058(3)	0.000(2)	–0.003(2)	–0.004(2)
O(1)	4*a*	0.1055(7)	0.8347(2)	0.1145(2)	0.098(3)	0.043(2)	0.094(3)	0.018(2)	0.004(3)	–0.009(2)
O(2)	4*a*	0.4562(8)	0.7825(2)	0.0630(2)	0.097(3)	0.052(2)	0.106(3)	–0.018(2)	0.038(3)	–0.006(2)
S(1)	4*a*	1.0366(3)	0.30335(7)	–0.11743(8)	0.0727(9)	0.0444(6)	0.0800(9)	0.0130(7)	0.0176(8)	–0.0023(6)
C(1)	4*a*	0.2284(8)	0.5145(3)	0.0985(2)	0.041(3)	0.042(2)	0.037(2)	0.000(2)	–0.004(2)	0.005(2)
C(2)	4*a*	0.0234(8)	0.5013(3)	0.1530(3)	0.046(3)	0.050(3)	0.040(2)	–0.007(2)	–0.004(2)	0.007(2)
C(3)	4*a*	–0.1068(9)	0.5745(3)	0.1914(3)	0.046(3)	0.071(3)	0.051(3)	–0.004(3)	0.008(2)	–0.002(3)
C(4)	4*a*	–0.0338(9)	0.6643(3)	0.1719(3)	0.052(3)	0.057(3)	0.051(3)	0.013(2)	0.004(3)	–0.007(2)
C(5)	4*a*	0.1687(8)	0.6760(3)	0.1183(3)	0.048(3)	0.036(2)	0.042(2)	0.003(2)	–0.002(2)	–0.001(2)
C(6)	4*a*	0.3005(8)	0.6058(3)	0.0814(2)	0.042(3)	0.048(3)	0.046(3)	–0.003(2)	0.007(2)	–0.002(2)
C(7)	4*a*	0.3697(8)	0.4382(3)	0.0593(3)	0.050(3)	0.030(2)	0.051(3)	–0.003(2)	–0.004(2)	0.001(2)
C(8)	4*a*	0.8751(8)	0.3937(3)	–0.0805(2)	0.045(3)	0.040(2)	0.041(2)	0.002(2)	–0.003(2)	–0.004(2)
C(9)	4*a*	1.1307(8)	0.5108(3)	–0.1574(3)	0.055(3)	0.054(3)	0.062(3)	–0.010(2)	0.005(2)	0.004(2)

References

1. Beraldo, H.; Lima, R.; Teixeira, L. R.; Moura, A. A.; West, D. X.: Crystal structures and IR, NMR and UV spectra of 4-formyl- and 4-acetylpyridine *N*(4)-methyl- and *N*(4)-ethylthiosemicarbazones. J. Mol. Struct. **559** (2001) 99-106.
2. Casas, J. S.; Castineiras, A.; Lobana, T. S.; Sanchez, A.; Sordo, J.; Garcia-Tasende, M. S.: The crystal and molecular structures of cyclohexanone thiosemicarbazone. J. Chem. Crystallogr. **31** (2001) 329-332.
3. Jouad, E. M.; Allain, M.; Khan, M. A.; Bouet, G. M.: Structural and spectral studies of thiosemicarbazones derived from 3-furaldehyde and 3-(2-furyl)prop-2-enal. J. Mol. Struct. **604** (2002) 205-209.
4. Swearingen, J. K.; Kaminsky, W.; West, D. X.: Structural and spectral studies of di-2-pyridyl ketone 3-piperidyl- and 3-hexamethyleneiminyl-thiosemicarbazone and their cobalt(II), nickel(II) and copper(II) complexes. Transit. Metal Chem. **27** (2002) 724-731.
5. Ferrari, M. B.; Capacchi, S.; Reffo, G.; Pelosi, G.; Tarasconi, P.; Albertini, R.; Pinelli, S.; Lunghi, P.: Synthesis, structural characterization and biological activity of *p*-fluorobenzaldehyde thiosemicarbazones and of a nickel complex. J. Inorg. Biochem. **81** (2000) 89-97.
6. Li, R.: 4-Methyl-1-(3-pyridylmethylidene)thiosemicarbazide. Acta Crystallogr. **E66** (2010) o3324.
7. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R.: Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. J. Chem. Soc. Perkin Trans. **2** (1987) S1-S19.
8. Valdés-Martínez, J.; Hernández-Ortega, S.; West, D. X.; Ives, J. S.; Bain, G. A.: Different structures for two very similar 2-benzoylpyridine azacyclothiosemicarbazones. Z. Kristallogr. **213** (1998) 246-248.
9. Basuli, F.; Peng, S.-M.; Bhattacharya, S.: Unusual coordination mode of thiosemicarbazone ligands. A search for the origin. Inorg. Chem. **39** (2000) 1120-1127.
10. Labisbal, E.; Haslow, K. D.; Sousa-Pedrares, A.; Valdés-Martínez, J.; Hernández-Ortega, S.; West, D. X.: Copper(II) and nickel(II) complexes of 5-methyl-2-hydroxyacetophenone *N*(4)-substituted thiosemicarbazones. Polyhedron **22** (2003) 2831-2837.
11. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.