Crystal structure of *N*-(methoxy)methanethioylbenzamide, $C_9H_9NO_2S$

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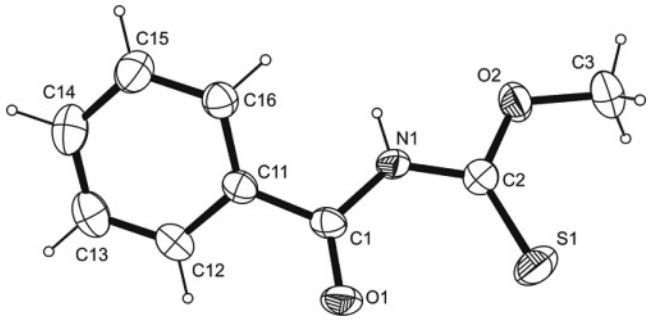

Abstract

$C_9H_9NO_2S$, orthorhombic, $Pna2_1$ (no. 33), a = 9.6168(2) Å, b = 9.0206(2) Å, c = 11.0006(2) Å, V = 954.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.0242, $wR_{ref}(F^2)$ = 0.0659, T = 200 K.

Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.32×0.40×0.59 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.04 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8536, 2286
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2200
$N(param)_{refined}$:	119
Programs:	SHELX [5], WinGX [6], MERCURY [7], PLATON [8]

Source of material

The title compound was obtained upon reacting benzoyl chloride with ammonium thiocyanate in acetone and, subsequently, with boiling methanol. Crystals suitable for the Xray analysis were obtained upon storage of the oily residue at room temperature for one week.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms) 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 group 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 [5]), with U_{iso}(H) set to 1.5U_{eq}(C). The nitrogen-bound H atom was placed in a calculated position (N–H 0.88 Å) and was included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(N).

Discussion

Chelating ligands have found widespread use in coordination chemistry. Coordination compounds formed by them show a markedly higher stability than coordination compounds formed from comparable but exclusively monodentate ligand systems. Mixed *N,S,O* ligand systems are especially interesting in this aspect as they offer a set of donor atoms of variable Lewis acidity and can, therefore, probe for prefereable binding sites. The incorporation of the aforementioned set of atoms in a mixed keto-thioketo-amide environment, in addition, offers the possibility of N–H tautomerization involving the two double-bonded atoms, thus enhancing the versatility of the ligand system. In continuation of our ongoing research on the field of *N,S,O* ligands, the title compound was synthesized and its crystal and molecular structure was determined. Two similar compounds – namely *syn*,*anti*-*O*,*O'*-dimethyl *N*,*N'*-(μ-phenylenedicarbonyl)bis(dithiocarbamate) and *anti*,*anti*-*O*,*O'*-dimethyl*N*,*N'*-(μ-phenylenedicarbonyl) bis(thiocarbamate) – have been reported in the literature [1]. The molecule shows widespread planarization among the *N*,*S*,*O* moiety. The least-squares plane defined by the non-hydrogen atoms of the sidechain (r.m.s = 0.0551 Å) shows the oxygen atom deviating most from this plane by 0.1039(8) Å. This finding can be rationalized by assuming amide-type resonance spanning the sidechain. However, the aromatic system does not seem to take part in this resonance as the least-squares plane defined by its carbon atoms intersects at an angle of 28.18(5)° with the least-squares plane just described. The length of the C–S bond, however, is not supportive of involving the latter in resonance as its value of 1.6253(12) Å is significantly below the most common values reported for molecular structures featuring comparable O–(C=S)–N moieties in the Cambridge Structural Database [2]. In the crystal, C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the corresponding atoms are observed next to classical hydrogen bonds of the N–H···O type. The C–H···O contacts are supported by one of the hydrogen atoms in *ortho* position to the keto functionality as well as one of the hydrogen atoms on the methyl group as donors. The double-bonded oxygen atom serves as acceptor in both cases as well as for the classical hydrogen bonds. In terms of graph-set analysis [3, 4], the descriptor for the C–H···O contacts is $C^1_1(5)C^1_1(7)$ on the unary level while the classical hydrogen bonds necessitate a $C^1_1(4)$ descriptor on the same level. The N–H···N hydrogen bonds connect the molecules to infinite chains along the crystallographic *a* axis. π-Stacking is not a prominent stabilizing factor in the crystal structure of the title compound with the shortest intercentroid distance between two centers of gravity measured at 5.6123(8) Å.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*a*	0.1421	0.2649	0.6081	0.035
H(3A)	4*a*	0.2141	0.5821	0.3524	0.076
H(3B)	4*a*	0.3544	0.5879	0.4303	0.076
H(3C)	4*a*	0.2200	0.6768	0.4753	0.076
H(12)	4*a*	–0.2092	0.1038	0.7968	0.044

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Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(13)	4*a*	–0.1975	–0.1392	0.8691	0.054
H(14)	4*a*	–0.0189	–0.2957	0.8048	0.058
H(15)	4*a*	0.1483	–0.2101	0.6678	0.05
H(16)	4*a*	0.1372	0.032	0.5934	0.039

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}
S(1)	4*a*	–0.05063(4)	0.55220(4)	0.48446(4)	0.0418(2)	0.0352(2)	0.0718(3)	0.0110(1)	–0.0056(2)	0.0088(2)
O(1)	4*a*	–0.16725(8)	0.3081(1)	0.6427(1)	0.0198(4)	0.0369(5)	0.0665(6)	0.0014(3)	0.0001(4)	–0.0012(4)
O(2)	4*a*	0.20781(9)	0.4583(1)	0.50282(9)	0.0296(4)	0.0474(5)	0.0472(6)	–0.0050(3)	0.0003(4)	0.0188(5)
N(1)	4*a*	0.06329(9)	0.3115(1)	0.5940(1)	0.0195(4)	0.0295(5)	0.0388(5)	0.0015(3)	–0.0026(4)	0.0032(4)
C(1)	4*a*	–0.0553(1)	0.2456(1)	0.6403(1)	0.0204(4)	0.0312(6)	0.0346(5)	–0.0033(4)	–0.0028(4)	–0.0051(5)
C(2)	4*a*	0.0729(1)	0.4415(1)	0.5283(1)	0.0294(5)	0.0282(6)	0.0308(6)	–0.0025(4)	–0.0038(4)	–0.0028(4)
C(3)	4*a*	0.2527(2)	0.5866(2)	0.4348(2)	0.0547(9)	0.0468(8)	0.0497(8)	–0.0092(7)	0.0122(7)	0.0148(6)
C(11)	4*a*	–0.0371(1)	0.0925(1)	0.6881(1)	0.0228(5)	0.0321(6)	0.0307(6)	–0.0042(4)	–0.0035(4)	–0.0024(5)
C(12)	4*a*	–0.1365(1)	0.0402(2)	0.7703(1)	0.0308(6)	0.0432(7)	0.0359(7)	–0.0058(5)	0.0032(5)	–0.0003(5)
C(13)	4*a*	–0.1296(2)	–0.1041(2)	0.8134(1)	0.0480(8)	0.0495(8)	0.0378(7)	–0.0121(6)	0.0041(6)	0.0075(6)
C(14)	4*a*	–0.0237(2)	–0.1969(2)	0.7752(1)	0.0648(9)	0.0361(7)	0.0437(8)	–0.0057(6)	0.0002(7)	0.0090(6)
C(15)	4*a*	0.0757(2)	–0.1460(2)	0.6936(1)	0.0490(7)	0.0334(6)	0.0428(7)	0.0034(5)	0.0010(6)	–0.0002(6)
C(16)	4*a*	0.0694(1)	–0.0022(1)	0.6496(1)	0.0311(5)	0.0319(6)	0.0343(6)	–0.0017(5)	0.0003(5)	–0.0008(5)

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