Crystal structure of *N*-(2-methyl-1-(5-thioxo-4,5-dihydro-1,3,4-oxadiazol-2-yl)propyl)benzamide, $C_{13}H_{15}N_3O_2S$

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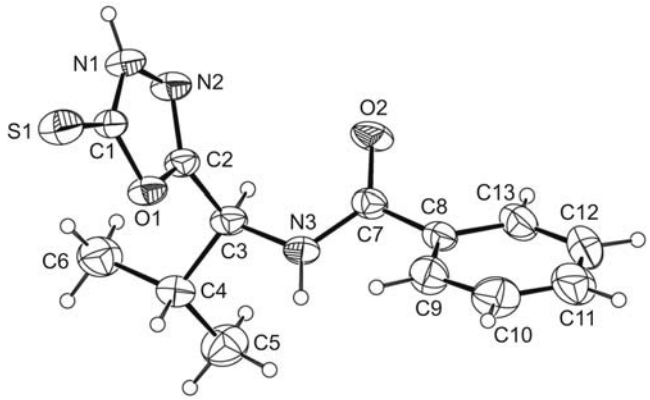

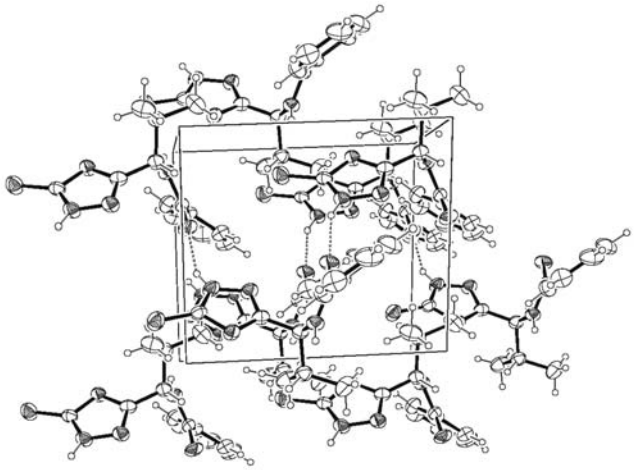

Abstract

$C_{13}H_{15}N_3O_2S$, monoclinic, $P2_1$ (no. 4), a = 9.051(1) Å, b = 9.585(1) Å, c = 9.153(1) Å, β = 114.466(1)°, V = 722.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.050, T = 298 K.

Source of material

To a stirred solution of L-valine methyl ester hydrochloride (0.03 mol) in CH_2Cl_2 (20 ml) was added triethylamine (0.06 mol) at 273 K. After 0.5 h, a solution of benzoic acid chloride (0.03 mol) in CH_2Cl_2 (10 ml) was added. The mixture was stirred for 2 h at 273 K, then allowed to warm to r.t. for 24 h. After washing with 10 % HCl, 1 N NaOH, water and saturated brine, the organic layer was evaporated in vacuo and the residue was recrystallized from methanol to give corresponding amide as a white solid. A mixture of the amide (0.02 mol) and 80 % hydrazine monohydrate (0.04 mol) in absolute methanol (20 ml) was heated under reflux over night. After cooling, a white solid was separated and recrystallized from ethanol to give corresponding hydrazide [1]. A mixture of the hydrazide (0.01 mol), KOH (0.01 mol), CS_2 (0.05 mol), and ethanol (70 ml) was heated under reflux with stirring for 12 h. Ethanol was distilled off under reduced pressure, the residue was dissolved in water and then acidified with 1 N HCl to pH 2 - 3. The solid obtained was filtered, washed with water, and recrystallized from 60 % aqueous ethanol [2]. Colourless needle-shaped single crystals of the title compound suitable for X-ray diffraction analysis were obtained by slow evaporation of the mixed solvent ethanol/water (3:1, *v*/*v*) at room temperature for ten days (m.p. 146 - 147 °C).

Experimental details

All H atoms attached to C were positioned geometrically and treated as riding with (dC—H) = 0.96 Å (methyl) or 0.93 Å (aromatic) with U_{iso}(H) = 1.2 U_{eq}(aromatic) or U_{iso}(H) = 1.5 U_{eq}(methyl).

Discussion

The present oxadiazole derivate is in continuation to our previous work of the thiadiazole scaffold prepared compounds and their biological activity [3]. The title compound shows thiol-thione tautomerism in solution, there is a evident thiol peak at 14.2 ppm in ^{1}H NMR spectra. The crystal structure of the title compound corresponds to the thione form.

The observed absolute crystal structure, indicated by the Flack's parameter of –0.04(8), is in accordance with the asymmetric direction of the synthetic pathway (figure, top). The oxadiazole ring is essentially planar and is inclined at 66.67° with respect to the benzene ring. The N2=C2 and S1=C1 double bonds agree with the corresponding distances in three structures containing similar systems [4-6]. The conformations of the N—H and C=O bonds are *anti* with respect to each other. In the crystal structure, molecules are linked by intermolecular N–H···O hydrogen bonds forming a three-dimensional framework (figure, bottom).

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.13 × 0.17 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.25 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3677, 2346
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1578
$N(param)_{refined}$:	174
Programs:	SHELXS-97, SHELXL-97 [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.6099	0.0498	–0.0235	0.070
H(3)	2*a*	0.9242	0.4500	0.4620	0.064
H(3A)	2*a*	0.8251	0.4809	0.1408	0.064
H(4)	2*a*	1.1243	0.3625	0.3553	0.072
H(5A)	2*a*	1.2392	0.5776	0.3295	0.135
H(5B)	2*a*	1.1167	0.5991	0.4085	0.135
H(5C)	2*a*	1.0649	0.6361	0.2271	0.135
H(6A)	2*a*	1.0284	0.4329	0.0274	0.133
H(6B)	2*a*	1.0580	0.2804	0.0953	0.133
H(6C)	2*a*	1.2042	0.3840	0.1403	0.133
H(9)	2*a*	0.7978	0.3866	0.6273	0.083
H(10)	2*a*	0.7229	0.4291	0.8371	0.103
H(11)	2*a*	0.5762	0.6278	0.8317	0.120
H(12)	2*a*	0.4926	0.7741	0.6137	0.113
H(13)	2*a*	0.5473	0.7212	0.3955	0.084

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*a*	0.6797(3)	0.0992(3)	0.0521(3)	0.053(2)	0.063(2)	0.043(2)	–0.012(2)	0.004(1)	–0.007(1)
N(2)	2*a*	0.6964(3)	0.2415(3)	0.0405(3)	0.054(2)	0.064(2)	0.042(2)	–0.007(2)	0.004(1)	0.001(2)
N(3)	2*a*	0.8500(3)	0.4586(2)	0.3662(2)	0.045(2)	0.065(2)	0.036(1)	0.006(1)	0.002(1)	0.001(1)
O(1)	2*a*	0.8726(2)	0.1605(2)	0.2737(2)	0.054(1)	0.056(2)	0.038(1)	–0.006(1)	0.0042(9)	0.001(1)
O(2)	2*a*	0.5969(2)	0.5260(2)	0.2065(2)	0.050(1)	0.084(2)	0.050(1)	0.015(1)	–0.008(1)	0.010(1)
S(1)	2*a*	0.8102(1)	–0.1129(1)	0.26314(9)	0.0746(6)	0.0655(6)	0.0658(6)	–0.0108(6)	0.0125(4)	0.0006(5)
C(1)	2*a*	0.7827(3)	0.0459(3)	0.1921(3)	0.041(2)	0.060(2)	0.046(2)	–0.006(2)	0.012(2)	–0.009(2)
C(2)	2*a*	0.8135(3)	0.2742(4)	0.1736(3)	0.045(2)	0.067(3)	0.034(2)	–0.002(2)	0.010(2)	–0.004(2)
C(3)	2*a*	0.8825(3)	0.4157(3)	0.2286(3)	0.049(2)	0.059(3)	0.039(2)	–0.001(2)	0.006(1)	0.001(2)
C(4)	2*a*	1.0643(3)	0.4247(3)	0.2651(3)	0.050(2)	0.066(3)	0.053(2)	–0.004(2)	0.012(2)	0.002(2)
C(5)	2*a*	1.1271(4)	0.5731(3)	0.3119(4)	0.088(3)	0.083(3)	0.099(3)	–0.027(2)	0.040(2)	–0.012(2)
C(6)	2*a*	1.0913(3)	0.3759(4)	0.1183(3)	0.071(2)	0.121(3)	0.080(2)	–0.016(3)	0.038(2)	–0.011(3)
C(7)	2*a*	0.7035(3)	0.5117(3)	0.3423(3)	0.046(2)	0.045(2)	0.050(2)	0.002(2)	0.008(2)	0.007(2)
C(8)	2*a*	0.6766(3)	0.5461(3)	0.4886(3)	0.040(2)	0.049(2)	0.052(2)	0.001(2)	0.009(2)	0.004(2)
C(9)	2*a*	0.7318(3)	0.4625(3)	0.6221(4)	0.071(2)	0.069(3)	0.062(2)	0.012(2)	0.021(2)	0.011(2)
C(10)	2*a*	0.6907(4)	0.4896(5)	0.7500(4)	0.087(3)	0.108(4)	0.060(2)	–0.004(3)	0.027(2)	0.014(2)
C(11)	2*a*	0.6018(4)	0.6071(5)	0.7457(5)	0.067(3)	0.158(5)	0.083(3)	0.001(3)	0.039(2)	–0.012(3)
C(12)	2*a*	0.5509(4)	0.6939(5)	0.6149(5)	0.067(3)	0.118(4)	0.097(3)	0.026(2)	0.034(3)	–0.011(3)
C(13)	2*a*	0.5852(3)	0.6634(4)	0.4851(4)	0.052(2)	0.072(3)	0.077(3)	0.012(2)	0.018(2)	0.008(2)

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