Crystal structure of *N*-(2-nitrophenyl)-2-(propan-2-ylidene)hydrazinecarbothioamide, $C_{10}H_{12}N_4O_2S$

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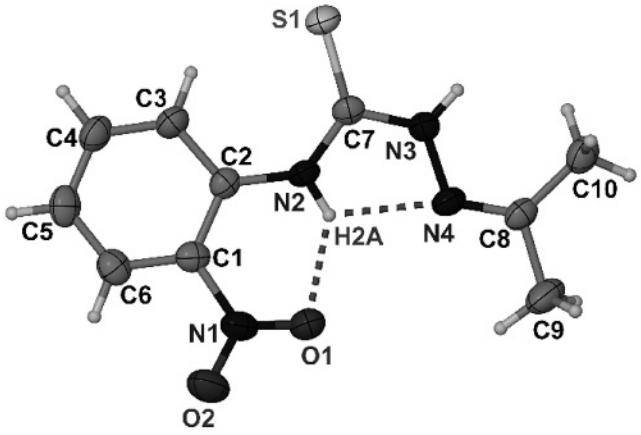

Abstract

$C_{10}H_{12}N_4O_2S$, monoclinic, *C*2/*c* (no. 15), $a = 32.331(6)$ Å, $b = 4.603(1)$ Å, $c = 16.254(3)$ Å, $\beta = 101.14(2)°$, $V = 2373.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0712$, $wR_{ref}(F^2) = 0.1756$, $T = 296$ K.

Table 1. Data collection and handling.

Crystal:	yellow flakes, size 0.15×0.20×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.69 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII CCD, φ and ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11230, 2087
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1284
$N(param)_{refined}$:	156
Programs:	SHELX [9]

Source of material

To a solution of hydrazine (2.4 mmol) in isopropanol (20 mL), 1-isothiocyanato-2-nitrobenzene (2 mmol) was added, and the reaction mixture was stirred in an ice-salt bath for 0.5 h. The separated solid was collected by filtration, washed with isopropanol three times and dried in air [1]. Besides the major product *N*-(2-nitrophenyl)hydrazinecarbothioamide, the by-product *N*-(2-nitrophenyl)-2-(propan-2-ylidene)hydrazinecarbothioamide was obtained, nevertheless the reaction mechanism to yield this compound is unclear. The yellow crystals of the title compound were deposited by evaporation of the solution of methylene chloride/methanol = 5:1 (*v*/*v*) at room temperature.

Discussion

Indolin-2-one has been demonstrated a conspicuous scaffold of a variety of new antitumor agents [2]. In addition, thiosemicarbazone derivatives have also drawn much attention for their potent antitumor activity [3, 4]. With the aim to identify new molecules with potential antiproliferative activity against tumor cells, we introduced piperazine-1-carbodithioate moiety into indolin-2-one to synthesize a new class of piperazine-1-carbothiohydrazide derivatives of indolin-2-one [5]. In order to investigate the effect of the piperazine moiety on antiproliferative activity, we carried out reactions of various phenyl isothiocyanates with an excess of hydrazine. However, an unexpected reaction occurred in the case of 2-nitrophenyl isothiocyanate, which led to the formation of the title compound. In the crystal structure of the title compound, the double bond between C7 and S1 has a length of 1.665(4) Å which is in good agreement with analogous structures [6]. The N3–N4 and N4–C8 bond lengths are 1.382(4) Å and 1.279(5) Å, respectively, and the values are within normal ranges and are comparable with those observed in the similar structures [7, 8]. In addition, two pairs of intramolecular hydrogen bonds are found: N2–H2A···O1 interaction, with the D···A distance of 2.629(4) Å, D–H···A angle of 135.2°; N2–H2A···N4 interaction, with the D···A distance of 2.576(5) Å and D–H···A angle of 114.1° (Figure). Finally, a 2D supramolecular aggregation of the title compound is furnished through another two groups of intermolecular H-bonding interaction between methyl hydrogen atoms (C10) and nitryl oxygen atom (O2).

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	8*f*	0.1287	0.3995	0.3828	0.063
H(3B)	8*f*	0.1359	0.1013	0.2134	0.067
H(3A)	8*f*	0.0363	0.7319	0.2862	0.077
H(4A)	8*f*	0.0001	1.0670	0.3447	0.085
H(5A)	8*f*	0.0260	1.2486	0.4773	0.084
H(6A)	8*f*	0.0894	1.0778	0.5505	0.078
H(9A)	8*f*	0.2204	–0.0482	0.4430	0.133
H(9B)	8*f*	0.2540	–0.0995	0.3867	0.133
H(9C)	8*f*	0.2256	–0.3573	0.4058	0.133
H(10A)	8*f*	0.1704	–0.2676	0.2081	0.110
H(10B)	8*f*	0.2146	–0.3925	0.2500	0.110
H(10C)	8*f*	0.2114	–0.0882	0.2059	0.110

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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)	8*f*	0.07444(3)	0.4965(3)	0.18008(6)	0.0627(7)	0.0857(8)	0.0549(6)	0.0145(6)	–0.0027(5)	0.0042(6)
O(1)	8*f*	0.1589(1)	0.4908(8)	0.4955(2)	0.071(2)	0.097(3)	0.069(2)	0.019(2)	–0.007(2)	–0.010(2)
O(2)	8*f*	0.1552(1)	0.8466(9)	0.5774(2)	0.078(2)	0.128(3)	0.068(2)	–0.010(2)	0.002(2)	–0.025(2)
N(1)	8*f*	0.1410(1)	0.707(1)	0.5140(2)	0.056(2)	0.087(3)	0.048(2)	–0.011(2)	0.008(2)	–0.002(2)
N(2)	8*f*	0.10944(9)	0.4835(7)	0.3468(2)	0.041(2)	0.062(2)	0.050(2)	0.003(2)	–0.003(1)	0.002(2)
N(3)	8*f*	0.1360(1)	0.1841(8)	0.2609(2)	0.050(2)	0.063(2)	0.053(2)	0.003(2)	0.005(2)	–0.005(2)
N(4)	8*f*	0.1660(1)	0.1061(8)	0.3300(2)	0.045(2)	0.070(2)	0.054(2)	0.003(2)	0.001(1)	0.007(2)
C(1)	8*f*	0.1015(1)	0.802(1)	0.4620(2)	0.048(2)	0.067(3)	0.052(2)	–0.009(2)	0.011(2)	0.005(2)
C(2)	8*f*	0.0867(1)	0.6920(9)	0.3810(2)	0.043(2)	0.054(2)	0.056(2)	–0.003(2)	0.012(2)	0.006(2)
C(3)	8*f*	0.0476(1)	0.801(1)	0.3396(3)	0.044(2)	0.076(3)	0.067(2)	0.004(2)	0.003(2)	–0.003(2)
C(4)	8*f*	0.0258(1)	1.001(1)	0.3746(3)	0.048(2)	0.085(3)	0.079(3)	0.012(3)	0.014(2)	0.006(3)
C(5)	8*f*	0.0411(1)	1.109(1)	0.4538(3)	0.062(3)	0.068(3)	0.089(3)	0.001(3)	0.037(2)	0.001(2)
C(6)	8*f*	0.0788(1)	1.008(1)	0.4969(3)	0.067(3)	0.069(3)	0.064(2)	–0.007(3)	0.025(2)	–0.002(2)
C(7)	8*f*	0.1068(1)	0.3887(9)	0.2672(2)	0.040(2)	0.052(2)	0.054(2)	–0.011(2)	0.004(2)	0.000(2)
C(8)	8*f*	0.1943(1)	–0.0766(9)	0.3192(2)	0.040(2)	0.065(3)	0.066(2)	0.001(2)	0.007(2)	0.009(2)
C(9)	8*f*	0.2265(1)	–0.152(1)	0.3955(3)	0.061(3)	0.125(4)	0.077(3)	0.025(3)	0.006(2)	0.021(3)
C(10)	8*f*	0.1980(1)	–0.219(1)	0.2387(3)	0.054(2)	0.083(3)	0.083(3)	0.012(2)	0.015(2)	0.004(3)

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