Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Sulfanylidene-1,2-dihydropyridine-3-carbohydrazide

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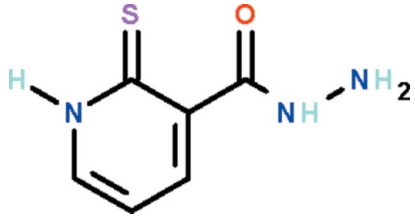
Received 24 August 2010; accepted 1 September 2010

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.003 Å; R factor = 0.034; wR factor = 0.090; data-to-parameter ratio = 12.6.

All non-H atoms of the title compound, $C_6H_7N_3OS$, which exists in the thione form, lie in a common plane (r.m.s. of non-H atoms = 0.08 Å). The amino group of the –NH–NH_2 substituent forms an intramolecular hydrogen bond to the S atom. The terminal –NH_2 group is pyramidally coordinated; it forms a weak N—H···O and a weak N—H···S hydrogen bond. Furthermore, the N atom is an acceptor for a C—H···N contact. The amino group of the ring is a hydrogen-bond donor to the carbonyl O atom of an adjacent molecule, this interaction giving rise to a linear chain motif running along the b axis.

Related literature

For the synthesis of 3-mercaptonicotinoylhydrazide from 3-mercaptonicotinic acid, see: Katz *et al.* (1958). For the synthesis of 2-(3,5-di-*tert*-butyl-4-hydroxybenzylsulfanyl)nicotinic acid, see: Mansor *et al.* (2008).



Experimental

Crystal data

$C_6H_7N_3OS$ M_r = 169.21
Triclinic, $P\overline{1}$
a = 7.1952 (2) Å
b = 7.4279 (2) Å
c = 7.7492 (2) Å
α = 88.205 (2)°
β = 64.201 (2)°
γ = 72.072 (2)°
V = 352.22 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 123 K
0.35 × 0.05 × 0.01 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.874, T_{max} = 0.996
3311 measured reflections
1619 independent reflections
1391 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.090
S = 1.08
1619 reflections
128 parameters
7 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.88 (1)	1.95 (2)	2.751 (2)	152 (2)
N2—H2···S1	0.89 (1)	2.24 (2)	3.007 (2)	145 (2)
N3—H3···O1^{ii}	0.88 (2)	2.36 (3)	3.214 (2)	166 (3)
N3—H4···S1^{iii}	0.88 (3)	2.85 (3)	3.4173 (18)	124 (2)
C2—H2A···N3^{iv}	0.94 (1)	2.69 (2)	3.323 (4)	125 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $x, y+1, z$; (iv) $x+1, y-1, z-1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5335).

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supporting information

Acta Cryst. (2010). E**66**, o2516 [doi:10.1107/S160053681003521X]

2-Sulfanylidene-1,2-dihydropyridine-3-carbohydrazide

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S1. Comment

3-Mercaptonicotinylcarbohydrazide is mentioned in the chemical (patent) literature in the context of its synthesis from 3-mercaptonicotinic acid (Katz *et al.*, 1958). This compound was the surprise product of the reaction between ethyl 2-(3,5-di-*tert*-butyl-4-hydroxybenzylsulfanyl)nicotinate and hydrazine. The compound exists in the thione form. The molecule of pryidyl-2(1*H*)-thione-3-carbohydrazide (Scheme I, Fig. 1) is planar (r.m.s. of non-H atoms 0.08 Å). In the six-membered ring, the two carbon–carbon double bonds are regarded as being localized. The amino –NH– group of the –NH–NH_2 substituent forms an intramolecular hydrogen bond to the double-bond sulfur atom. The terminal –NH_2 group is pyramidally coordinated; it does not engage in hydrogen bonding. The amino –NH– group of the ring is hydrogen-bond donor to the double-bond oxygen atom an adjacent molecule, this interaction giving rise to a linear chain motif running along the *b*-axis of the triclinic unit cell (Fig. 2).

S2. Experimental

The synthesis of colorless 2-(3,5-di-*tert*-butyl-4-hydroxybenzylsulfanyl)nicotinic acid was described earlier (Mansor *et al.*, 2008); the acid was first converted to the ethyl ester. The ester (0.80 g, 2 mmol) was dissolved in ethanol (15 ml) and to this was added hydrazine hydrate (0.20 ml, 4 mmol). The mixture was heated for 24 h. The solvent was removed to give a brown gummy solid; this was recrystallized from hexane to afford orange plate-like crystals.

S3. Refinement

All H-atoms were located in a difference Fourier map, and were refined isotropically with distance restraints of C–H 0.95±0.01 Å and N–H 0.88±0.01 Å.

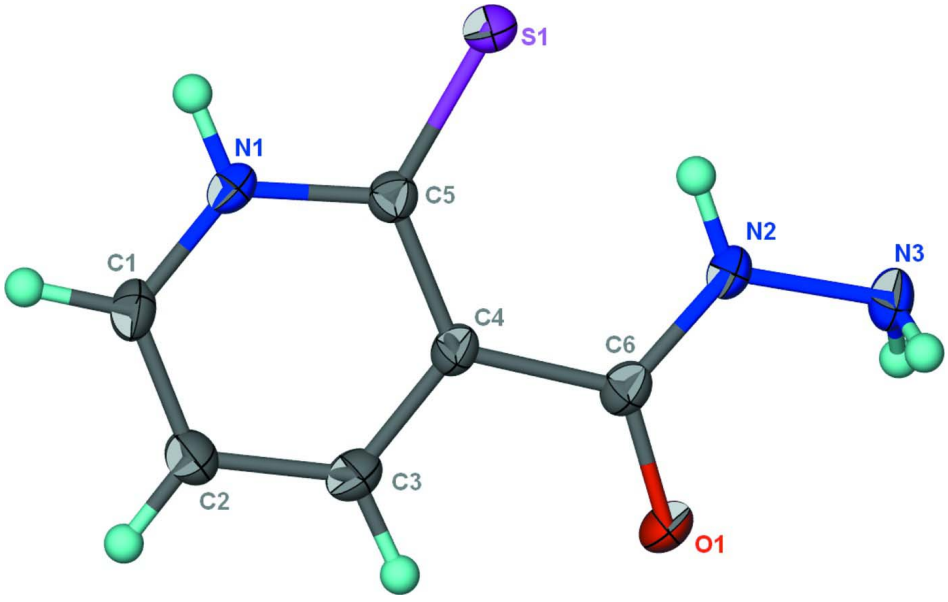

Figure 1

Anisotropic displacement ellipsoid plot (Barbour, 2001) of $C_6H_7N_3OS$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

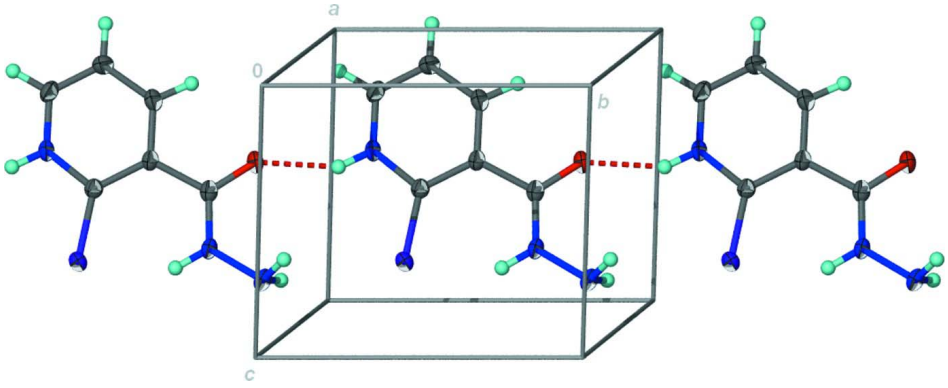

Figure 2

Hydrogen-bonded chain structure.

2-Sulfanylidene-1,2-dihydropyridine-3-carbohydrazide

Crystal data

$C_6H_7N_3OS$
M_r = 169.21
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.1952 (2) Å
b = 7.4279 (2) Å
c = 7.7492 (2) Å
α = 88.205 (2)°
β = 64.201 (2)°
γ = 72.072 (2)°
V = 352.22 (2) Å^3
Z = 2
F(000) = 176
D_x = 1.595 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1745 reflections
θ = 2.9–28.3°
μ = 0.40 mm^{-1}
T = 123 K
Plate, orange
0.35 × 0.05 × 0.01 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.874, T_{max} = 0.996
3311 measured reflections
1619 independent reflections
1391 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.5°, θ_{min} = 2.9°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.090
S = 1.08
1619 reflections
128 parameters
7 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 0.3308P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.58477 (8)	0.32161 (7)	0.76922 (7)	0.02102 (15)
O1	0.7744 (2)	0.81569 (18)	0.44198 (19)	0.0210 (3)
N1	0.8505 (3)	0.1589 (2)	0.4153 (2)	0.0165 (3)
N2	0.5443 (3)	0.7318 (2)	0.7129 (2)	0.0191 (3)
N3	0.4375 (3)	0.9211 (2)	0.8063 (2)	0.0218 (4)
C1	1.0002 (3)	0.1308 (3)	0.2289 (3)	0.0182 (4)
C2	1.0636 (3)	0.2790 (3)	0.1432 (3)	0.0199 (4)
C3	0.9635 (3)	0.4575 (3)	0.2526 (3)	0.0181 (4)
C4	0.8069 (3)	0.4870 (2)	0.4421 (3)	0.0147 (4)
C5	0.7505 (3)	0.3285 (2)	0.5345 (3)	0.0148 (4)
C6	0.7070 (3)	0.6906 (2)	0.5353 (3)	0.0160 (4)
H1	0.805 (4)	0.064 (3)	0.466 (3)	0.036 (7)*
H2	0.505 (4)	0.638 (3)	0.776 (3)	0.039 (7)*
H3	0.404 (4)	0.991 (3)	0.724 (3)	0.036 (7)*
H4	0.533 (3)	0.956 (4)	0.827 (4)	0.032 (7)*
H1A	1.059 (3)	0.0051 (17)	0.165 (3)	0.020 (5)*
H2A	1.171 (3)	0.260 (3)	0.0141 (17)	0.027 (6)*
H3A	1.002 (4)	0.565 (2)	0.199 (3)	0.021 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0251 (3)	0.0148 (2)	0.0172 (2)	−0.00847 (18)	−0.00306 (19)	0.00297 (16)
O1	0.0259 (7)	0.0123 (6)	0.0214 (7)	−0.0081 (5)	−0.0063 (6)	0.0033 (5)
N1	0.0190 (8)	0.0107 (7)	0.0189 (8)	−0.0055 (6)	−0.0072 (6)	0.0025 (6)

N2	0.0210 (8)	0.0102 (7)	0.0194 (8)	−0.0041 (6)	−0.0039 (7)	−0.0003 (6)
N3	0.0250 (9)	0.0114 (7)	0.0216 (8)	−0.0023 (6)	−0.0061 (7)	−0.0017 (6)
C1	0.0199 (9)	0.0125 (8)	0.0192 (9)	−0.0020 (7)	−0.0080 (8)	−0.0016 (7)
C2	0.0196 (9)	0.0176 (9)	0.0161 (9)	−0.0041 (7)	−0.0036 (7)	0.0011 (7)
C3	0.0208 (9)	0.0138 (8)	0.0200 (9)	−0.0065 (7)	−0.0090 (8)	0.0047 (7)
C4	0.0155 (8)	0.0110 (8)	0.0171 (8)	−0.0034 (7)	−0.0075 (7)	0.0016 (6)
C5	0.0143 (8)	0.0137 (8)	0.0160 (8)	−0.0041 (7)	−0.0067 (7)	0.0016 (7)
C6	0.0163 (8)	0.0125 (8)	0.0199 (9)	−0.0041 (7)	−0.0091 (7)	0.0023 (7)

Geometric parameters (Å, º)

S1—C5	1.696 (2)	N3—H4	0.88 (1)
O1—C6	1.246 (2)	C1—C2	1.365 (3)
N1—C1	1.348 (2)	C1—H1A	0.95 (1)
N1—C5	1.376 (2)	C2—C3	1.395 (3)
N1—H1	0.88 (1)	C2—H2A	0.94 (1)
N2—C6	1.327 (2)	C3—C4	1.380 (3)
N2—N3	1.416 (2)	C3—H3A	0.95 (1)
N2—H2	0.89 (1)	C4—C5	1.433 (2)
N3—H3	0.88 (1)	C4—C6	1.507 (2)
C1—N1—C5	125.85 (15)	C3—C2—H2A	121.7 (14)
C1—N1—H1	118.5 (17)	C4—C3—C2	122.34 (17)
C5—N1—H1	115.6 (17)	C4—C3—H3A	116.8 (14)
C6—N2—N3	121.63 (15)	C2—C3—H3A	120.9 (14)
C6—N2—H2	119.0 (17)	C3—C4—C5	119.45 (16)
N3—N2—H2	119.3 (17)	C3—C4—C6	115.35 (15)
N2—N3—H3	106.3 (17)	C5—C4—C6	125.20 (16)
N2—N3—H4	107.0 (17)	N1—C5—C4	114.58 (15)
H3—N3—H4	109 (2)	N1—C5—S1	116.57 (13)
N1—C1—C2	119.76 (16)	C4—C5—S1	128.82 (14)
N1—C1—H1A	116.8 (14)	O1—C6—N2	121.97 (16)
C2—C1—H1A	123.4 (14)	O1—C6—C4	119.33 (16)
C1—C2—C3	117.83 (17)	N2—C6—C4	118.66 (15)
C1—C2—H2A	120.5 (14)		
C5—N1—C1—C2	−0.3 (3)	C3—C4—C5—S1	173.23 (15)
N1—C1—C2—C3	−2.1 (3)	C6—C4—C5—S1	−7.1 (3)
C1—C2—C3—C4	0.7 (3)	N3—N2—C6—O1	0.2 (3)
C2—C3—C4—C5	3.0 (3)	N3—N2—C6—C4	−177.57 (17)
C2—C3—C4—C6	−176.77 (17)	C3—C4—C6—O1	−2.5 (3)
C1—N1—C5—C4	3.8 (3)	C5—C4—C6—O1	177.77 (17)
C1—N1—C5—S1	−174.60 (15)	C3—C4—C6—N2	175.28 (17)
C3—C4—C5—N1	−4.9 (3)	C5—C4—C6—N2	−4.4 (3)
C6—C4—C5—N1	174.76 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88 (1)	1.95 (2)	2.751 (2)	152 (2)
N2—H2···S1	0.89 (1)	2.24 (2)	3.007 (2)	145 (2)
N3—H3···O1^{ii}	0.88 (2)	2.36 (3)	3.214 (2)	166 (3)
N3—H4···S1^{iii}	0.88 (3)	2.85 (3)	3.4173 (18)	124 (2)
C2—H2*A*···N3^{iv}	0.94 (1)	2.69 (2)	3.323 (4)	125 (2)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*, *y*+1, *z*; (iv) *x*+1, *y*−1, *z*−1.