5-Amino-1,3-benzothiazole-2(3H)-thione

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The two independent molecules of the title compound, $C_7H_6N_2S_2$, are linked by two secondary amino–thione hydrogen bonds [3.344 (3) and 3.376 (3) Å] to form a flat pseudo-centrosymmetric dimer.

Comment

Mercaptobenzothiazole exists in the thione form in the solid state (Chesick & Donohue, 1971; Radha, 1985). The deprotonated anion forms a large number of N,S-chelated metal complexes, e.g. cadmium di(benzothiazolyl-2-thiolate) (Hursthouse et al., 1990) and tetramethylammonium tris-(benzothiazolyl-2-thiolate)nickelate (Rasper et al., 1990); the diorganotin derivatives show cytotoxocity (Xanthopoulou et al., 2003). Among the substituted compounds, the 5-chloro derivative has been extensively studied in view of its use as a drug (Antoniadis et al., 2003).

(I)
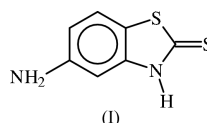
The 5-amino-substituted compound, (I), exists with two molecules per asymmetric unit; these are linked by a pair of hydrogen bonds to form a pseudo-centrosymmetric dimer (Fig. 1 and Table 2). The parent compound, mercaptobenzothiazole, also exists as a hydrogen-bonded dimer (Chesick & Donohue, 1971; Radha, 1985). The molecules feature both long [S1—C1 1.740 (3) Å and S1—C2 1.751 (3) Å; S1a—C1a 1.753 (3) Å and S1a—C2a 1.762 (3) Å] and short [S2—C1 1.688 (3) Å and S2a—C1a 1.672 (3) Å] C—S bonds (Table 1).
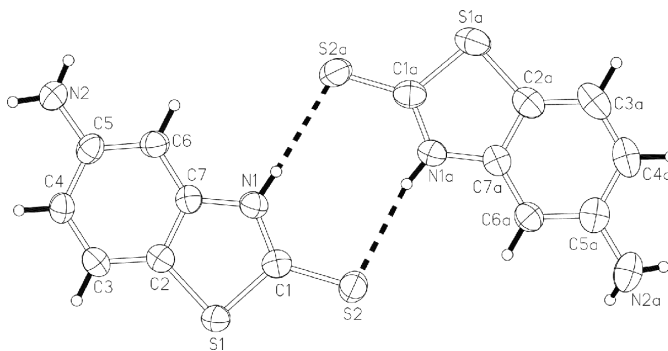
Figure 1
ORTEPII (Johnson, 1976) plot of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

Hence, the title compound can be regarded as the thione tautomer in the solid state.

In the crystal structure the 'dimers' are hydrogen bonded to symmetry-related molecules, forming a zigzag sheet-like structure (Table 2).

Experimental

An ethanol solution (50 ml) of *m*-phenylenediamine (0.22 g, 2 mmol) and carbon disulfude (15 ml, 2.4 mmol), kept at 273 K, was stirred for 2 h. The solution was then heated at reflux for 12 h. The reaction was carried out under an N_2 atmosphere. The solution was poured into water to afford a solid material that was recrystallized from ethanol.

Crystal data

$C_7H_6N_2S_2$	$D_x = 1.526$ Mg m^{-3}
$M_r = 182.26$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1662
$a = 5.1041 (2)$ Å	reflections
$b = 20.3859 (7)$ Å	$\theta = 2.4–23.3°$
$c = 15.3378 (5)$ Å	$\mu = 0.60$ mm^{-1}
$\beta = 96.279 (2)°$	$T = 298 (2)$ K
$V = 1586.4 (1)$ Å^3	Block, yellow
$Z = 8$	$0.32 \times 0.12 \times 0.09$ mm

Data collection

Bruker SMART APEX area-detector diffractometer	2332 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.046$
φ and ω scans	$\theta_{max} = 27.5°$
Absorption correction: none	$h = -5 \rightarrow 6$
9371 measured reflections	$k = -26 \rightarrow 19$
3531 independent reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.056$	independent and constrained
$wR(F^2) = 0.125$	refinement
$S = 0.95$	$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2]$
3531 reflections	where $P = (F_o^2 + 2F_c^2)/3$
223 parameters	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.34$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.740 (3)	S1a—C1a	1.753 (3)
S1—C2	1.751 (3)	S1a—C2a	1.762 (3)
S2—C1	1.688 (3)	S2a—C1a	1.672 (3)
N1—C1	1.344 (4)	N1a—C1a	1.350 (4)
N1—C7	1.402 (4)	N1a—C7a	1.392 (4)
N2—C5	1.391 (4)	N2a—C5a	1.410 (4)
C1—S1—C2	92.1 (1)	C1a—S1a—C2a	92.5 (2)
C1—N1—C7	116.8 (3)	C1a—N1a—C7a	117.5 (3)
N1—C1—S1	109.8 (2)	N1a—C1a—S1a	108.7 (2)
N1—C1—S2	128.2 (2)	N1a—C1a—S2a	127.4 (2)
S1—C1—S2	122.0 (2)	S1a—C1a—S2a	123.9 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1n···S2a	0.86 (1)	2.52 (1)	3.376 (3)	177 (3)
N2—H2n1···N2a^i	0.86 (1)	2.39 (1)	3.223 (5)	163 (3)
N2—H2n2···S2a^{ii}	0.85 (1)	2.87 (2)	3.641 (3)	151 (3)
N1a—H1na···S2	0.86 (1)	2.51 (1)	3.344 (3)	164 (2)
N2a—H2nb···S2^{iii}	0.86 (1)	2.96 (2)	3.685 (3)	143 (3)
N2a—H2nb···S1a^{iv}	0.86 (1)	3.11 (3)	3.726 (4)	130 (3)

Symmetry codes: (i) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $-x, 1-y, 1-z$; (iii) $1+x, y, z$; (iv) $1+x, \frac{3}{2}-y, \frac{1}{2}+z$.

The aromatic H atoms were placed at calculated positions (C—H = 0.93 Å) in the riding-model approximation; the U_{iso}(H) values were set equal to 1.2U_{eq}(parent C atom). The N-bound H atoms were located and refined with an N—H = 0.86 (1) Å distance restraint.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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