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5-Bromo-1*H*-thieno[2,3-*d*]imidazole

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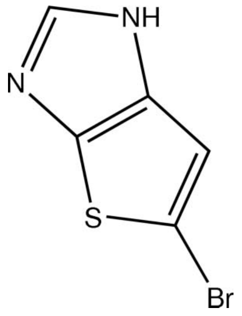
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.036; wR factor = 0.098; data-to-parameter ratio = 17.4.

The crystal structure of the title compound, $C_5H_3BrN_2S$, shows that bromination of 1*H*-thieno[2,3-*d*]imidazole with *N*-bromosuccinimide in acetonitrile occurs at position 5 of the bicyclic system. The molecule is almost planar, with a mean deviation of 0.015 Å from the least-squares plane through all the non-H atoms. In the crystal, N—H···N hydrogen bonds link the molecules into infinite *C*(4) chains running along [101].

Related literature

For a related structure involving the thieno[2,3-*d*]imidazole fragment, see: Busetti *et al.* (1989).



Experimental

Crystal data

$C_5H_3BrN_2S$
M_r = 203.06
Monoclinic, $P2_1/n$
a = 3.8917 (11) Å
b = 17.118 (5) Å
c = 9.405 (3) Å
β = 91.359 (3)°
V = 626.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 6.79 mm^{-1}
T = 100 K
0.32 × 0.18 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.220, T_{max} = 0.580
9691 measured reflections
1441 independent reflections
1270 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.08
1441 reflections
83 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···N2^i	0.88	2.04	2.903 (4)	165

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5547).

References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
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Busetti, V., Guerrera, F., Siracusa, M. A., Ajo, D. & De Zuane, F. (1989). *Z. Kristallogr.* **187**, 187–191.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o2021   [**doi:10.1107/S1600536810027224**]

5-Bromo-1*H*-thieno[2,3-*d*]imidazole

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Comment

Bromination of 1*H*-thieno[2,3-*d*]imidazole by bromosuccinimide in acetonitrile may occur either at position 2,5 or 6. The present X-ray study showed that substitution occurs in fact at position 5; the molecular structure of the title compound, representing the major product of bromination is shown in Fig. 1.

The molecule of the title compound is planar; maximum deviation of the Br1 atom from the mean plane of all non-H atoms of the molecule is equal to 0.029 (3) Å. To the best of our knowledge, this is the first structural study of thieno[2,3-*d*]imidazole derivative with the isolated bicyclic system. In the only closely related molecule, studied by the single-crystal X-ray diffraction earlier (Busetti *et al.*, 1989), the thieno[2,3-*d*]imidazole system is fused with the benzene ring, thus forming a tricyclic molecule. The geometry of the thienoimidazole fragment of the tricyclic molecule is very similar to that of the title compound.

There is one symmetry independent intermolecular H-bond in the structure (Table 1), which is responsible for the formation of infinite chains of molecules running along the [101] direction of the crystal (Fig. 2).

Experimental

To a solution of 1*H*-thieno[2,3-*d*]imidazole (16 mg, 0.13 mmol) in 0.75 ml of acetonitrile at 0°C was added dropwise *N*-bromosuccinimide (21 mg, 0.12 mmol) in 0.25 ml of acetonitrile. The reaction mixture was stirred at 0°C for 0.5 hr. The reaction mixture was diluted with 10 ml of 1 N NaOH, and the aqueous layer was extracted with EtOAc (3 × 15 ml). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The product was purified by flash chromatography (silica gel, 0–70% EtOAc/heptane) to give 22 mg (81%) 5-bromo-1*H*-thieno[2,3-*d*]imidazole as an off white solid.

Light brown needles of (I) were grown by slow evaporation of a 20/20/60 methanol/dichloromethane/toluene solution

Refinement

All H atoms were placed in geometrically calculated positions (N—H 0.88 Å, C—H 0.95 Å) and included in the refinement in the riding motion approximation. The U_{iso}(H) were set to $1.2U_{eq}$ of the carrying atom. The highest residual peak of 1.41 e/Å^3 is located at 0.91 Å from the Br1 atom.

Figures

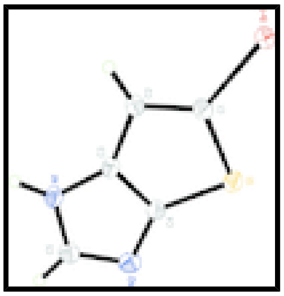

Fig. 1. Molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms are drawn as circles with arbitrary small radius.

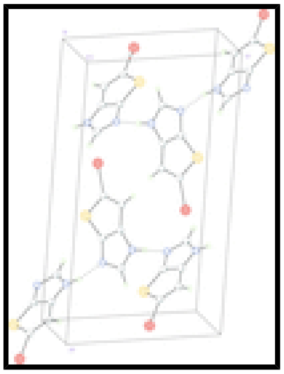

Fig. 2. Packing diagram of (I) viewed approximately down the *a* axis.

5-Bromo-1*H*-thieno[2,3-*d*]imidazole

Crystal data

$C_5H_3BrN_2S$

$M_r = 203.06$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 3.8917$ (11) Å

$b = 17.118$ (5) Å

$c = 9.405$ (3) Å

$\beta = 91.359$ (3)°

$V = 626.4$ (3) Å^3

$Z = 4$

$F(000) = 392$

$D_x = 2.153$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4198 reflections

$\theta = 2.4$–27.4°

$\mu = 6.79$ mm^{-1}

$T = 100$ K

Needle, light brown

0.32 × 0.18 × 0.09 mm

Data collection

Bruker APEX CCD diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2001)

$T_{min} = 0.220$, $T_{max} = 0.580$

1441 independent reflections

1270 reflections with $I > 2\sigma(I)$

$R_{int} = 0.043$

$\theta_{max} = 28.2°$, $\theta_{min} = 2.4°$

$h = -5 \rightarrow 5$

$k = -22 \rightarrow 21$

9691 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.9841P]$ where $P = (F_o^2 + 2F_c^2)/3$
1441 reflections	$(\Delta/\sigma)_{max} < 0.001$
83 parameters	$\Delta\rho_{max} = 1.41$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.81$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.78267 (9)	0.43247 (2)	0.25169 (4)	0.01969 (18)
S1	0.4398 (2)	0.58614 (6)	0.13967 (10)	0.0204 (3)
N1	0.4603 (8)	0.71893 (18)	0.4614 (3)	0.0186 (7)
H1N	0.5141	0.7276	0.5515	0.022*
N2	0.2480 (8)	0.7397 (2)	0.2389 (3)	0.0212 (7)
C1	0.6366 (9)	0.5359 (2)	0.2806 (4)	0.0178 (7)
C2	0.6719 (9)	0.5760 (2)	0.4074 (4)	0.0159 (7)
H2	0.7747	0.5568	0.4932	0.019*
C3	0.5239 (9)	0.6521 (2)	0.3853 (4)	0.0169 (7)
C4	0.3908 (9)	0.6662 (2)	0.2503 (4)	0.0168 (7)
C5	0.2976 (10)	0.7690 (2)	0.3697 (4)	0.0206 (8)
H5	0.2262	0.8200	0.3960	0.025*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0235 (2)	0.0164 (3)	0.0190 (3)	0.00184 (12)	−0.00180 (14)	−0.00335 (13)

S1	0.0251 (5)	0.0207 (5)	0.0153 (5)	0.0007 (3)	−0.0021 (4)	−0.0008 (4)
N1	0.0240 (16)	0.0179 (16)	0.0140 (16)	−0.0007 (12)	−0.0001 (12)	−0.0003 (13)
N2	0.0225 (16)	0.0183 (18)	0.0227 (18)	−0.0007 (11)	−0.0005 (13)	0.0031 (13)
C1	0.0189 (17)	0.0149 (18)	0.0196 (19)	−0.0004 (13)	0.0011 (13)	−0.0008 (15)
C2	0.0201 (17)	0.0141 (17)	0.0137 (18)	−0.0012 (13)	0.0033 (13)	0.0018 (13)
C3	0.0195 (17)	0.0171 (18)	0.0140 (18)	−0.0024 (13)	−0.0009 (13)	0.0002 (14)
C4	0.0204 (17)	0.0140 (17)	0.0161 (19)	−0.0002 (14)	−0.0006 (13)	0.0018 (14)
C5	0.0258 (19)	0.0154 (18)	0.021 (2)	0.0007 (14)	0.0012 (15)	0.0020 (15)

Geometric parameters (Å, °)

Br1—C1	1.882 (4)	N2—C4	1.378 (5)
S1—C4	1.734 (4)	C1—C2	1.379 (5)
S1—C1	1.742 (4)	C2—C3	1.438 (5)
N1—C5	1.362 (5)	C2—H2	0.9500
N1—C3	1.375 (5)	C3—C4	1.381 (5)
N1—H1N	0.8800	C5—H5	0.9500
N2—C5	1.338 (5)		
C4—S1—C1	89.20 (18)	C3—C2—H2	126.4
C5—N1—C3	106.3 (3)	N1—C3—C4	105.3 (3)
C5—N1—H1N	126.8	N1—C3—C2	139.1 (3)
C3—N1—H1N	126.8	C4—C3—C2	115.6 (3)
C5—N2—C4	102.8 (3)	N2—C4—C3	111.9 (3)
C2—C1—S1	116.5 (3)	N2—C4—S1	136.4 (3)
C2—C1—Br1	124.6 (3)	C3—C4—S1	111.6 (3)
S1—C1—Br1	118.9 (2)	N2—C5—N1	113.6 (3)
C1—C2—C3	107.1 (3)	N2—C5—H5	123.2
C1—C2—H2	126.4	N1—C5—H5	123.2

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···N2^{i}	0.88	2.04	2.903 (4)	165

Symmetry codes: (i) x+1/2, −y+3/2, z+1/2.

Fig. 1

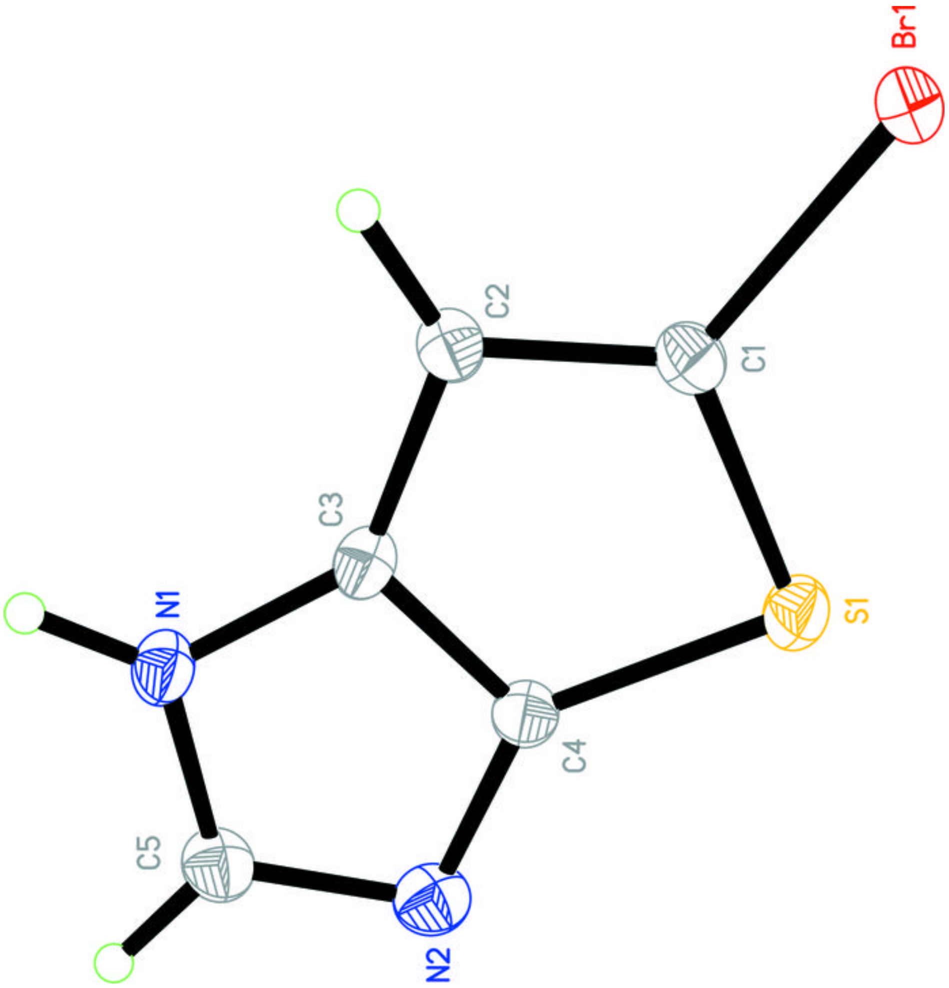

Fig. 2