

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

8-Bromo-3,4-dihydro-2H-1,3-thiazino-[2,3:2',1']imidazo[5',4'-b]pyridine

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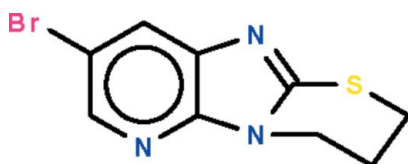
Received 6 April 2010; accepted 6 April 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; disorder in main residue; R factor = 0.024; wR factor = 0.064; data-to-parameter ratio = 24.4.

The imidazopyridine ring system in the title compound, $\text{C}_9\text{H}_8\text{BrN}_3\text{S}$, is almost planar [r.m.s. deviation of the C and N atoms = 0.007 (1) Å]. The S and methylene C atoms connected to the five-membered ring lie within this plane. The remaining two methylene groups of the thiazine ring are disordered over two sets of sites in a 0.817 (5):0.183 (5) ratio.

Related literature

The parent tricyclic condensed imidazole (without bromine) has been patented as a pharmaceutical; see: Hideg *et al.* (1975, 1976). For other compounds synthesized from 6-bromo-1H-imidazo[4,5-b]pyridine-2(3H)-thione, see: Liszkiewicz *et al.* (2007); Prasad *et al.* (1986); Yutilov & Svertilova (1988).



Experimental

Crystal data

$\text{C}_9\text{H}_8\text{BrN}_3\text{S}$
 $M_r = 270.15$
 Monoclinic, $C2/c$
 $a = 20.2738$ (3) Å
 $b = 13.2786$ (2) Å
 $c = 7.3169$ (1) Å
 $\beta = 102.193$ (1)°
 $V = 1925.33$ (5) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 4.45$ mm⁻¹
 $T = 100$ K
 $0.46 \times 0.14 \times 0.12$ mm

Data collection

Bruker X8 APEXII diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.234$, $T_{\max} = 0.618$
 30460 measured reflections
 3561 independent reflections
 3003 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 Standard reflections: 0

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.064$
 $S = 0.99$
 3561 reflections
 146 parameters
 14 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.49$ e Å⁻³
 $\Delta\rho_{\min} = -0.55$ e Å⁻³

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).

The authors thank the University Sidi Mohammed Ben Abdallah, the Université Mohammed V-Agdal and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5242).

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supporting information

Acta Cryst. (2010). E66, o1079 [https://doi.org/10.1107/S1600536810012778]

8-Bromo-3,4-dihydro-2H-1,3-thiazino[2,3:2',1']imidazo[5',4'-b]pyridine

Hend Bel Ghacham, Youssef Kandri Rodi, Frédéric Capet, El Mokhtar Essassi and Seik Weng Ng

S1. Comment

Commerically-available 6-bromo-1*H*-imidazo[4,5-*b*]pyridine-2(3*H*)-thione has been used to react with a range of organic compounds to furnish chemicals having useful biological activities (Liszkiewicz *et al.*, 2007; Prasad *et al.*, 1986; Yutilov & Svertilova, 1988). The compound reacts with 1-chloropropanal under catalytic conditions to yield the title tricyclic condensed imidazole (Scheme I, Fig. 1). The imidazopyridine fused ring is planar. One ethylene fragment of the six-membered ring is twisted such that one atom lies above and the other below the plane. This fragment is disordered over two positions.

S2. Experimental

6-Bromo-1*H*-imidazo[4,5-*b*]pyridine-2(3*H*)-thione (1 mmol), potassium carbonate (4 mmol), tetra-*n*-butylammonium bromide (0.1 mmol) and 1-chloro-propanol (1.5 mmol) in DMF (15 ml) were stirred for 72 h. After completion of reaction (as monitored by TLC), the salt was filtered and the solvent removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel using chloroform/hexane (1/1) as eluent. Colorless crystals were isolated when the solvent was allowed to evaporate.

S3. Refinement

H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U(\text{C})$.

The two methylene atoms next to the S atom are disordered over two sites; the disorder refined to an 0.817 (5):0.183 (5) ratio. The pair of S—C distances were restrained to be equal within 0.01 Å of each other, as were the pair of C—C distances. The anisotropic temperature factors of the primed atoms were restrained to be nearly isotropic.

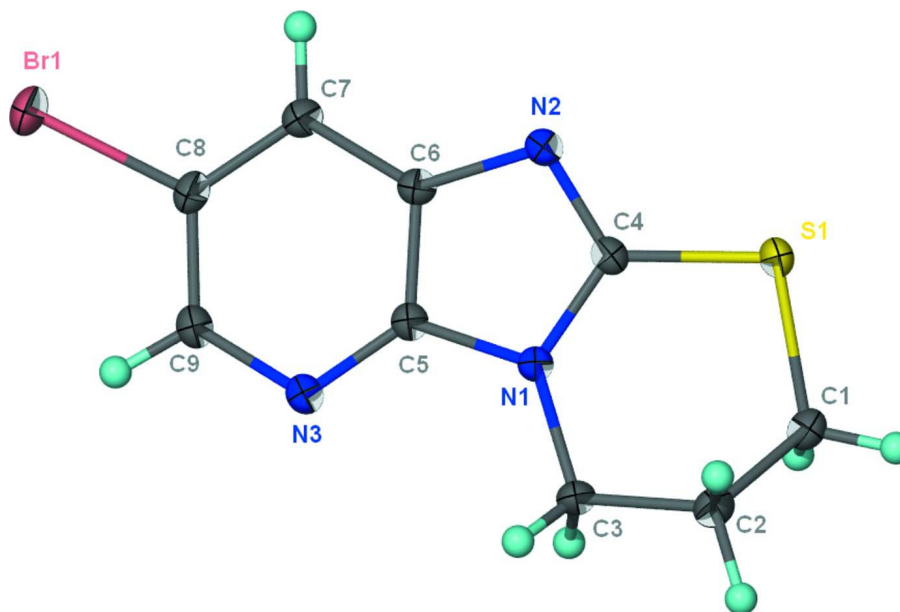


Figure 1

Anisotropic displacement ellipsoid plot (Barbour, 2001) of $C_9H_8BrN_3O$ at the 70% probability level; H atoms are drawn as spheres of an arbitrary radius. The disorder is not shown.

8-Bromo-3,4-dihydro-2H1,3-thiazino[2,3:2',1']imidazo[5',4'-b]pyridine

Crystal data

$C_9H_8BrN_3O$
 $M_r = 270.15$
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 Hall symbol: $-C 2yc$
 $a = 20.2738 (3) \text{ \AA}$
 $b = 13.2786 (2) \text{ \AA}$
 $c = 7.3169 (1) \text{ \AA}$
 $\beta = 102.193 (1)^\circ$
 $V = 1925.33 (5) \text{ \AA}^3$
 $Z = 8$

$F(000) = 1072$
 $D_x = 1.864 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 9070 reflections
 $\theta = 2.8\text{--}32.5^\circ$
 $\mu = 4.45 \text{ mm}^{-1}$
 $T = 100 \text{ K}$
 Block, colourless
 $0.46 \times 0.14 \times 0.12 \text{ mm}$

Data collection

Bruker X8 APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.234$, $T_{\max} = 0.618$

30460 measured reflections
 3561 independent reflections
 3003 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 32.8^\circ$, $\theta_{\min} = 1.9^\circ$
 $h = -30 \rightarrow 30$
 $k = -20 \rightarrow 20$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.064$
 $S = 0.99$

3561 reflections
 146 parameters
 14 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.6536P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.446434 (7)	0.655625 (11)	0.45346 (2)	0.02338 (5)	
S1	0.082325 (17)	0.50817 (3)	0.60465 (5)	0.01612 (7)	
N1	0.20317 (6)	0.43515 (8)	0.54957 (17)	0.0139 (2)	
N2	0.19469 (6)	0.60483 (9)	0.56459 (18)	0.0162 (2)	
N3	0.31734 (6)	0.42166 (9)	0.50005 (18)	0.0167 (2)	
C1	0.07654 (9)	0.37320 (13)	0.6425 (4)	0.0175 (4)	0.817 (5)
H1A	0.0993	0.3568	0.7726	0.021*	0.817 (5)
H1B	0.0285	0.3537	0.6256	0.021*	0.817 (5)
C2	0.10897 (9)	0.31333 (13)	0.5076 (3)	0.0178 (4)	0.817 (5)
H2A	0.0888	0.3342	0.3780	0.021*	0.817 (5)
H2B	0.0991	0.2409	0.5196	0.021*	0.817 (5)
C1'	0.0642 (4)	0.3746 (5)	0.5409 (16)	0.0186 (18)	0.183 (5)
H1'A	0.0233	0.3527	0.5836	0.022*	0.183 (5)
H1'B	0.0556	0.3670	0.4033	0.022*	0.183 (5)
C2'	0.1237 (3)	0.3089 (6)	0.6309 (11)	0.0158 (18)	0.183 (5)
H2'A	0.1106	0.2371	0.6148	0.019*	0.183 (5)
H2'B	0.1360	0.3232	0.7667	0.019*	0.183 (5)
C3	0.18508 (7)	0.32823 (10)	0.5435 (2)	0.0179 (3)	
H3A	0.2062	0.2962	0.6639	0.021*	0.817 (5)
H3B	0.2030	0.2947	0.4433	0.021*	0.817 (5)
H3C	0.2240	0.2887	0.6118	0.021*	0.183 (5)
H3D	0.1748	0.3051	0.4119	0.021*	0.183 (5)
C4	0.16459 (7)	0.51691 (10)	0.57248 (19)	0.0142 (2)	
C5	0.26416 (7)	0.47390 (10)	0.52582 (19)	0.0140 (2)	
C6	0.25763 (7)	0.57918 (10)	0.53377 (19)	0.0143 (2)	
C7	0.31223 (7)	0.63821 (10)	0.5118 (2)	0.0166 (2)	
H7	0.3111	0.7097	0.5143	0.020*	
C8	0.36844 (7)	0.58455 (10)	0.4857 (2)	0.0158 (2)	
C9	0.37001 (7)	0.47932 (11)	0.4812 (2)	0.0175 (3)	
H9	0.4101	0.4471	0.4641	0.021*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01399 (7)	0.02031 (8)	0.03740 (10)	-0.00406 (5)	0.00897 (6)	0.00137 (6)
S1	0.01303 (14)	0.01364 (14)	0.02374 (16)	0.00071 (11)	0.00854 (12)	-0.00036 (12)
N1	0.0120 (5)	0.0103 (4)	0.0206 (5)	-0.0002 (4)	0.0058 (4)	-0.0006 (4)
N2	0.0136 (5)	0.0117 (5)	0.0246 (6)	0.0011 (4)	0.0068 (4)	0.0003 (4)
N3	0.0131 (5)	0.0136 (5)	0.0244 (6)	0.0008 (4)	0.0065 (4)	-0.0004 (4)
C1	0.0156 (8)	0.0145 (7)	0.0240 (11)	-0.0020 (6)	0.0079 (7)	0.0010 (7)

C2	0.0155 (7)	0.0133 (7)	0.0255 (11)	-0.0024 (6)	0.0066 (7)	-0.0022 (6)
C1'	0.020 (4)	0.015 (3)	0.023 (5)	-0.005 (3)	0.009 (3)	-0.001 (3)
C2'	0.016 (3)	0.013 (3)	0.020 (4)	-0.001 (2)	0.005 (3)	0.002 (3)
C3	0.0153 (6)	0.0099 (5)	0.0301 (7)	-0.0009 (4)	0.0088 (5)	-0.0011 (5)
C4	0.0128 (5)	0.0125 (5)	0.0183 (6)	0.0014 (4)	0.0054 (4)	-0.0002 (5)
C5	0.0123 (5)	0.0122 (5)	0.0179 (6)	-0.0001 (4)	0.0043 (4)	-0.0003 (4)
C6	0.0132 (5)	0.0114 (5)	0.0187 (6)	0.0005 (4)	0.0041 (5)	0.0006 (4)
C7	0.0144 (6)	0.0128 (5)	0.0230 (6)	-0.0008 (4)	0.0047 (5)	0.0008 (5)
C8	0.0119 (5)	0.0153 (6)	0.0208 (6)	-0.0022 (4)	0.0046 (5)	0.0011 (5)
C9	0.0128 (6)	0.0160 (6)	0.0250 (7)	0.0010 (5)	0.0067 (5)	0.0002 (5)

Geometric parameters (Å, °)

Br1—C8	1.8986 (13)	C1'—C2'	1.521 (13)
S1—C4	1.7367 (14)	C1'—H1'A	0.9900
S1—C1	1.8211 (18)	C1'—H1'B	0.9900
S1—C1'	1.851 (6)	C2'—C3	1.536 (6)
N1—C4	1.3689 (17)	C2'—H2'A	0.9900
N1—C5	1.3836 (17)	C2'—H2'B	0.9900
N1—C3	1.4647 (17)	C3—H3A	0.9900
N2—C4	1.3243 (17)	C3—H3B	0.9900
N2—C6	1.3844 (17)	C3—H3C	0.9900
N3—C5	1.3286 (17)	C3—H3D	0.9900
N3—C9	1.3445 (18)	C5—C6	1.4067 (18)
C1—C2	1.521 (3)	C6—C7	1.3931 (19)
C1—H1A	0.9900	C7—C8	1.391 (2)
C1—H1B	0.9900	C7—H7	0.9500
C2—C3	1.522 (2)	C8—C9	1.3982 (19)
C2—H2A	0.9900	C9—H9	0.9500
C2—H2B	0.9900		
C4—S1—C1	100.42 (7)	N1—C3—C2	111.68 (12)
C4—S1—C1'	100.1 (3)	N1—C3—C2'	111.7 (3)
C4—N1—C5	105.63 (11)	N1—C3—H3A	109.3
C4—N1—C3	128.79 (12)	C2—C3—H3A	109.3
C5—N1—C3	125.55 (11)	N1—C3—H3B	109.3
C4—N2—C6	103.85 (11)	C2—C3—H3B	109.3
C5—N3—C9	113.77 (12)	H3A—C3—H3B	107.9
C2—C1—S1	111.42 (14)	N1—C3—H3C	109.3
C2—C1—H1A	109.3	C2'—C3—H3C	109.3
S1—C1—H1A	109.3	N1—C3—H3D	109.3
C2—C1—H1B	109.3	C2'—C3—H3D	109.3
S1—C1—H1B	109.3	H3C—C3—H3D	107.9
H1A—C1—H1B	108.0	N2—C4—N1	114.41 (12)
C1—C2—C3	112.43 (15)	N2—C4—S1	121.96 (10)
C1—C2—H2A	109.1	N1—C4—S1	123.61 (10)
C3—C2—H2A	109.1	N3—C5—N1	126.67 (12)
C1—C2—H2B	109.1	N3—C5—C6	127.66 (13)

C3—C2—H2B	109.1	N1—C5—C6	105.67 (11)
H2A—C2—H2B	107.8	N2—C6—C7	131.50 (12)
C2'—C1'—S1	110.1 (6)	N2—C6—C5	110.44 (12)
C2'—C1'—H1'A	109.6	C7—C6—C5	118.06 (12)
S1—C1'—H1'A	109.6	C8—C7—C6	114.94 (12)
C2'—C1'—H1'B	109.6	C8—C7—H7	122.5
S1—C1'—H1'B	109.6	C6—C7—H7	122.5
H1'A—C1'—H1'B	108.2	C7—C8—C9	122.59 (13)
C1'—C2'—C3	111.2 (6)	C7—C8—Br1	119.37 (10)
C1'—C2'—H2'A	109.4	C9—C8—Br1	118.04 (10)
C3—C2'—H2'A	109.4	N3—C9—C8	122.97 (13)
C1'—C2'—H2'B	109.4	N3—C9—H9	118.5
C3—C2'—H2'B	109.4	C8—C9—H9	118.5
H2'A—C2'—H2'B	108.0		
C4—S1—C1—C2	-42.19 (16)	C1—S1—C4—N1	10.57 (15)
C1'—S1—C1—C2	49.0 (7)	C1'—S1—C4—N1	-12.8 (4)
S1—C1—C2—C3	67.0 (2)	C9—N3—C5—N1	-179.92 (13)
C4—S1—C1'—C2'	44.5 (7)	C9—N3—C5—C6	0.4 (2)
C1—S1—C1'—C2'	-48.5 (7)	C4—N1—C5—N3	179.51 (14)
S1—C1'—C2'—C3	-69.0 (8)	C3—N1—C5—N3	-2.5 (2)
C4—N1—C3—C2	17.2 (2)	C4—N1—C5—C6	-0.78 (15)
C5—N1—C3—C2	-160.32 (14)	C3—N1—C5—C6	177.23 (13)
C4—N1—C3—C2'	-19.3 (4)	C4—N2—C6—C7	179.69 (15)
C5—N1—C3—C2'	163.2 (3)	C4—N2—C6—C5	-0.67 (16)
C1—C2—C3—N1	-52.1 (2)	N3—C5—C6—N2	-179.37 (14)
C1—C2—C3—C2'	44.8 (5)	N1—C5—C6—N2	0.92 (16)
C1'—C2'—C3—N1	54.3 (7)	N3—C5—C6—C7	0.3 (2)
C1'—C2'—C3—C2	-42.7 (5)	N1—C5—C6—C7	-179.37 (12)
C6—N2—C4—N1	0.15 (16)	N2—C6—C7—C8	178.98 (14)
C6—N2—C4—S1	-178.61 (10)	C5—C6—C7—C8	-0.6 (2)
C5—N1—C4—N2	0.41 (16)	C6—C7—C8—C9	0.3 (2)
C3—N1—C4—N2	-177.51 (14)	C6—C7—C8—Br1	179.90 (10)
C5—N1—C4—S1	179.16 (10)	C5—N3—C9—C8	-0.9 (2)
C3—N1—C4—S1	1.2 (2)	C7—C8—C9—N3	0.6 (2)
C1—S1—C4—N2	-170.77 (14)	Br1—C8—C9—N3	-179.09 (11)
C1'—S1—C4—N2	165.9 (4)		