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3-Bromo-2-[4-(methylsulfonyl)phenyl]-5,6,7,8-tetrahydro-1,3-benzothiazolo[3,2-a]imidazole

Alexander S. Bunev,^{a*} Elena V. Sukhonosova,^b Vladimir E. Statsyuk,^a Gennady I. Ostapenko^a and Victor N. Khrustalev^c

^aDepartment of Chemistry and Chemical Technology, Togliatti State University, 14 Belorusskaya St, Togliatti 445667, Russian Federation, ^bDepartment of Organic, Bioorganic and Medicinal Chemistry, Samara State University, 1 Akademician Pavlov St, Samara 443011, Russian Federation, and ^cX-Ray Structural Centre, A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, B-334, Moscow 119991, Russian Federation

Correspondence e-mail: a.s.bunev@gmail.com

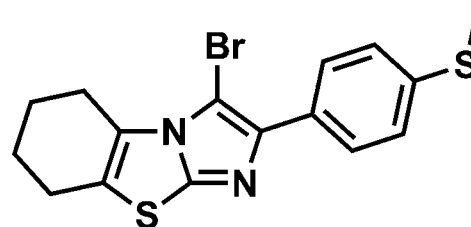
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.030; wR factor = 0.073; data-to-parameter ratio = 23.6.

In the title molecule, $\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{S}_2$, the central imidazo[2,1-*b*]thiazole fragment is almost planar (r.m.s. deviation = 0.012 Å), and the fused 5,6,7,8-tetrahydrobenzene ring adopts an unsymmetrical half-chair conformation. The dihedral angle between the imidazo[2,1-*b*]thiazole and benzene planes is 18.25 (4)°. The terminal methylsulfonyl substituent lies practically within the benzene plane [the dihedral angle between the corresponding planes is 7.20 (10)°] and is turned toward the C—Br bond. In the crystal, molecules form infinite chains along [100] via secondary Br⋯N interactions [3.1861 (16) Å]. The chains are arranged at van der Waals distances.

Related literature

For applications of imidazo[2,1-*b*][1,3]benzothiazoles, see: Ager *et al.* (1988); Sanfilippo *et al.* (1988); Barchéath *et al.* (2005); Andreani *et al.* (2008); Chao *et al.* (2009); Kumbhare *et al.* (2011); Chandak *et al.* (2013). For the crystal structures of related compounds, see: Landreau *et al.* (2002); Adib *et al.* (2008); Fun, Asik *et al.* (2011); Fun, Hemamalini *et al.* (2011); Ghabbour *et al.* (2012); Bunev *et al.* (2013, 2014).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{15}\text{BrN}_2\text{S}_2$	$\gamma = 101.938$ (1)°
$M_r = 379.34$	$V = 771.03$ (6) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.3132$ (3) Å	Mo $K\alpha$ radiation
$b = 7.5663$ (3) Å	$\mu = 2.93$ mm ⁻¹
$c = 14.4543$ (7) Å	$T = 120$ K
$\alpha = 95.033$ (1)°	$0.15 \times 0.10 \times 0.10$ mm
$\beta = 97.188$ (1)°	

Data collection

Bruker APEXII CCD diffractometer	10352 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	4508 independent reflections
$T_{\min} = 0.668$, $T_{\max} = 0.758$	3927 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	191 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.67$ e Å ⁻³
4508 reflections	$\Delta\rho_{\text{min}} = -0.32$ e Å ⁻³

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RK2426).

References

- Adib, M., Sheibani, E., Zhu, L.-G. & Bijanzadeh, H. R. (2008). *Synlett*, pp. 2941–2944.
- Ager, I. R., Barnes, A. C., Danswan, G. W., Hairsine, P. W., Kay, D. P., Kennewell, P. D., Matharu, S. S., Miller, P. & Robson, P. (1988). *J. Med. Chem.* **31**, 1098–1115.
- Andreani, A., Burnelli, S., Granaola, M., Leoni, A., Locatelli, A., Morigi, R., Rambaldi, M., Varoli, L., Calonghi, N., Cappadone, C., Farruggia, G., Zini, M., Stefanelli, C., Masotti, L., Radin, N. S. & Shoemaker, R. H. (2008). *J. Med. Chem.* **51**, 809–816.
- Barchéath, S. D., Tawatao, R. I., Corr, V., Carson, D. I. & Cottam, H. B. (2005). *J. Med. Chem.* **48**, 6409–6422.
- Bruker (2001). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2003). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2005). APEX2. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bunev, A. S., Sukhonosova, E. V., Statsyuk, V. E., Ostapenko, G. I. & Khrustalev, V. N. (2014). *Acta Cryst.* **E70**, o143–o144.

- Buney, A. S., Sukhonosova, E. V., Syrazhetdinova, D. R., Statsyuk, V. E., Ostapenko, G. I. & Khrustalev, V. N. (2013). *Acta Cryst.* **E69**, o531.
- Chandak, N., Bhardwaj, J. K., Sharma, R. K. & Sharma, P. K. (2013). *Eur. J. Med. Chem.* **59**, 203–208.
- Chao, Q., Sprankle, K. G., Grotzfeld, R. M., Lai, A. G., Carter, T. A., Velasco, A. M., Gunawardane, R. N., Cramer, M. D., Gardner, M. F., James, J., Zarrinkar, P. P., Patel, H. K. & Bhagwat, S. S. (2009). *J. Med. Chem.* **52**, 7808–7816.
- Fun, H.-K., Asik, S. I. J., Himaja, M., Munirajasekhar, D. & Sarojini, B. K. (2011). *Acta Cryst.* **E67**, o2810.
- Fun, H.-K., Hemamalini, M., Umesha, K., Sarojini, B. K. & Narayana, B. (2011). *Acta Cryst.* **E67**, o3265–o3266.
- Ghabbour, H. A., Chia, T. S. & Fun, H.-K. (2012). *Acta Cryst.* **E68**, o1631–o1632.
- Kumbhare, R. M., Kumar, K. V., Ramaiah, M. J., Dadmal, T., Pushpavalli, S. N., Mukhopadhyay, D., Divya, B., Devi, T. A., Kosurkar, U. & Pal-Bhadra, M. (2011). *Eur. J. Med. Chem.* **46**, 4258–4266.
- Landreau, C., Deniaud, D., Evain, M., Reliquet, A. & Meslin, J.-C. (2002). *J. Chem. Soc. Perkin Trans. 1*, pp. 741–745.
- Sanfilippo, P. J., Urbanski, M., Press, J. B., Dubinsky, B. & Moore, J. B. Jr (1988). *J. Med. Chem.* **31**, 2221–2227.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2014). E70, o596–o597 [doi:10.1107/S1600536814008976]

3-Bromo-2-[4-(methylsulfanyl)phenyl]-5,6,7,8-tetrahydro-1,3-benzothiazolo[3,2-a]imidazole

Alexander S. Bunev, Elena V. Sukhonosova, Vladimir E. Statsyuk, Gennady I. Ostapenko and Victor N. Khrustalev

S1. Comment

Imidazo[2,1-*b*][1,3]benzothiazole are of great interest due to their biological properties. These compounds and their derivatives demonstrate the antitumor (Andreani *et al.*, 2008), antiallergic (Ager *et al.*, 1988), anesthetic (Sanfilippo *et al.*, 1988) and anti-cancer (Kumbhare *et al.*, 2011) activities as well as the inhibition activity of apoptosis in testicular germ cells (Chandak *et al.*, 2013), lymphocytes (Barchéath *et al.*, 2005), and FMS-like tyrosine kinase-3 (FLT3) (Chao *et al.*, 2009).

In this work, a new halogensubstituted 5,6,7,8-tetrahydrobenzo[d]imidazo[2,1-*b*]thiazole, C₁₆H₁₅BrN₂S₂, **I**, was prepared by the reaction of 5,6,7,8-tetrahydrobenzo[d]imidazo[2,1-*b*]thiazole with bromine at room temperature (Fig. 1), and its structure was unambiguously established by the X-ray diffraction study (Fig. 2).

In the title molecule (**I**) the central imidazo[2,1-*b*]thiazole fragment is almost planar (r.m.s. deviation = 0.012 Å), and the fused 5,6,7,8-tetrahydrobenzene ring adopts an unsymmetrical *half-chair* conformation (the C6 and C7 carbon atoms are out of the plane passed through the other atoms of the ring by -0.246 (2) and 0.508 (2) Å, respectively). The bond lengths and angles within the molecule of **I** are in a good agreement with those found in the related compounds (Landreau *et al.*, 2002; Adib *et al.*, 2008; Fun, Asik *et al.*, 2011; Fun, Hemamalini *et al.*, 2011; Ghabbour *et al.*, 2012; Bunev *et al.*, 2013, 2014). The dihedral angle between the imidazo[2,1-*b*]thiazole and benzene planes is 18.25 (4)°. The terminal methylthio substituent lies practically within the benzene plane (the dihedral angle between the corresponding planes is 7.20 (10)°) and is turned toward the C—Br bond.

In the crystal, the molecules of **I** form infinite chains along [100] by intermolecular secondary Br1⋯N1ⁱ interactions (3.1861 (16) Å) (Fig. 3). The chains are arranged at van der Waals distances. Symmetry code: (i) 1 + *x*, *y*, *z*.

S2. Experimental

A solution of bromine (139 μL, 430.4 mg, 2.69 mmol) in dry CHCl₃ (10 mL) was added to a solutions 2-(4-(methylthio)phenyl)-5,6,7,8-tetrahydrobenzo[d]imidazo[2,1-*b*]thiazole (808.3 mg, 2.69 mmol) in dry CHCl₃ (30 mL). The reaction mixture was stirred at room temperature for 3 h. the solvent was evaporated from the reaction mixture on rotavapor. The crude product was diluted with 5% solution Na₂CO₃ in water (25 mL). The precipitate was filtered and crystallized from DMF. Yield is 75%. The single-crystal of the product **I** was obtained by slow crystallization from DMF. M.p. = 439–441 K. IR (KBr), ν/cm⁻¹: 3131, 3073, 1580, 1523, 1501, 1337, 1144, 815, 714. ¹H NMR (600 MHz, DMSO-*d*₆, 304 K): 7.63 (d, 2H, *J* = 8.9), 7.54 (d, 2H, *J* = 8.9), 3.39–3.33 (m, 2H), 3.02–2.96 (m, 2H), 2.45 (s, 3H), 1.91–1.81 (m, 4H). Anal. Calcd for C₁₆H₁₅BrN₂S: C, 50.66; H, 3.99. Found: C, 50.57; H, 4.08.

S3. Refinement

All hydrogen atoms were placed in the calculated positions with $C-H = 0.95-0.99 \text{ \AA}$ and refined in the riding model with fixed isotropic displacement parameters: $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl group and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups.

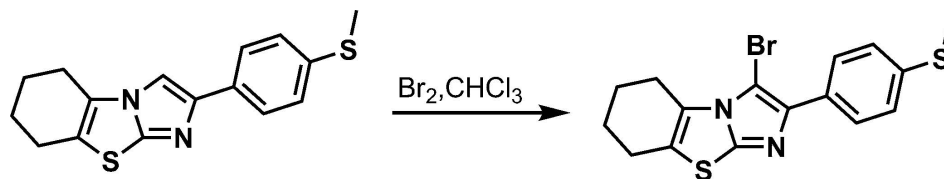


Figure 1

The synthesis of 3-bromo-2-[4-(methylsulfanyl)phenyl]-5,6,7,8-tetrahydro-1,3-benzothiazolo[3,2-*a*]imidazole.

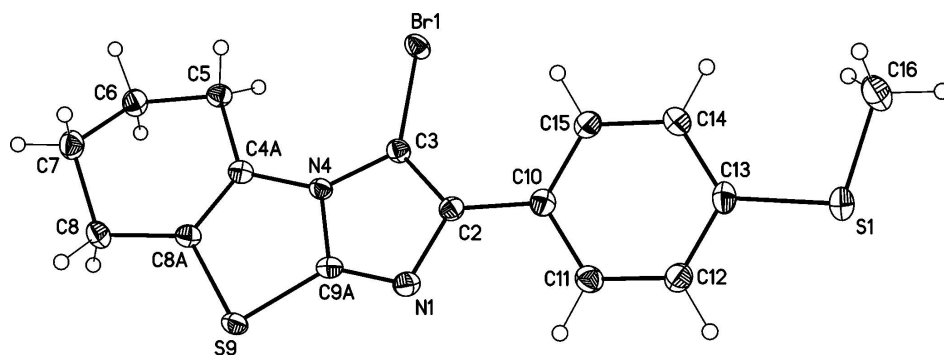


Figure 2

Molecular structure of **I**. Displacement ellipsoids are presented at the 50% probability level. H atoms are depicted as small spheres of arbitrary radius.

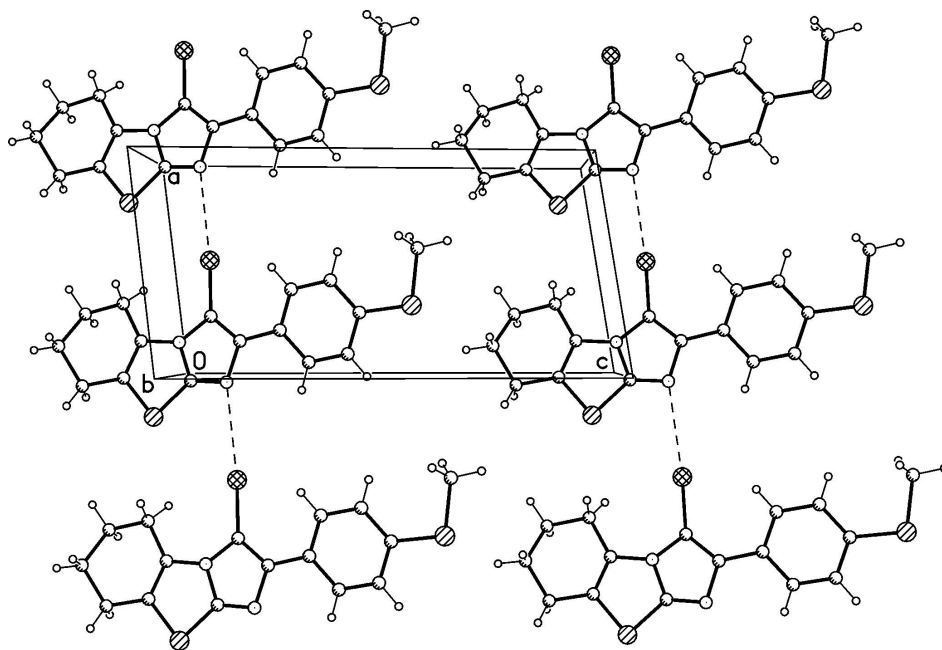


Figure 3

A portion of the crystal structure of **I** demonstrating the chains along [100]. The intermolecular secondary Br...N interactions are depicted by dashed lines.

3-Bromo-2-[4-(methylsulfonyl)phenyl]-5,6,7,8-tetrahydro-1,3-benzothiazolo[3,2-a]imidazole

Crystal data

$C_{16}H_{15}BrN_2S_2$

$M_r = 379.34$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.3132$ (3) Å

$b = 7.5663$ (3) Å

$c = 14.4543$ (7) Å

$\alpha = 95.033$ (1)°

$\beta = 97.188$ (1)°

$\gamma = 101.938$ (1)°

$V = 771.03$ (6) Å³

$Z = 2$

$F(000) = 384$

$D_x = 1.634$ Mg m⁻³

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

Cell parameters from 4428 reflections

$\theta = 2.8$ – 32.3 °

$\mu = 2.93$ mm⁻¹

$T = 120$ K

Prism, colourless

$0.15 \times 0.10 \times 0.10$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2003)

$T_{\min} = 0.668$, $T_{\max} = 0.758$

10352 measured reflections

4508 independent reflections

3927 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 30.0$ °, $\theta_{\min} = 2.8$ °

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.073$
 $S = 1.05$
 4508 reflections
 191 parameters
 0 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
 $w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.1351P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.67 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.52846 (2)	0.33371 (2)	0.103656 (13)	0.01782 (6)
S1	0.31673 (8)	0.75383 (8)	0.55165 (4)	0.02712 (12)
N1	-0.0318 (2)	0.3490 (2)	0.10823 (11)	0.0169 (3)
C2	0.1565 (3)	0.3866 (2)	0.15151 (13)	0.0150 (3)
C3	0.2697 (2)	0.3284 (2)	0.09002 (13)	0.0146 (3)
N4	0.1494 (2)	0.2541 (2)	0.00724 (10)	0.0136 (3)
C4A	0.1551 (3)	0.1754 (2)	-0.08424 (13)	0.0147 (3)
C5	0.3302 (3)	0.1399 (2)	-0.11797 (13)	0.0159 (3)
H5A	0.3921	0.0696	-0.0739	0.019*
H5B	0.4195	0.2568	-0.1199	0.019*
C6	0.2819 (3)	0.0326 (3)	-0.21646 (14)	0.0194 (4)
H6A	0.3978	0.0462	-0.2464	0.023*
H6B	0.2372	-0.0981	-0.2106	0.023*
C7	0.1308 (3)	0.0964 (3)	-0.27918 (13)	0.0208 (4)
H7A	0.1110	0.0295	-0.3429	0.025*
H7B	0.1735	0.2276	-0.2844	0.025*
C8	-0.0560 (3)	0.0635 (3)	-0.23845 (13)	0.0186 (4)
H8A	-0.1458	0.1253	-0.2726	0.022*
H8B	-0.1133	-0.0684	-0.2457	0.022*
C8A	-0.0175 (3)	0.1366 (2)	-0.13656 (13)	0.0154 (3)
S9	-0.19453 (6)	0.18940 (6)	-0.07481 (3)	0.01700 (10)
C9A	-0.0272 (2)	0.2722 (2)	0.02379 (13)	0.0153 (3)
C10	0.2059 (3)	0.4782 (2)	0.24789 (13)	0.0164 (3)
C11	0.0607 (3)	0.4836 (3)	0.30255 (14)	0.0191 (4)
H11	-0.0658	0.4267	0.2767	0.023*

C12	0.0991 (3)	0.5705 (3)	0.39362 (14)	0.0204 (4)
H12	-0.0014	0.5733	0.4291	0.024*
C13	0.2850 (3)	0.6542 (3)	0.43388 (13)	0.0199 (4)
C14	0.4292 (3)	0.6527 (3)	0.37994 (14)	0.0232 (4)
H14	0.5554	0.7108	0.4058	0.028*
C15	0.3898 (3)	0.5664 (3)	0.28802 (14)	0.0217 (4)
H15	0.4900	0.5676	0.2520	0.026*
C16	0.5684 (3)	0.8198 (3)	0.58283 (16)	0.0302 (5)
H16A	0.6001	0.8615	0.6502	0.045*
H16B	0.6187	0.9185	0.5472	0.045*
H16C	0.6242	0.7154	0.5682	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01313 (9)	0.02030 (10)	0.01932 (10)	0.00599 (7)	-0.00109 (6)	-0.00219 (7)
S1	0.0271 (3)	0.0327 (3)	0.0173 (2)	0.0007 (2)	0.0029 (2)	-0.0057 (2)
N1	0.0157 (7)	0.0163 (7)	0.0187 (8)	0.0026 (6)	0.0042 (6)	0.0015 (6)
C2	0.0154 (8)	0.0140 (8)	0.0158 (8)	0.0029 (7)	0.0033 (7)	0.0023 (6)
C3	0.0134 (8)	0.0155 (8)	0.0154 (8)	0.0051 (7)	0.0010 (6)	0.0008 (6)
N4	0.0109 (7)	0.0153 (7)	0.0145 (7)	0.0034 (6)	0.0011 (5)	0.0010 (6)
C4A	0.0145 (8)	0.0121 (8)	0.0175 (9)	0.0030 (6)	0.0023 (7)	0.0016 (6)
C5	0.0140 (8)	0.0160 (8)	0.0186 (9)	0.0050 (7)	0.0036 (7)	0.0004 (7)
C6	0.0195 (9)	0.0217 (9)	0.0179 (9)	0.0083 (8)	0.0030 (7)	-0.0010 (7)
C7	0.0221 (9)	0.0247 (10)	0.0159 (9)	0.0070 (8)	0.0025 (7)	-0.0004 (7)
C8	0.0178 (9)	0.0193 (9)	0.0167 (9)	0.0036 (7)	-0.0016 (7)	-0.0013 (7)
C8A	0.0136 (8)	0.0140 (8)	0.0182 (8)	0.0025 (7)	0.0028 (7)	0.0007 (6)
S9	0.01080 (19)	0.0210 (2)	0.0186 (2)	0.00355 (17)	0.00092 (16)	0.00057 (17)
C9A	0.0119 (8)	0.0160 (8)	0.0186 (8)	0.0030 (7)	0.0033 (7)	0.0031 (7)
C10	0.0192 (9)	0.0129 (8)	0.0167 (8)	0.0027 (7)	0.0028 (7)	0.0010 (6)
C11	0.0176 (9)	0.0174 (9)	0.0208 (9)	0.0017 (7)	0.0021 (7)	0.0001 (7)
C12	0.0211 (9)	0.0208 (9)	0.0193 (9)	0.0037 (8)	0.0051 (7)	0.0010 (7)
C13	0.0252 (10)	0.0187 (9)	0.0145 (8)	0.0037 (8)	0.0019 (7)	-0.0011 (7)
C14	0.0196 (9)	0.0252 (10)	0.0208 (10)	-0.0006 (8)	0.0014 (7)	-0.0028 (8)
C15	0.0205 (9)	0.0235 (10)	0.0194 (9)	0.0009 (8)	0.0063 (7)	-0.0012 (8)
C16	0.0286 (11)	0.0311 (12)	0.0249 (11)	-0.0003 (9)	-0.0030 (9)	-0.0030 (9)

Geometric parameters (Å, °)

Br1—C3	1.8693 (18)	C7—H7B	0.9900
S1—C13	1.7673 (19)	C8—C8A	1.498 (3)
S1—C16	1.793 (2)	C8—H8A	0.9900
N1—C9A	1.312 (2)	C8—H8B	0.9900
N1—C2	1.400 (2)	C8A—S9	1.7529 (19)
C2—C3	1.391 (2)	S9—C9A	1.7354 (19)
C2—C10	1.467 (3)	C10—C15	1.399 (3)
C3—N4	1.391 (2)	C10—C11	1.405 (3)
N4—C9A	1.374 (2)	C11—C12	1.387 (3)

N4—C4A	1.411 (2)	C11—H11	0.9500
C4A—C8A	1.349 (2)	C12—C13	1.403 (3)
C4A—C5	1.492 (2)	C12—H12	0.9500
C5—C6	1.537 (3)	C13—C14	1.389 (3)
C5—H5A	0.9900	C14—C15	1.396 (3)
C5—H5B	0.9900	C14—H14	0.9500
C6—C7	1.524 (3)	C15—H15	0.9500
C6—H6A	0.9900	C16—H16A	0.9800
C6—H6B	0.9900	C16—H16B	0.9800
C7—C8	1.537 (3)	C16—H16C	0.9800
C7—H7A	0.9900		
C13—S1—C16	103.71 (10)	C8A—C8—H8B	109.9
C9A—N1—C2	104.13 (15)	C7—C8—H8B	109.9
C3—C2—N1	110.13 (16)	H8A—C8—H8B	108.3
C3—C2—C10	130.54 (17)	C4A—C8A—C8	124.20 (17)
N1—C2—C10	119.33 (16)	C4A—C8A—S9	113.31 (14)
C2—C3—N4	106.03 (15)	C8—C8A—S9	122.44 (13)
C2—C3—Br1	131.99 (14)	C9A—S9—C8A	89.99 (9)
N4—C3—Br1	121.98 (13)	N1—C9A—N4	114.32 (16)
C9A—N4—C3	105.38 (15)	N1—C9A—S9	134.58 (14)
C9A—N4—C4A	114.32 (15)	N4—C9A—S9	111.08 (13)
C3—N4—C4A	140.26 (16)	C15—C10—C11	117.62 (17)
C8A—C4A—N4	111.27 (16)	C15—C10—C2	123.61 (17)
C8A—C4A—C5	124.77 (17)	C11—C10—C2	118.73 (17)
N4—C4A—C5	123.97 (16)	C12—C11—C10	121.15 (18)
C4A—C5—C6	110.25 (15)	C12—C11—H11	119.4
C4A—C5—H5A	109.6	C10—C11—H11	119.4
C6—C5—H5A	109.6	C11—C12—C13	120.61 (18)
C4A—C5—H5B	109.6	C11—C12—H12	119.7
C6—C5—H5B	109.6	C13—C12—H12	119.7
H5A—C5—H5B	108.1	C14—C13—C12	118.75 (18)
C7—C6—C5	112.55 (15)	C14—C13—S1	124.86 (16)
C7—C6—H6A	109.1	C12—C13—S1	116.38 (15)
C5—C6—H6A	109.1	C13—C14—C15	120.45 (19)
C7—C6—H6B	109.1	C13—C14—H14	119.8
C5—C6—H6B	109.1	C15—C14—H14	119.8
H6A—C6—H6B	107.8	C14—C15—C10	121.38 (18)
C6—C7—C8	110.44 (16)	C14—C15—H15	119.3
C6—C7—H7A	109.6	C10—C15—H15	119.3
C8—C7—H7A	109.6	S1—C16—H16A	109.5
C6—C7—H7B	109.6	S1—C16—H16B	109.5
C8—C7—H7B	109.6	H16A—C16—H16B	109.5
H7A—C7—H7B	108.1	S1—C16—H16C	109.5
C8A—C8—C7	109.02 (15)	H16A—C16—H16C	109.5
C8A—C8—H8A	109.9	H16B—C16—H16C	109.5
C7—C8—H8A	109.9		

C9A—N1—C2—C3	-0.4 (2)	C8—C8A—S9—C9A	-175.86 (16)
C9A—N1—C2—C10	178.60 (16)	C2—N1—C9A—N4	0.5 (2)
N1—C2—C3—N4	0.2 (2)	C2—N1—C9A—S9	-178.31 (16)
C10—C2—C3—N4	-178.66 (17)	C3—N4—C9A—N1	-0.4 (2)
N1—C2—C3—Br1	-178.84 (14)	C4A—N4—C9A—N1	-178.63 (15)
C10—C2—C3—Br1	2.3 (3)	C3—N4—C9A—S9	178.71 (12)
C2—C3—N4—C9A	0.07 (19)	C4A—N4—C9A—S9	0.45 (19)
Br1—C3—N4—C9A	179.24 (12)	C8A—S9—C9A—N1	177.7 (2)
C2—C3—N4—C4A	177.6 (2)	C8A—S9—C9A—N4	-1.11 (14)
Br1—C3—N4—C4A	-3.2 (3)	C3—C2—C10—C15	17.2 (3)
C9A—N4—C4A—C8A	0.7 (2)	N1—C2—C10—C15	-161.53 (18)
C3—N4—C4A—C8A	-176.6 (2)	C3—C2—C10—C11	-164.91 (19)
C9A—N4—C4A—C5	-179.12 (16)	N1—C2—C10—C11	16.3 (3)
C3—N4—C4A—C5	3.5 (3)	C15—C10—C11—C12	-1.1 (3)
C8A—C4A—C5—C6	-6.7 (3)	C2—C10—C11—C12	-179.12 (17)
N4—C4A—C5—C6	173.18 (16)	C10—C11—C12—C13	-0.5 (3)
C4A—C5—C6—C7	39.6 (2)	C11—C12—C13—C14	1.7 (3)
C5—C6—C7—C8	-63.1 (2)	C11—C12—C13—S1	-177.96 (15)
C6—C7—C8—C8A	49.1 (2)	C16—S1—C13—C14	-6.6 (2)
N4—C4A—C8A—C8	175.79 (16)	C16—S1—C13—C12	173.04 (16)
C5—C4A—C8A—C8	-4.3 (3)	C12—C13—C14—C15	-1.2 (3)
N4—C4A—C8A—S9	-1.6 (2)	S1—C13—C14—C15	178.47 (16)
C5—C4A—C8A—S9	178.26 (14)	C13—C14—C15—C10	-0.5 (3)
C7—C8—C8A—C4A	-17.4 (3)	C11—C10—C15—C14	1.7 (3)
C7—C8—C8A—S9	159.79 (14)	C2—C10—C15—C14	179.55 (18)
C4A—C8A—S9—C9A	1.59 (15)		
