

Crystal structure of 2-[(naphthalen-2-yl)methyl]isothiouonium bromide

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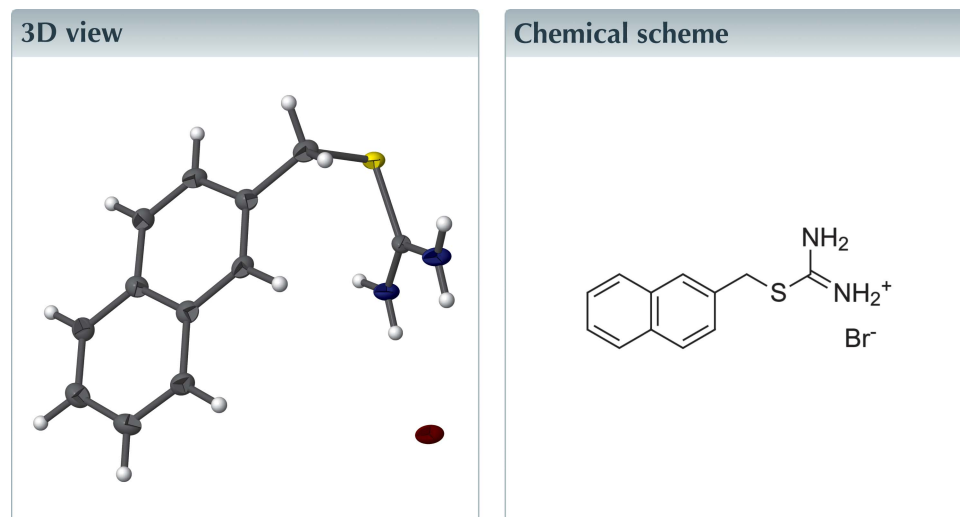
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Structural data: full structural data are available from iucrdata.iucr.org

Herein we report the crystal structure of 2-[(naphthalen-2-yl)methyl]isothiouonium bromide, $C_{12}H_{13}N_2S^+ \cdot Br^-$, which crystallizes in the monoclinic $P2_1/c$ centrosymmetric space group. The asymmetric unit contains one 2-[(naphthalen-2-yl)methyl]isothiouonium cation and one bromide anion. The methylene carbon lies in plane of the naphthalene core. In comparison with reference structures, elongation of C–S bonds as well as tilting of the isothiouonium group is observed. Given the ionic nature of the compound, the structure is held by charge-assisted N–H \cdots Br hydrogen bonds, with a noteworthy contribution of dipole–dipole interactions, which form bilayers in the structure. The bilayers are held by the weak London forces.



Structure description

Isothiouonium salts have been investigated because of their ability to bind anions by charge-assisted hydrogen bonds (Yeo & Hong, 1998; Seong *et al.*, 2004). Despite their potential in crystal engineering, only 23 crystal structures of 2-(arylmethyl)isothiouonium salts are present in the CSD (Groom *et al.*, 2016). In our studies of isothiouonia, we have managed to synthesize and crystallize naphthalene-2-ylmethyl-bearing isothiouonium bromide, and we report here its structure and a comparison with similar crystal structures.

The title compound crystallizes in the monoclinic $P2_1/c$ centrosymmetric space group with one 2-[(naphthalen-2-yl)methyl]isothiouonium cation and one bromide anion in the asymmetric unit, see Fig. 1. The naphthalene core is almost perfectly planar, with a maximum deviation of 0.026 (3) Å for atom C6. The C11 atom can be considered to be in the plane of naphthalene core, with a deviation of 0.039 (3) Å from the mean plane. The single bonds around carbon C11 and S1 allow for the free rotation of the isothiouonium group.

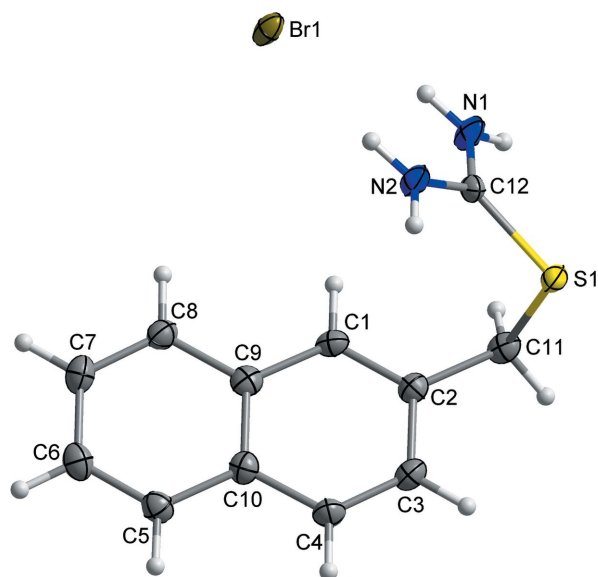


Figure 1
The title compound showing the numbering scheme with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

There are no 2-[(naphthalen-2-yl)methyl]isothiuronium structures in the the CSD; therefore, we decided to compare the title compound with 2-benzylisothiuronium structures. The published structures of 2-benzylisothiuronium can be divided according to the $C_{ar}-C_{me}-S-C_{th}$ torsion angle into linear and non-linear groups. Since the relevant torsion angle of the title compound is $-68.1(3)^\circ$, only the non-linear 2-benzylisothiuronium, will be used as a reference group [CCDC codes EBIFOK (Ishii *et al.*, 2000), IGECIG (Raptopoulou *et al.*, 2002), JALSOE (Mikolajczyk *et al.*, 1989), SEFRUQ (Barker & Powell, 1998), TAWVAP (Stergiou *et al.*, 2005), TOBNEE (Gayathri *et al.*, 2008) and YOCRUE (Fun *et al.*, 2008)]. The C2–C11 bond length of $1.495(5) \text{ \AA}$ in the title compound is within the usually observed values among the reference group,

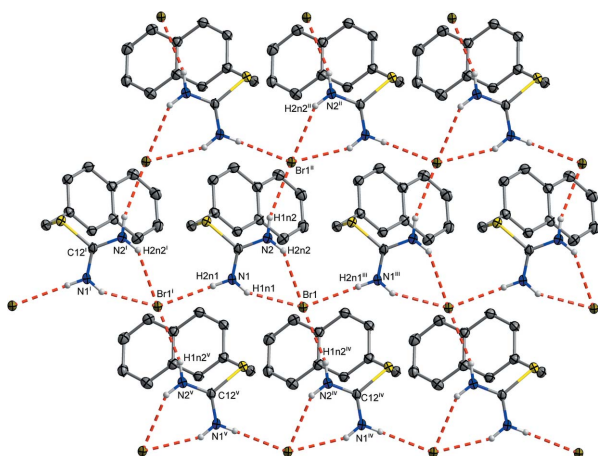


Figure 2
The charge-assisted hydrogen bonds in the title compound. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Symmetry codes: (i) $x, y - 1, z$; (ii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iii) $x, y + 1, z$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1n1 \cdots Br1$	0.86 (3)	2.54 (3)	3.332 (3)	153 (3)
$N1-H2n1 \cdots Br1^i$	0.86 (2)	2.49 (2)	3.350 (3)	180 (3)
$N2-H1n2 \cdots Br1^{ii}$	0.860 (19)	2.55 (3)	3.381 (3)	164 (4)
$N2-H2n2 \cdots Br1$	0.86 (3)	2.68 (3)	3.434 (3)	147 (3)

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

while the C11–S1 and S1–C12 bond lengths of $1.855(3) \text{ \AA}$ and $1.771(3) \text{ \AA}$ respectively are larger than usually observed, with average values of 1.819 \AA and 1.739 \AA . The C2–C11–S1 and C11–S1–C12 angles of $111.7(2)$ and $96.98(15)^\circ$, respectively, are less obtuse than the average values among the reference group, 115.21 and 103.91° . This deviation is most likely caused by the difference of electronic behaviour between the benzyl group and the 2-naphthylmethyl unit.

The C11–S1 bond is almost perpendicular to the naphthalene core, with C1–C2–C11–S1 and C3–C2–C11–S1 torsion angle values of $91.8(3)$ and $-88.0(3)^\circ$, respectively. Among the reference group, such a conformation is unusual, with average values being 61.45 and 120.53° . The isothiuronium group is significantly tilted, with C11–S1–C12–N1 and C11–S1–C12–N2 torsion angles of $-68.5(3)$ and $110.7(3)^\circ$, respectively. Such a tilt is not observed among the reference group, where the average values are 20.46 and 160.94° . The tilting of the group can be explained by the steric demands of the 2-naphthylmethyl unit on the packing.

The N–H \cdots Br charge-assisted hydrogen bonds (Table 1) have the most significant impact on crystal structure of 2-[(naphthalen-2-yl)methyl]isothiuronium bromide, with every isothiuronium cation forming three hydrogen bonds, one of them bifurcated, with bromide anions. This is a major difference from the structure of 2-benzylisothiuronium chloride (Barker & Powell, 1998), the only structure of 2-arylmethylisothiuronium with simple halide anion, where the isothiuronium group forms four charge-assisted hydrogen bonds with four different chloride anions. The charge-assisted hydrogen bonds form layers in the structure

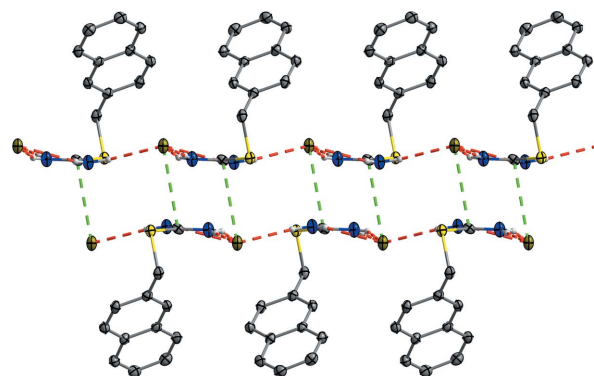


Figure 3
The bilayers formed in the title compound by charge-assisted hydrogen bonds, depicted in red, and dipole–dipole interactions, depicted in green. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₃ N ₂ S ⁺ ·Br ⁻
<i>M_r</i>	297.2
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.2976 (8), 6.1294 (2), 12.2221 (6)
β (°)	99.070 (4)
<i>V</i> (Å ³)	1205.65 (9)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	6.04
Crystal size (mm)	0.21 × 0.08 × 0.01
Data collection	
Diffractometer	Rigaku Oxford Diffraction Gemini ultra, AtlasS2
Absorption correction	Analytical <i>CrysAlis PRO</i> (Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.522, 0.917
No. of measured, independent and observed [<i>I</i> > 3 σ (<i>I</i>)] reflections	12512, 2162, 1699
<i>R</i> _{int}	0.057
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.598
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.081, 1.18
No. of reflections	2162
No. of parameters	157
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.48, -0.36

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SUPERFLIP* (Palatinus & Chapuis, 2007), *MCE* (Rohlíček & Hušák, 2007), *DIAMOND* (Brandenburg & Putz, 1999), *JANA2006* (Petricek *et al.*, 2014) and *publCIF* (Westrip, 2010).

through five chains, N1—H1n1···Br1···H2n1ⁱⁱⁱ—N1ⁱⁱⁱ, and N2—H1n2···Br1ⁱⁱ···H2n2ⁱⁱ—N2ⁱⁱ classified as *C*₁²(4) and N1—H1n1···Br1···H1n2^{iv}—N2^{iv}—C12^{iv}—N1^{iv}, N1—H2n1···Br1ⁱ···H1n2^v—N2^v—C12^v—N1^v, and N1—H2n1···Br1ⁱ···H2n2ⁱ—N2ⁱ—C12ⁱ—N1ⁱ classified as *C*₁²(6) [symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x*, −*y* + $\frac{3}{2}$, *z* − $\frac{1}{2}$; (iii) *x*, *y* + 1, *z*; (iv) *x*, −*y* + $\frac{3}{2}$, *z* + $\frac{1}{2}$; (v) *x*, −*y* + $\frac{1}{2}$, *z* + $\frac{1}{2}$], see Fig. 2. The layers are connected by dipole–dipole interactions between C12 and Br1^{vi} [symmetry code: (vi) −*x*, *y* − $\frac{1}{2}$, −*z* + $\frac{1}{2}$] with a distance of 3.535 (4) Å into bilayers along the (100) plane, see Fig. 3. The bilayers are held by weak London forces only.

Synthesis and crystallization

Thiourea (0.23 g, 3 mmol) was dissolved in 25 ml of anhydrous acetonitrile. The solution was then treated with 2-(bromo-

methyl)naphthalene (0.55 g, 2.5 mmol). The reaction mixture was stirred for 4 h at room temperature. The resulting white precipitate was filtered and washed with diethyl ether and left to dry at room temperature, resulting in yield 0.72 g (97%) of 2-[(naphthalen-2-yl)methyl]isothiuronium bromide.

The 2-[(naphthalen-2-yl)methyl]isothiuronium bromide (20 mg) was dissolved in 10 ml of methanol and left to slowly evaporate at room temperature. After 5 d, colorless platelets were collected.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2020). 5, x201511 [https://doi.org/10.1107/S2414314620015114]

Crystal structure of 2-[(naphthalen-2-yl)methyl]isothiuronium bromide

Václav Eigner

2-[(Naphthalen-2-yl)methyl]isothiuronium bromide

Crystal data

$C_{12}H_{13}N_2S^+Br^-$
 $M_r = 297.2$
 Monoclinic, $P2_1/c$
 Hall symbol: -P 2ycb
 $a = 16.2976$ (8) Å
 $b = 6.1294$ (2) Å
 $c = 12.2221$ (6) Å
 $\beta = 99.070$ (4)°
 $V = 1205.65$ (9) Å³
 $Z = 4$

$F(000) = 600$
 $D_x = 1.637$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
 Cell parameters from 3162 reflections
 $\theta = 7.4$ – 67.1 °
 $\mu = 6.04$ mm⁻¹
 $T = 120$ K
 Platelet, colourless
 $0.21 \times 0.08 \times 0.01$ mm

Data collection

Rigaku Oxford Diffraction Gemini ultra,
 AtlasS2
 diffractometer
 Radiation source: X-ray tube
 Mirror monochromator
 Detector resolution: 5.1783 pixels mm⁻¹
 ω scans
 Absorption correction: analytical
 CrysAlisPro (Rigaku OD, 2015)

$T_{\min} = 0.522$, $T_{\max} = 0.917$
 12512 measured reflections
 2162 independent reflections
 1699 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\max} = 67.2$ °, $\theta_{\min} = 5.5$ °
 $h = -19 \rightarrow 18$
 $k = -7 \rightarrow 6$
 $l = -14 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.081$
 $S = 1.18$
 2162 reflections
 157 parameters
 4 restraints
 40 constraints

H atoms treated by a mixture of independent
 and constrained refinement
 Weighting scheme based on measured s.u.'s $w =$
 $1/(\sigma^2(I) + 0.0016I^2)$
 $(\Delta/\sigma)_{\max} = 0.017$
 $\Delta\rho_{\max} = 0.48$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.12634 (2)	0.79627 (6)	0.40347 (3)	0.02124 (12)
S1	0.09471 (5)	0.11747 (14)	0.09911 (6)	0.0181 (2)
N1	0.09225 (19)	0.2979 (5)	0.2973 (2)	0.0222 (9)
N2	0.08363 (19)	0.5365 (5)	0.1520 (2)	0.0221 (9)
C1	0.2898 (2)	0.3770 (6)	0.1961 (3)	0.0188 (10)

C2	0.2633 (2)	0.2128 (6)	0.1229 (3)	0.0193 (10)
C3	0.2926 (2)	0.2072 (6)	0.0196 (3)	0.0211 (10)
C4	0.3465 (2)	0.3612 (6)	-0.0066 (3)	0.0224 (11)
C5	0.4332 (2)	0.6914 (6)	0.0454 (3)	0.0222 (10)
C6	0.4595 (2)	0.8519 (6)	0.1203 (3)	0.0252 (11)
C7	0.4283 (2)	0.8638 (6)	0.2208 (3)	0.0245 (11)
C8	0.3725 (2)	0.7122 (6)	0.2466 (3)	0.0222 (10)
C9	0.3453 (2)	0.5398 (6)	0.1715 (3)	0.0192 (10)
C10	0.3751 (2)	0.5322 (6)	0.0686 (3)	0.0198 (10)
C11	0.2043 (2)	0.0410 (6)	0.1493 (3)	0.0208 (10)
C12	0.0894 (2)	0.3369 (5)	0.1920 (3)	0.0177 (10)
H1c1	0.270001	0.38133	0.266045	0.0226*
H1c3	0.27426	0.093362	-0.032466	0.0253*
H1c4	0.365563	0.354385	-0.076939	0.0269*
H1c5	0.45425	0.686312	-0.023628	0.0266*
H1c6	0.499614	0.957074	0.104151	0.0302*
H1c7	0.44616	0.979455	0.272054	0.0294*
H1c8	0.351646	0.722293	0.315701	0.0267*
H1c11	0.211892	0.018125	0.227929	0.0249*
H2c11	0.216623	-0.09448	0.115986	0.0249*
H1n1	0.096 (3)	0.403 (5)	0.344 (3)	0.0267*
H2n1	0.101 (3)	0.169 (3)	0.324 (3)	0.0267*
H1n2	0.091 (3)	0.552 (7)	0.0843 (11)	0.0266*
H2n2	0.086 (3)	0.646 (4)	0.196 (3)	0.0266*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0348 (2)	0.01257 (19)	0.01671 (19)	0.00035 (15)	0.00505 (13)	0.00032 (13)
S1	0.0234 (4)	0.0138 (4)	0.0174 (4)	-0.0010 (3)	0.0041 (3)	-0.0024 (3)
N1	0.0367 (16)	0.0108 (14)	0.0198 (15)	0.0000 (13)	0.0066 (12)	0.0011 (12)
N2	0.0337 (16)	0.0142 (15)	0.0193 (14)	-0.0026 (12)	0.0068 (12)	-0.0022 (11)
C1	0.0220 (16)	0.0188 (17)	0.0164 (16)	0.0038 (14)	0.0056 (12)	0.0012 (13)
C2	0.0202 (16)	0.0183 (17)	0.0191 (16)	0.0011 (14)	0.0023 (12)	0.0005 (14)
C3	0.0262 (17)	0.0185 (17)	0.0184 (16)	0.0016 (14)	0.0026 (13)	-0.0028 (14)
C4	0.0249 (17)	0.025 (2)	0.0180 (16)	-0.0020 (14)	0.0058 (13)	-0.0025 (13)
C5	0.0228 (17)	0.0234 (19)	0.0205 (17)	-0.0008 (15)	0.0040 (13)	0.0018 (14)
C6	0.0248 (17)	0.023 (2)	0.0274 (18)	-0.0030 (14)	0.0024 (14)	0.0036 (14)
C7	0.0276 (18)	0.0184 (18)	0.0262 (18)	-0.0023 (14)	0.0001 (14)	-0.0011 (14)
C8	0.0227 (17)	0.0231 (19)	0.0207 (17)	0.0005 (14)	0.0029 (13)	-0.0045 (14)
C9	0.0176 (16)	0.0199 (18)	0.0192 (16)	0.0035 (13)	0.0001 (12)	0.0013 (13)
C10	0.0216 (16)	0.0179 (18)	0.0195 (16)	0.0006 (14)	0.0017 (13)	0.0019 (13)
C11	0.0270 (18)	0.0173 (18)	0.0183 (16)	0.0041 (14)	0.0043 (13)	0.0026 (13)
C12	0.0190 (16)	0.0127 (18)	0.0228 (16)	-0.0014 (12)	0.0077 (12)	-0.0003 (12)

Geometric parameters (Å, °)

S1—C11	1.855 (3)	C4—C10	1.423 (5)
S1—C12	1.771 (3)	C4—H1c4	0.96
N1—C12	1.302 (4)	C5—C6	1.366 (5)
N1—H1n1	0.86 (3)	C5—C10	1.419 (5)
N1—H2n1	0.86 (2)	C5—H1c5	0.96
N2—C12	1.316 (4)	C6—C7	1.404 (5)
N2—H1n2	0.860 (19)	C6—H1c6	0.96
N2—H2n2	0.86 (3)	C7—C8	1.372 (5)
C1—C2	1.370 (5)	C7—H1c7	0.96
C1—C9	1.411 (5)	C8—C9	1.424 (5)
C1—H1c1	0.96	C8—H1c8	0.96
C2—C3	1.419 (5)	C9—C10	1.419 (5)
C2—C11	1.495 (5)	C11—H1c11	0.96
C3—C4	1.361 (5)	C11—H2c11	0.96
C3—H1c3	0.96		
C11—S1—C12	96.98 (15)	C5—C6—H1c6	119.84
C12—N1—H1n1	121 (2)	C7—C6—H1c6	119.84
C12—N1—H2n1	122 (3)	C6—C7—C8	120.7 (3)
H1n1—N1—H2n1	117 (3)	C6—C7—H1c7	119.63
C12—N2—H1n2	117 (3)	C8—C7—H1c7	119.63
C12—N2—H2n2	120 (2)	C7—C8—C9	120.3 (3)
H1n2—N2—H2n2	121 (4)	C7—C8—H1c8	119.84
C2—C1—C9	121.8 (3)	C9—C8—H1c8	119.84
C2—C1—H1c1	119.12	C1—C9—C8	122.1 (3)
C9—C1—H1c1	119.12	C1—C9—C10	119.1 (3)
C1—C2—C3	118.9 (3)	C8—C9—C10	118.7 (3)
C1—C2—C11	121.5 (3)	C4—C10—C5	122.6 (3)
C3—C2—C11	119.5 (3)	C4—C10—C9	118.3 (3)
C2—C3—C4	120.8 (3)	C5—C10—C9	119.2 (3)
C2—C3—H1c3	119.59	S1—C11—C2	111.7 (2)
C4—C3—H1c3	119.58	S1—C11—H1c11	109.47
C3—C4—C10	121.1 (3)	S1—C11—H2c11	109.47
C3—C4—H1c4	119.45	C2—C11—H1c11	109.47
C10—C4—H1c4	119.45	C2—C11—H2c11	109.47
C6—C5—C10	120.7 (3)	H1c11—C11—H2c11	107.17
C6—C5—H1c5	119.66	S1—C12—N1	119.8 (3)
C10—C5—H1c5	119.66	S1—C12—N2	118.4 (3)
C5—C6—C7	120.3 (3)	N1—C12—N2	121.8 (3)
C9—C1—C2—C3	0.0 (2)	C7—C8—C9—C10	-1.8 (5)
C9—C1—C2—C11	-179.8 (3)	C8—C9—C1—C2	179.4 (3)
C1—C2—C3—C4	0.3 (5)	C10—C9—C1—C2	-0.6 (5)
C11—C2—C3—C4	-179.9 (3)	C4—C10—C9—C1	1.0 (5)
C2—C3—C4—C10	0.0 (3)	C4—C10—C9—C8	-179.0 (3)
C3—C4—C10—C5	178.0 (3)	C5—C10—C9—C1	-177.8 (3)

C3—C4—C10—C9	-0.7 (5)	C5—C10—C9—C8	2.2 (5)
C4—C10—C5—C6	-179.5 (3)	C1—C2—C11—S1	91.8 (3)
C9—C10—C5—C6	-0.8 (5)	C3—C2—C11—S1	-88.0 (3)
C10—C5—C6—C7	-1.1 (5)	C2—C11—S1—C12	-68.1 (3)
C5—C6—C7—C8	1.5 (5)	C11—S1—C12—N1	-68.5 (3)
C6—C7—C8—C9	0.0 (3)	C11—S1—C12—N2	110.7 (3)
C7—C8—C9—C1	178.2 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1 <i>n</i> 1...Br1	0.86 (3)	2.54 (3)	3.332 (3)	153 (3)
N1—H2 <i>n</i> 1...Br1 ⁱ	0.86 (2)	2.49 (2)	3.350 (3)	180 (3)
N2—H1 <i>n</i> 2...Br1 ⁱⁱ	0.860 (19)	2.55 (3)	3.381 (3)	164 (4)
N2—H2 <i>n</i> 2...Br1	0.86 (3)	2.68 (3)	3.434 (3)	147 (3)

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) *x*, -*y*+3/2, *z*-1/2.