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(*S*)-2-[(2-Ammoniophenyl)sulfanylmethyl]pyrrolidinium dibromide

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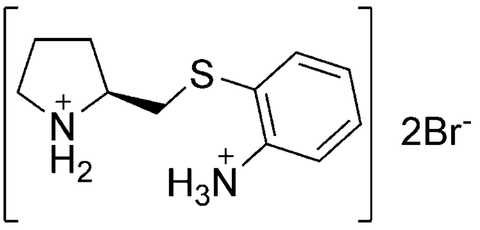
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.014 Å; R factor = 0.058; wR factor = 0.134; data-to-parameter ratio = 21.0.

In the title compound, $C_{11}H_{18}N_2S^{2+}\cdot 2Br^-$, the pyrrolidine ring displays a half-chair conformation, with the flap C atom lying 0.522 (5) Å out of the plane of the other four atoms. The methylene C atom, which connects the pyrrolidinium ring and the thioether group, is displaced from the plane of four pyrrolidinium atoms by 0.690 (6) Å in the same direction as the flap C atom. The plane of four pyrrolidinium atoms is almost perpendicular to the benzene ring [dihedral angle = 75.02 (4)°]. The crystal structure is stabilized by hydrogen bonds between the N and Br atoms.

Related literature

The synthesis of (*S*)-(+)-2-bromomethylpyrrolidine hydrobromide was described by Xu *et al.* (2006). The development of asymmetric organocatalysis was reviewed by Seayad & List (2005).



Experimental

Crystal data

$C_{11}H_{18}N_2S^{2+}\cdot 2Br^-$
M_r = 370.15
Orthorhombic, $P2_12_12_1$
a = 7.9399 (9) Å
b = 10.8427 (13) Å
c = 17.658 (2) Å
V = 1520.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.45 mm^{-1}
T = 293 (2) K
0.49 × 0.42 × 0.36 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.103, T_{max} = 0.137
8969 measured reflections
3311 independent reflections
1808 reflections with $I > 2\sigma(I)$
R_{int} = 0.136

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.134
S = 0.83
3311 reflections
158 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}
Absolute structure: Flack (1983), 1394 Friedel pairs
Flack parameter: 0.00 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*E*···Br1^{i}	0.83 (8)	2.39 (8)	3.201 (9)	169 (10)
N2—H2*D*···Br2^{ii}	0.84 (6)	2.48 (4)	3.277 (9)	159 (8)
N2—H2*C*···Br1	0.84 (7)	2.47 (7)	3.298 (9)	173 (8)
N1—H1*B*···Br2	0.90	2.47	3.355 (7)	169
N1—H1*A*···Br2^{ii}	0.90	2.33	3.224 (7)	170

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; 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: PK2105).

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supporting information

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(*S*)-2-[(2-Ammoniophenyl)sulfanylmethyl]pyrrolidinium dibromide

Bailin Li, Shuai Zhang, Yifeng Wang and Shuping Luo

S1. Comment

In recent years, the field of asymmetric organocatalysis has developed rapidly, attracting an increasing number of research groups around the world (Seayad & List, 2005). The title compound, readily synthesized from commercially available *L*-proline and 2-aminobenzenethiol, could act as an organocatalyst in the Michael addition of ketones to nitro-styrenes. The reaction gave the desired Michael adducts in good yields and high enantioselectivities. The structure of (*S*)-2-((2-ammoniophenylthio)methyl)pyrrolidinium dibromide is shown in Fig. 1.

The crystal is built of doubly protonated cations and bromide anions. The pyrrolidine ring displays a half-chair conformation, with the flap C atom lying 0.522 (5) Å from the remaining four atoms of the pyrrolidine which are almost coplanar. The methylene C atom, which connects the pyrrolidinium ring and the thioether group, is displaced from the plane of four pyrrolidinium atoms by 0.690 (6) Å in the same direction, as the flap C atom. The plane of four pyrrolidinium ring atoms is almost perpendicular to the benzene ring [dihedral angle 75.02 (4) °]. The crystal structure is stabilized by hydrogen-bonds between the N and Br atoms. The molecular packing of the title compound showing H-bridge interactions between cationic-anionic groups is shown in Fig. 2.

S2. Experimental

The title compound was synthesized by treating 2-aminobenzenethiol (1.25 g,10 mmol) with (*S*)-2-bromomethyl-pyrrolidine hydrobromide (2.47 g,10 mmol) in MeCN (30 ml) under stirring at 353 K for 24 h (yield 87%). The compound (*S*)-2-bromomethylpyrrolidine hydrobromide was obtained from commercially available *L*-proline by reduction with $NaBH_4$ and subsequent bromination with PBr_3 (Xu *et al.*, 2006). Suitable crystals of the title compound were obtained by slow evaporation of an ethanol solution at room temperature.

S3. Refinement

All carbon-bonded H atoms were placed in calculated positions with C—H = 0.93 Å (C_{ar}), C—H = 0.98 Å (R_3CH), C—H = 0.97 Å (R_2CH_2) and refined using a riding model, with U_{iso}(H)=1.2_{eq}(C). NH_3 hydrogen atoms were located in a difference map and refined with an N—H distance restraint of 0.83 (1) Å, with U value being 0.06, 0.06, 0.09 respectively, while NH_2 hydrogens were treated using a riding model with N—H distance of 0.90 Å.

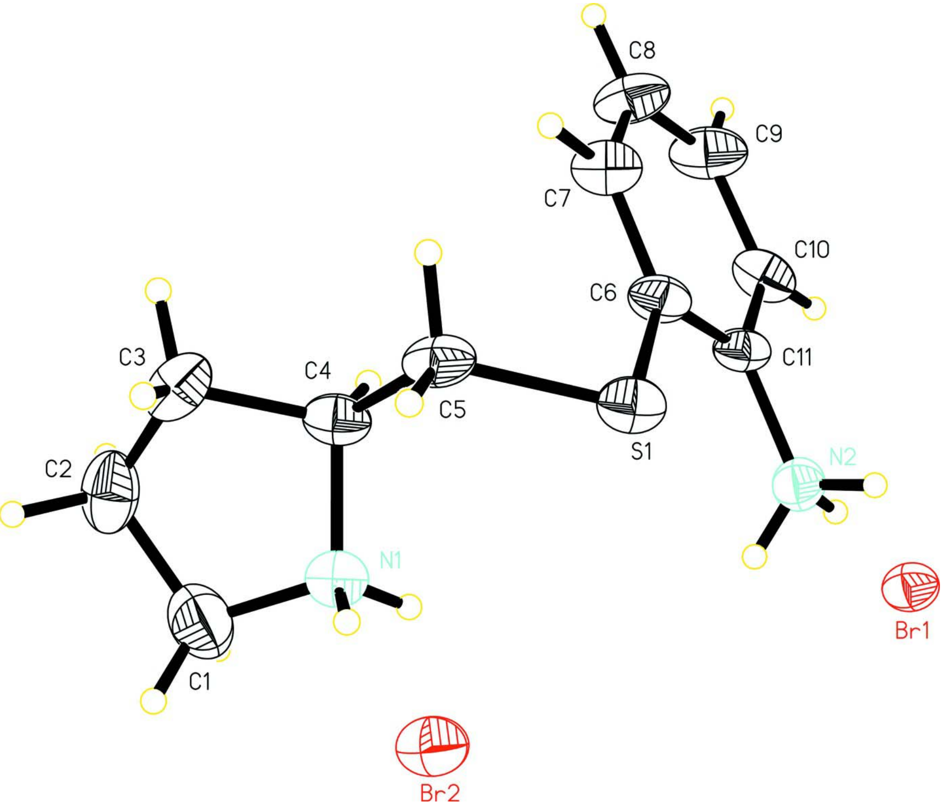

Figure 1

The asymmetric unit of the title compound with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

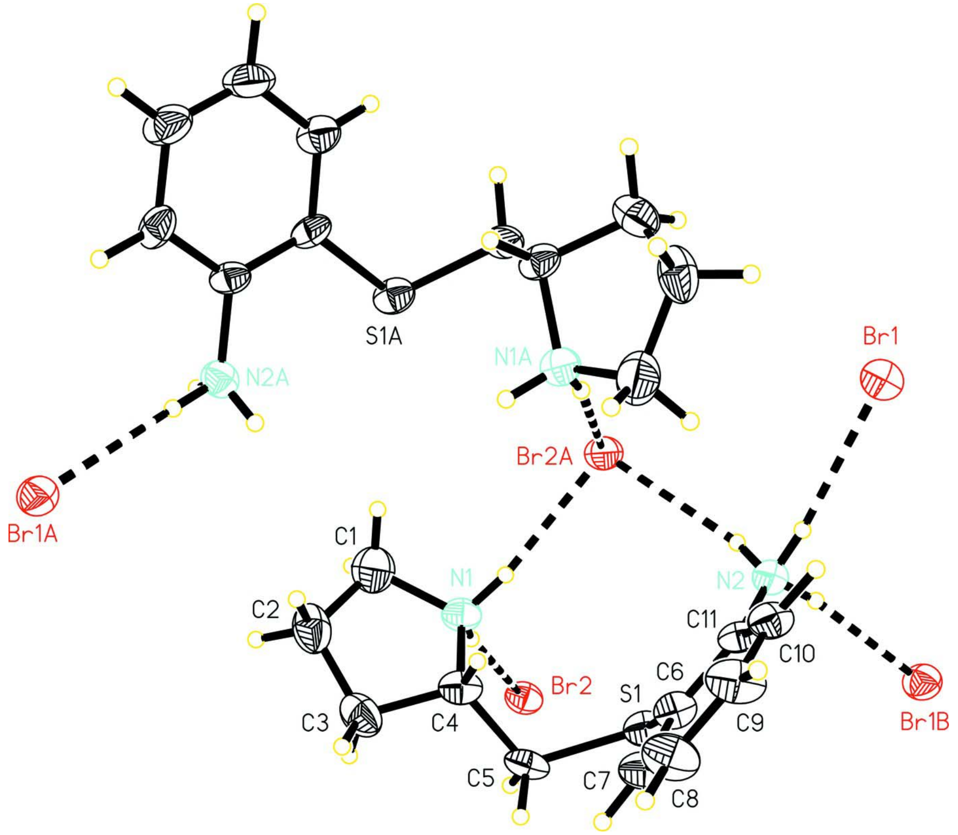

Figure 2

The molecular packing of the title compound showing H-bridge interactions between cationic-anionic groups.

(*S*)-2-[(2-Ammoniophenyl)sulfanylmethyl]pyrrolidinium dibromide

Crystal data

$C_{11}H_{18}N_2S^{2+}\cdot 2Br^-$	$F(000) = 736$
$M_r = 370.15$	$D_x = 1.617$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1525 reflections
$a = 7.9399$ (9) Å	$\theta = 4.4$–$38.3°$
$b = 10.8427$ (13) Å	$\mu = 5.45$ mm^{-1}
$c = 17.658$ (2) Å	$T = 293$ K
$V = 1520.2$ (3) Å^3	Prismatic, colorless
$Z = 4$	0.49 × 0.42 × 0.37 mm

Data collection

Bruker SMART CCD area-detector diffractometer	8969 measured reflections
Radiation source: fine-focus sealed tube	3311 independent reflections
Graphite monochromator	1808 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.136$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{\text{max}} = 27.0°$, $\theta_{\text{min}} = 2.2°$
$T_{\text{min}} = 0.103$, $T_{\text{max}} = 0.137$	$h = -9\rightarrow10$
	$k = -13\rightarrow12$
	$l = -22\rightarrow18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.134$
$S = 0.83$
3311 reflections
158 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0005 (1)
Absolute structure: Flack (1983), 1394 Friedel pairs
Absolute structure parameter: 0.00 (2)

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 $F^2 > 2\sigma(F^2)$ 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	0.30470 (12)	−0.24305 (9)	−0.08797 (5)	0.0559 (3)
Br2	−0.38177 (12)	0.34415 (8)	0.06967 (5)	0.0526 (3)
S1	−0.0443 (3)	0.1034 (2)	0.14946 (13)	0.0524 (6)
N1	0.0399 (9)	0.3571 (6)	0.0600 (4)	0.0502 (18)
H1A	0.0636	0.2939	0.0288	0.060*
H1B	−0.0728	0.3650	0.0630	0.060*
N2	0.1147 (12)	−0.0815 (8)	0.0452 (5)	0.0487 (18)
C1	0.1159 (18)	0.4726 (9)	0.0308 (7)	0.083 (3)
H1C	0.0296	0.5273	0.0111	0.100*
H1D	0.1959	0.4549	−0.0093	0.100*
C2	0.2025 (14)	0.5297 (9)	0.0973 (7)	0.072 (3)
H2A	0.3237	0.5225	0.0921	0.087*
H2B	0.1735	0.6164	0.1013	0.087*
C3	0.1443 (14)	0.4625 (9)	0.1640 (6)	0.068 (3)
H3A	0.0420	0.4990	0.1840	0.081*
H3B	0.2297	0.4627	0.2033	0.081*
C4	0.1120 (12)	0.3339 (8)	0.1362 (4)	0.049 (2)
H4	0.2194	0.2901	0.1309	0.059*
C5	−0.0079 (11)	0.2577 (8)	0.1852 (4)	0.052 (2)
H5A	−0.1150	0.3004	0.1885	0.062*
H5B	0.0381	0.2519	0.2359	0.062*
C6	0.1553 (11)	0.0316 (8)	0.1640 (5)	0.047 (2)

C7	0.2504 (11)	0.0537 (9)	0.2270 (5)	0.056 (3)
H7	0.2117	0.1092	0.2632	0.068*
C8	0.4032 (13)	−0.0049 (10)	0.2382 (6)	0.073 (3)
H8	0.4680	0.0138	0.2805	0.087*
C9	0.4579 (14)	−0.0887 (10)	0.1879 (6)	0.071 (3)
H9	0.5602	−0.1285	0.1956	0.085*
C10	0.3611 (11)	−0.1161 (8)	0.1239 (5)	0.053 (2)
H10	0.3980	−0.1750	0.0893	0.063*
C11	0.2112 (12)	−0.0555 (8)	0.1123 (5)	0.045 (2)
H2C	0.157 (10)	−0.127 (6)	0.012 (4)	0.06 (3)*
H2D	0.094 (12)	−0.032 (6)	0.010 (3)	0.06 (3)*
H2E	0.043 (10)	−0.135 (7)	0.054 (6)	0.09 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0514 (6)	0.0627 (5)	0.0536 (6)	0.0081 (5)	−0.0055 (4)	−0.0024 (5)
Br2	0.0526 (6)	0.0614 (5)	0.0438 (5)	0.0072 (5)	−0.0041 (4)	−0.0022 (5)
S1	0.0412 (14)	0.0682 (15)	0.0479 (14)	0.0052 (12)	0.0015 (11)	0.0049 (12)
N1	0.045 (4)	0.060 (4)	0.046 (4)	0.007 (4)	0.004 (3)	−0.001 (4)
N2	0.054 (5)	0.048 (5)	0.044 (5)	−0.003 (5)	0.002 (5)	−0.002 (4)
C1	0.105 (10)	0.061 (7)	0.084 (8)	0.010 (7)	0.005 (8)	0.006 (6)
C2	0.055 (7)	0.055 (6)	0.107 (10)	0.005 (5)	0.010 (7)	−0.017 (6)
C3	0.062 (8)	0.074 (7)	0.067 (7)	−0.006 (6)	−0.007 (6)	−0.021 (6)
C4	0.038 (5)	0.066 (6)	0.044 (5)	0.015 (5)	0.000 (4)	0.003 (5)
C5	0.053 (6)	0.070 (6)	0.033 (4)	0.019 (6)	0.002 (4)	−0.009 (5)
C6	0.033 (6)	0.062 (6)	0.046 (5)	0.008 (4)	−0.006 (4)	0.010 (4)
C7	0.043 (6)	0.077 (7)	0.048 (6)	0.012 (5)	0.003 (5)	0.000 (5)
C8	0.062 (8)	0.102 (8)	0.055 (7)	0.010 (7)	−0.022 (6)	−0.008 (6)
C9	0.054 (7)	0.103 (8)	0.056 (7)	0.028 (7)	−0.005 (6)	−0.001 (6)
C10	0.046 (6)	0.061 (6)	0.051 (5)	0.022 (5)	0.011 (5)	0.010 (4)
C11	0.044 (6)	0.059 (6)	0.031 (5)	0.000 (5)	0.000 (4)	0.007 (4)

Geometric parameters (Å, º)

Br1—H2C	2.47 (7)	C3—C4	1.500 (12)
Br2—H1B	2.4665	C3—H3A	0.9700
S1—C6	1.784 (8)	C3—H3B	0.9700
S1—C5	1.811 (9)	C4—C5	1.529 (12)
N1—C1	1.483 (12)	C4—H4	0.9800
N1—C4	1.484 (10)	C5—H5A	0.9700
N1—H1A	0.9000	C5—H5B	0.9700
N1—H1B	0.9000	C6—C7	1.366 (11)
N2—C11	1.438 (11)	C6—C11	1.388 (11)
N2—H2C	0.84 (7)	C7—C8	1.383 (13)
N2—H2D	0.84 (6)	C7—H7	0.9300
N2—H2E	0.83 (8)	C8—C9	1.343 (13)
C1—C2	1.495 (14)	C8—H8	0.9300

C1—H1C	0.9700	C9—C10	1.399 (13)
C1—H1D	0.9700	C9—H9	0.9300
C2—C3	1.460 (13)	C10—C11	1.374 (12)
C2—H2A	0.9700	C10—H10	0.9300
C2—H2B	0.9700		

C6—S1—C5	102.2 (4)	N1—C4—C3	101.8 (7)
C1—N1—C4	107.5 (8)	N1—C4—C5	111.3 (7)
C1—N1—H1A	110.2	C3—C4—C5	115.1 (8)
C4—N1—H1A	110.2	N1—C4—H4	109.4
C1—N1—H1B	110.2	C3—C4—H4	109.4
C4—N1—H1B	110.2	C5—C4—H4	109.4
H1A—N1—H1B	108.5	C4—C5—S1	113.7 (6)
C11—N2—H2C	118 (6)	C4—C5—H5A	108.8
C11—N2—H2D	126 (6)	S1—C5—H5A	108.8
H2C—N2—H2D	87 (7)	C4—C5—H5B	108.8
C11—N2—H2E	111 (7)	S1—C5—H5B	108.8
H2C—N2—H2E	90 (9)	H5A—C5—H5B	107.7
H2D—N2—H2E	117 (10)	C7—C6—C11	118.6 (8)
N1—C1—C2	105.3 (9)	C7—C6—S1	122.1 (7)
N1—C1—H1C	110.7	C11—C6—S1	119.1 (7)
C2—C1—H1C	110.7	C6—C7—C8	121.3 (9)
N1—C1—H1D	110.7	C6—C7—H7	119.3
C2—C1—H1D	110.7	C8—C7—H7	119.3
H1C—C1—H1D	108.8	C9—C8—C7	120.0 (10)
C3—C2—C1	106.3 (8)	C9—C8—H8	120.0
C3—C2—H2A	110.5	C7—C8—H8	120.0
C1—C2—H2A	110.5	C8—C9—C10	120.1 (9)
C3—C2—H2B	110.5	C8—C9—H9	120.0
C1—C2—H2B	110.5	C10—C9—H9	120.0
H2A—C2—H2B	108.7	C11—C10—C9	119.6 (9)
C2—C3—C4	104.7 (7)	C11—C10—H10	120.2
C2—C3—H3A	110.8	C9—C10—H10	120.2
C4—C3—H3A	110.8	C10—C11—C6	120.3 (8)
C2—C3—H3B	110.8	C10—C11—N2	119.4 (8)
C4—C3—H3B	110.8	C6—C11—N2	120.3 (8)
H3A—C3—H3B	108.9		

C4—N1—C1—C2	−12.2 (11)	C11—C6—C7—C8	2.8 (14)
N1—C1—C2—C3	−12.1 (11)	S1—C6—C7—C8	178.6 (8)
C1—C2—C3—C4	31.4 (11)	C6—C7—C8—C9	−2.4 (15)
C1—N1—C4—C3	30.7 (10)	C7—C8—C9—C10	0.5 (16)
C1—N1—C4—C5	153.8 (8)	C8—C9—C10—C11	1.0 (15)
C2—C3—C4—N1	−38.0 (10)	C9—C10—C11—C6	−0.6 (13)
C2—C3—C4—C5	−158.6 (8)	C9—C10—C11—N2	178.2 (9)
N1—C4—C5—S1	64.5 (8)	C7—C6—C11—C10	−1.3 (12)
C3—C4—C5—S1	179.7 (7)	S1—C6—C11—C10	−177.2 (6)
C6—S1—C5—C4	69.0 (6)	C7—C6—C11—N2	180.0 (8)

C5—S1—C6—C7	38.7 (8)	S1—C6—C11—N2	4.1 (11)
C5—S1—C6—C11	−145.6 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*E*···Br1^{i}	0.83 (8)	2.39 (8)	3.201 (9)	169 (10)
N2—H2*D*···Br2^{ii}	0.84 (6)	2.48 (4)	3.277 (9)	159 (8)
N2—H2*C*···Br1	0.84 (7)	2.47 (7)	3.298 (9)	173 (8)
N1—H1*B*···Br2	0.90	2.47	3.355 (7)	169
N1—H1*A*···Br2^{ii}	0.90	2.33	3.224 (7)	170

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