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(*S*)-2-(Pyrrolidinium-2-ylmethylsulfanyl)-pyridinium dibromide

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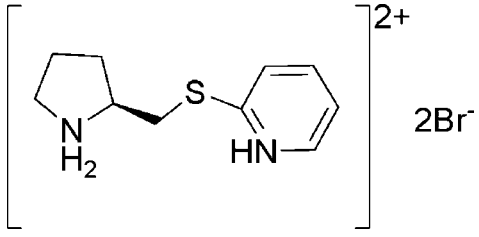
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.013 Å; R factor = 0.037; wR factor = 0.108; data-to-parameter ratio = 23.0.

In the title compound, $C_{10}H_{16}N_2S^{2+}\cdot 2Br^-$, the pyrrolidine ring displays an envelope conformation, with the flap C atom lying 0.484 (5) Å out of the plane of the rest of the pyrrolidine ring. The thioether group connects the pyridine ring and the 2-methylpyrrolidine group. Both pyrrolidine NH bonds form hydrogen bonds to the bromide anions. These hydrogen bonds link the cations and anions in a helical chain along the *c* axis.

Related literature

For related literature, see: Ishii *et al.* (2004); Xu *et al.* (2007); Larson (1970).



Experimental

Crystal data

$C_{10}H_{16}N_2S^{2+}\cdot 2Br^-$
M_r = 356.12
Trigonal, $P3_2$
a = 8.9892 (9) Å
c = 15.4567 (14) Å
V = 1081.66 (18) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 5.76 mm^{-1}
T = 296 (1) K
0.35 × 0.30 × 0.23 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi,1995)
T_{min} = 0.162, T_{max} = 0.266
10585 measured reflections
3169 independent reflections
1902 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.108
S = 1.01
3169 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 1037 Friedel pairs
Flack parameter: 0.017 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H2···Br1	0.86	2.45	3.278 (7)	163
N1—H3···Br1^{i}	0.86	2.43	3.271 (5)	165

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

We thank Professor Jian-Ming Gu of Zhejiang University for his help.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2087).

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S1. Comment

In recent years, proline and its derivatives have been studied extensively because of their ability to catalyze a large number of reactions (Ishii *et al.*, 2004). The title compound is a hydrobromide of an ionic compound that was synthesized from *L*-proline. It was prepared as a kind of ionic organocatalyst for use in the asymmetric Michael addition of carbonyl compounds to nitroalkenes (Xu *et al.*, 2007). The compound consists of two ionic pairs, protonated ammoniums and Br^- anions. The chiral atom C1 has the expected S conformation, and the C1/C3/C4/N1 atoms of pyrrolidine are almost coplanar. The distance of atom C2 to the C1/C3/C4/N1 mean plane is 0.484 (5) Å, while the distance of atom C5 to the plane is 0.865 (9) Å. In addition, the dihedral angle of the C1/N1/C3/C4 mean plane and the pyridine ring is 67.82 (4) °. The thioether group connects the pyridine ring and the 2-methylpyrrolidine group, the torsion angle of C6—S1—C5—C1 is 97.13 (4) °.

S2. Experimental

The title compound was readily synthesized by treating 2-mercaptopyridine with (*S*)-(+)-2-bromomethylpyrrolidine hydrobromide in MeCN. The compound (*S*)-(+)-2-bromomethylpyrrolidine hydrobromide was obtained from commercially available *L*-proline by reduction with $NaBH_4$ and subsequent bromination with PBr_3. Suitable crystals were obtained by slow evaporation of methanol at room temperature.

S3. Refinement

All H atoms were placed in calculated positions with C—H=0.98 Å (*sp*), C—H=0.97 Å (sp2), C—H=0.93 Å (aromatic), N—H=0.86 Å and included in the final cycles of refinement as a riding model, with $U_{iso}(H)=1.2U_{eq}$ of the carrier atoms.

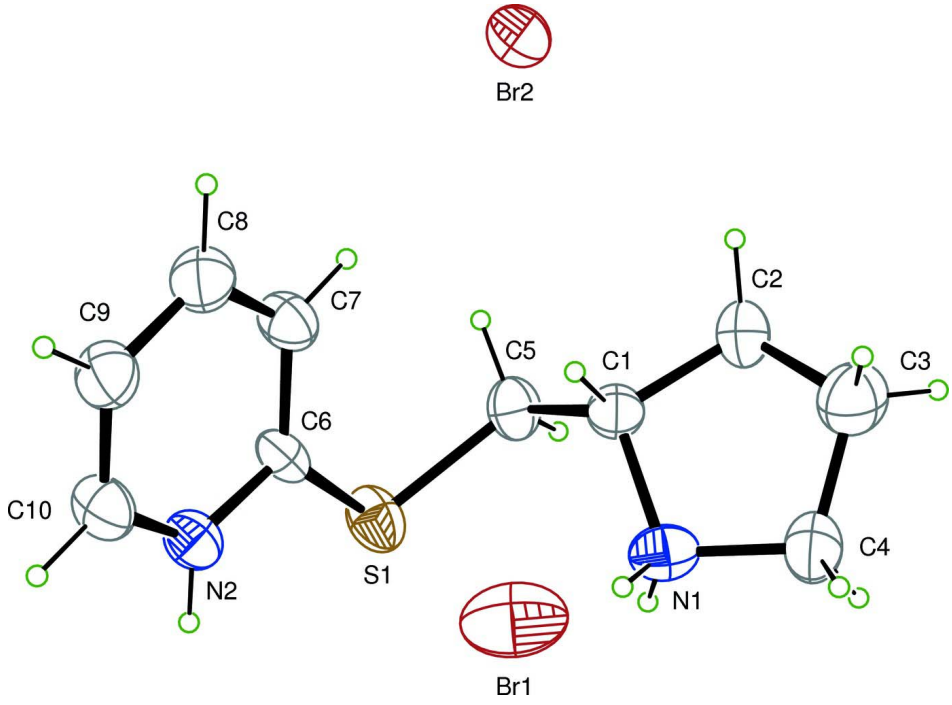

Figure 1

The asymmetric unit of the title compound, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 40% probability level.

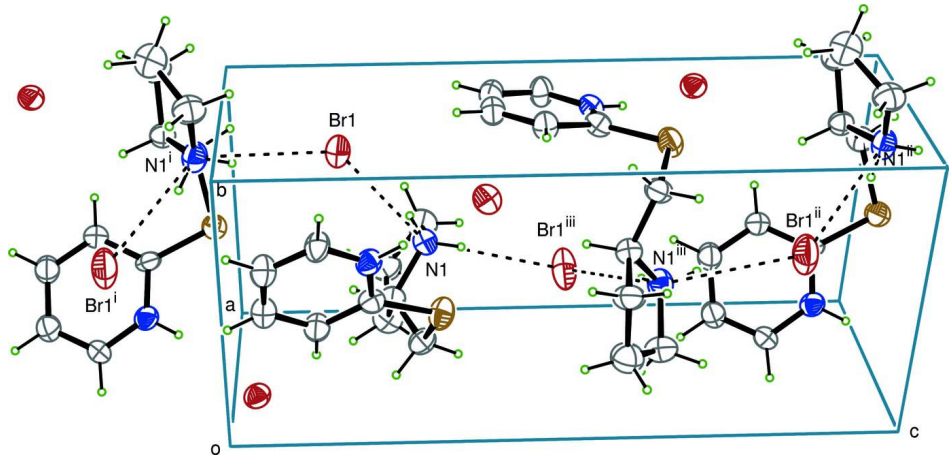

Figure 2

Hydrogen bonding in the title compound. Symmetry codes: (i) 1-y, 1+x-y, -1/3+z; (ii) 1-y, 1+x-y, 2/3+z; (iii) -x+y, 1-x, 1/3+z.

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Crystal data

$C_{10}H_{16}N_2S^{2+}\cdot 2Br^-$
$M_r = 356.12$
Trigonal, $P3_2$
Hall symbol: P 32

$a = 8.9892\ (9)$ Å
$c = 15.4567\ (14)$ Å
$V = 1081.66\ (18)$ Å^3
$Z = 3$

$F(000)$ = 528.00
D_x = 1.640 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5169 reflections
θ = 3.7–27.4°
μ = 5.76 mm^{-1}
T = 296 K
Chunk, colorless
0.35 × 0.30 × 0.23 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi,1995)
T_{min} = 0.162, T_{max} = 0.266
10585 measured reflections
3169 independent reflections
1902 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.061
θ_{max} = 27.4°
h = −11→11
k = −11→10
l = −18→20

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.108
S = 1.01
3169 reflections
138 parameters
0 restraints
H-atom parameters constrained
$w = 1/[0.7600\sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max}$ = 0.013
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Extinction correction: Larson (1970) Crystallographic Computing eq. 22
Extinction coefficient: 385 (18)
Absolute structure: Flack (1983), 1037 Friedel Pairs
Absolute structure parameter: 0.017 (2)

Special details

Refinement. Refinement using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.51453 (17)	0.87503 (13)	0.16904 (9)	0.1032 (4)
Br2	0.10004 (11)	0.14553 (10)	0.04190 (9)	0.0605 (2)
S1	0.0678 (3)	0.4733 (3)	0.31433 (12)	0.0671 (7)
N1	0.4515 (9)	0.5570 (8)	0.2963 (3)	0.067 (2)
N2	0.0359 (7)	0.6865 (8)	0.2110 (3)	0.053 (2)
C1	0.3184 (9)	0.4069 (9)	0.2462 (4)	0.053 (2)
C2	0.3905 (11)	0.2858 (11)	0.2388 (5)	0.071 (3)
C3	0.5771 (13)	0.4004 (16)	0.2379 (8)	0.086 (5)
C4	0.6121 (14)	0.5513 (18)	0.2933 (7)	0.077 (5)
C5	0.1434 (10)	0.3261 (10)	0.2879 (4)	0.059 (2)
C6	0.0388 (9)	0.5412 (9)	0.2143 (4)	0.050 (2)
C7	0.0160 (10)	0.4576 (10)	0.1352 (4)	0.059 (2)
C8	−0.0040 (10)	0.5283 (11)	0.0612 (4)	0.066 (2)
C9	−0.0037 (10)	0.6817 (12)	0.0635 (4)	0.067 (2)
C10	0.0138 (10)	0.7576 (11)	0.1396 (4)	0.062 (2)
H1	0.3105	0.4460	0.1880	0.064*
H2	0.4673	0.6511	0.2735	0.080*
H3	0.4187	0.5509	0.3491	0.080*

H7	0.0144	0.3534	0.1330	0.071*
H8	−0.0180	0.4724	0.0087	0.079*
H9	−0.0154	0.7310	0.0130	0.080*
H10	0.0108	0.8593	0.1432	0.074*
H21	0.3560	0.2085	0.2879	0.085*
H22	0.3522	0.2195	0.1857	0.085*
H31	0.6169	0.4377	0.1793	0.103*
H32	0.6343	0.3421	0.2614	0.103*
H41	0.6450	0.5369	0.3511	0.092*
H42	0.7033	0.6564	0.2682	0.092*
H51	0.1477	0.2708	0.3409	0.071*
H52	0.0614	0.2403	0.2484	0.071*
H201	0.0494	0.7403	0.2590	0.064*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1369 (10)	0.0925 (8)	0.0513 (4)	0.0357 (7)	0.0061 (5)	0.0034 (4)
Br2	0.0670 (6)	0.0510 (5)	0.0630 (4)	0.0292 (4)	0.0073 (4)	0.0054 (3)
S1	0.0848 (16)	0.0802 (16)	0.0554 (11)	0.0555 (14)	0.0125 (10)	0.0098 (10)
N1	0.072 (4)	0.063 (4)	0.053 (3)	0.026 (4)	−0.001 (3)	−0.006 (3)
N2	0.055 (4)	0.055 (4)	0.053 (3)	0.029 (3)	0.011 (2)	0.003 (2)
C1	0.052 (4)	0.046 (4)	0.058 (4)	0.022 (4)	−0.001 (3)	−0.001 (3)
C2	0.055 (5)	0.082 (6)	0.084 (5)	0.040 (5)	0.000 (4)	−0.005 (4)
C3	0.070 (8)	0.088 (10)	0.090 (14)	0.032 (7)	0.004 (7)	−0.000 (10)
C4	0.061 (7)	0.083 (14)	0.093 (10)	0.041 (9)	−0.004 (6)	−0.003 (10)
C5	0.051 (5)	0.063 (5)	0.065 (5)	0.030 (4)	0.011 (3)	0.009 (3)
C6	0.056 (5)	0.041 (4)	0.060 (4)	0.030 (4)	0.008 (3)	−0.003 (3)
C7	0.075 (5)	0.056 (5)	0.055 (4)	0.040 (4)	0.002 (3)	0.002 (3)
C8	0.071 (6)	0.078 (6)	0.053 (4)	0.041 (5)	0.001 (3)	0.001 (4)
C9	0.077 (6)	0.082 (6)	0.053 (4)	0.049 (5)	−0.002 (3)	0.002 (4)
C10	0.088 (6)	0.061 (5)	0.050 (4)	0.048 (5)	0.002 (3)	0.009 (3)

Geometric parameters (Å, º)

S1—C5	1.811 (11)	N1—H3	0.860
S1—C6	1.729 (7)	N2—H201	0.860
N1—C1	1.496 (8)	C1—H1	0.980
N1—C4	1.471 (18)	C2—H21	0.970
N2—C6	1.321 (12)	C2—H22	0.970
N2—C10	1.339 (10)	C3—H31	0.970
C1—C2	1.524 (16)	C3—H32	0.970
C1—C5	1.508 (10)	C4—H41	0.970
C2—C3	1.465 (12)	C4—H42	0.970
C3—C4	1.499 (9)	C5—H51	0.970
C6—C7	1.396 (9)	C5—H52	0.970
C7—C8	1.363 (12)	C7—H7	0.930
C8—C9	1.379 (16)	C8—H8	0.930

C9—C10	1.329 (10)	C9—H9	0.930
N1—H2	0.860	C10—H10	0.930
C5—S1—C6	103.5 (4)	C1—C2—H22	110.8
C1—N1—C4	108.0 (8)	C3—C2—H21	110.8
C6—N2—C10	125.8 (6)	C3—C2—H22	110.8
N1—C1—C2	104.4 (7)	H21—C2—H22	109.5
N1—C1—C5	112.6 (6)	C2—C3—H31	110.3
C2—C1—C5	113.7 (6)	C2—C3—H32	110.3
C1—C2—C3	104.2 (8)	C4—C3—H31	110.3
C2—C3—C4	106.2 (11)	C4—C3—H32	110.3
N1—C4—C3	106.5 (8)	H31—C3—H32	109.5
S1—C5—C1	115.3 (6)	N1—C4—H41	110.2
S1—C6—N2	117.7 (5)	N1—C4—H42	110.2
S1—C6—C7	126.9 (7)	C3—C4—H41	110.2
N2—C6—C7	115.4 (7)	C3—C4—H42	110.2
C6—C7—C8	120.2 (9)	H41—C4—H42	109.5
C7—C8—C9	120.7 (7)	S1—C5—H51	108.0
C8—C9—C10	118.4 (8)	S1—C5—H52	108.0
N2—C10—C9	119.5 (10)	C1—C5—H51	108.0
C1—N1—H2	109.8	C1—C5—H52	108.0
C1—N1—H3	109.8	H51—C5—H52	109.5
C4—N1—H2	109.8	C6—C7—H7	119.9
C4—N1—H3	109.8	C8—C7—H7	119.9
H2—N1—H3	109.5	C7—C8—H8	119.7
C6—N2—H201	117.1	C9—C8—H8	119.7
C10—N2—H201	117.1	C8—C9—H9	120.8
N1—C1—H1	108.7	C10—C9—H9	120.8
C2—C1—H1	108.7	N2—C10—H10	120.2
C5—C1—H1	108.7	C9—C10—H10	120.2
C1—C2—H21	110.8		
C5—S1—C6—N2	−159.4 (5)	N1—C1—C5—S1	51.7 (8)
C5—S1—C6—C7	21.3 (8)	C2—C1—C5—S1	170.2 (5)
C6—S1—C5—C1	66.8 (5)	C5—C1—C2—C3	−153.7 (7)
C1—N1—C4—C3	2.2 (10)	C1—C2—C3—C4	32.4 (11)
C4—N1—C1—C2	17.3 (7)	C2—C3—C4—N1	−22.0 (12)
C4—N1—C1—C5	141.1 (8)	S1—C6—C7—C8	−179.4 (6)
C6—N2—C10—C9	−1.5 (12)	N2—C6—C7—C8	1.2 (11)
C10—N2—C6—S1	−179.6 (5)	C6—C7—C8—C9	−0.6 (10)
C10—N2—C6—C7	−0.1 (9)	C7—C8—C9—C10	−1.0 (12)
N1—C1—C2—C3	−30.6 (8)	C8—C9—C10—N2	2.1 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···Br1	0.86	2.45	3.278 (7)	163

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