# (S)-2-[(2-Ammoniophenyl)sulfanyl-methyl]pyrrolidinium dibromide

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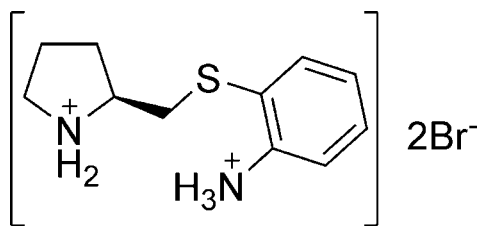Correspondence e-mail: bailinli1972@gmail.com

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

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

### Data collection

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

### Refinement

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

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N2—H2E$\cdots$Br1$^i$ | 0.83 (8) | 2.39 (8) | 3.201 (9) | 169 (10) |
| N2—H2D$\cdots$Br2$^{ii}$ | 0.84 (6) | 2.48 (4) | 3.277 (9) | 159 (8) |
| N2—H2C$\cdots$Br1 | 0.84 (7) | 2.47 (7) | 3.298 (9) | 173 (8) |
| N1—H1B$\cdots$Br2 | 0.90 | 2.47 | 3.355 (7) | 169 |
| N1—H1A$\cdots$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*.

## References

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**supplementary materials**

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

## B. Li, S. Zhang, Y. Wang and S. Luo

## 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 nitrostyrenes. 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.

## Experimental

The title compound was synthesized by treating 2-aminobenzenethiol (1.25 g,10 mmol) with (*S*)-2-bromomethylpyrrolidine 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.

## 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.
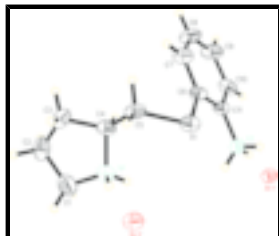
# supplementary materials

**Figures**



Fig. 1. The asymmetric unit of the title compound with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
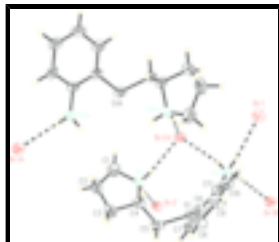


Fig. 2. The molecular packing of the title compound showing H-bridge interactions between cationic-anionic groups.

## (*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<br>$\lambda = 0.71073$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 1525 reflections |
| $a = 7.9399$ (9) Å | $\theta = 4.4–38.3º$ |
| $b = 10.8427$ (13) Å | $\mu = 5.45$ mm$^{-1}$ |
| $c = 17.658$ (2) Å | $T = 293$ (2) K |
| $V = 1520.2$ (3) Å$^3$ | Prismatic, colorless |
| $Z = 4$ | $0.49 \times 0.42 \times 0.37$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3311 independent reflections |
| Radiation source: fine-focus sealed tube | 1808 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.136$ |
| $T = 293(2)$ K | $\theta_{max} = 27.0º$ |
| $\varphi$ and $\omega$ scans | $\theta_{min} = 2.2º$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -9 \rightarrow 10$ |
| $T_{min} = 0.103$, $T_{max} = 0.137$ | $k = -13 \rightarrow 12$ |
| 8969 measured reflections | $l = -22 \rightarrow 18$ |

*Refinement*

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

| | | | |
|---|---|---|---|
| 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, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2E···Br1[i] | 0.83 (8) | 2.39 (8) | 3.201 (9) | 169 (10) |
| N2—H2D···Br2[ii] | 0.84 (6) | 2.48 (4) | 3.277 (9) | 159 (8) |
| N2—H2C···Br1 | 0.84 (7) | 2.47 (7) | 3.298 (9) | 173 (8) |
| N1—H1B···Br2 | 0.90 | 2.47 | 3.355 (7) | 169 |
| N1—H1A···Br2[ii] | 0.90 | 2.33 | 3.224 (7) | 170 |

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

**Fig. 1**

**Fig. 2**