

**(1*R*,3*S*)-1,2,2-Trimethylcyclopentane-1,3-diammonium sulfate**Zhao-Lian Chu,<sup>a</sup> Ying Fan,<sup>b</sup> Wei Huang<sup>a\*</sup> and Jian-Lan Liu<sup>b</sup>

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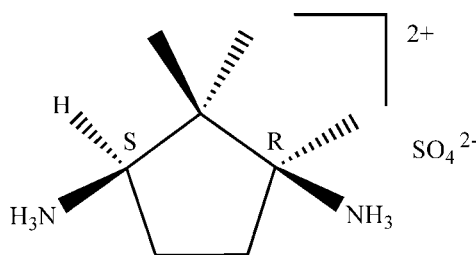
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Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.092; data-to-parameter ratio = 18.2.

In the title salt,  $\text{C}_8\text{H}_{20}\text{N}_2^{2+} \cdot \text{SO}_4^{2-}$ , a ten-membered hydrogen-bonded ring ( $\text{C}_3\text{H}_2\text{N}_2\text{O}_2\text{S}$ ) is observed involving the two ammonium groups and two O atoms of the sulfate ion. A three-dimensional hydrogen-bond network is constructed whereby every sulfate anion is linked to five adjacent (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-diammonium cations by  $\text{N}-\text{H} \cdots \text{O}$  interactions.

**Related literature**

For the synthesis of the title compound, see: Yang *et al.* (2001). For the structures of related organic camphor compounds, see: Huang, Qian *et al.* (2003, 2004); Qian, Liu & Huang (2007). For the structures of other transition metal coordination complexes (enantiomeric and racemic ligands), see: Huang, Zhou *et al.* (2004); Huang *et al.* (2005); Qian *et al.* (2003, 2006); Qian, Chu *et al.* (2007).

**Experimental***Crystal data* $\text{C}_8\text{H}_{20}\text{N}_2^{2+} \cdot \text{SO}_4^{2-}$  $M_r = 240.32$ Orthorhombic,  $P2_12_12_1$  $a = 6.5631$  (7) Å $b = 8.2864$  (9) Å $c = 19.872$  (2) Å $V = 1080.7$  (2) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.30$  mm<sup>-1</sup> $T = 291$  (2) K

0.14 × 0.12 × 0.10 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Bruker, 2000) $T_{\min} = 0.961$ ,  $T_{\max} = 0.969$ 

6729 measured reflections

2573 independent reflections

2530 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.057$ *Refinement* $R[F^2 > 2\sigma(F^2)] = 0.035$  $wR(F^2) = 0.092$  $S = 1.08$ 

2573 reflections

141 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.55$  e Å<sup>-3</sup>

Absolute structure: Flack (1983),

1008 Friedel pairs

Flack parameter: 0.05 (7)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O4}^{\text{i}}$	0.89	2.22	3.098 (2)	169
$\text{N1}-\text{H1B} \cdots \text{O3}$	0.89	1.85	2.7011 (19)	160
$\text{N1}-\text{H1C} \cdots \text{O1}^{\text{ii}}$	0.89	1.96	2.840 (2)	172
$\text{N2}-\text{H2A} \cdots \text{O4}$	0.89	1.97	2.844 (2)	169
$\text{N2}-\text{H2B} \cdots \text{O2}^{\text{iii}}$	0.89	1.97	2.833 (2)	162
$\text{N2}-\text{H2C} \cdots \text{O1}^{\text{iv}}$	0.89	2.13	2.969 (2)	157
$\text{N2}-\text{H2C} \cdots \text{O3}^{\text{iv}}$	0.89	2.48	3.185 (2)	137

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2395).

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**supplementary materials**

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## (1*R*,3*S*)-1,2,2-Trimethylcyclopentane-1,3-diammonium sulfate

Z.-L. Chu, Y. Fan, W. Huang and J.-L. Liu

### Comment

In our previous studies, we have reported the syntheses and crystal structures of a series of camphoric derivatives and some of their transition metal coordination complexes. Herein, we report the single-crystal structure of (*1R,3S*)-1,2,2-trimethylcyclopentane-1,3-diammonium sulfate.

The atom-numbering scheme of the title compound is shown in Fig. 1, while selected bond distances and bond angles are given in Table 1. Both of the amine groups are in the protonated form and the bond lengths and bond angles are in the normal ranges compared with the related compounds. A ten-membered hydrogen bonding ring (C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S) is observed between the two diammonium groups and the two oxygen atoms of divalent sulfate counterion.

In the crystal packing, a three-dimensional hydrogen-bond network is constructed where every sulfate group links five adjacent (*1R,3S*)-1,2,2-trimethylcyclopentane-1,3-diammonium dications by means of N—H···O hydrogen bonding interactions (Fig. 2).

### Experimental

The title compound is prepared *via* a literature method we have mentioned before expect that a dilute sulfuric acid (6.0 mol/L) aqueous solution is used instead of concentrated hydrochloric acid. Single crystals suitable for X-ray diffraction measurement were formed after 1 week in water by slow evaporation at room temperature in air. Anal. Calcd. for C<sub>8</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>S: C, 39.98; H, 8.39; O, 11.66%. Found: C, 40.01; H, 8.33; O, 11.74%. FT—IR (KBr pellets, cm<sup>-1</sup>): 3441 (*s*), 2972 (*s*), 1602 (*versus*), 1552 (*s*), 1123 (*s*), and 1083 (*s*). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ = 0.96 (*s*, 3H), 1.04 (*s*, 3H), 1.24 (*s*, 3H), 1.70–1.73 (*m*, 1H), 1.82–1.87 (*m*, 1H), 2.03–2.06 (*m*, 1H), 2.07–2.19 (*m*, 1H), 3.46–3.49 (*t*, 1H).

### Refinement

The non-hydrogen atoms were refined anisotropically, whereas the H atoms were placed in geometrically idealized positions (C—H = 0.96–0.97 Å and N—H = 0.89 Å) and refined as riding atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  (for methyl C and nitrogen atoms) or  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the other C atoms.

Figures

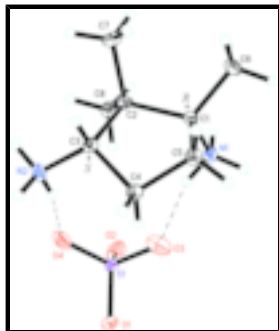


Fig. 1. A drawing of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

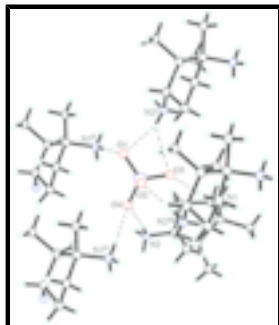


Fig. 2. A perspective view of the N—H...O hydrogen-bond contacts in the crystal packing of the title compound. Hydrogen bonds are indicated as dashed lines. [Symmetry codes: (i)  $-x, 1/2 + y, 1/2 - z$ ; (ii)  $-x, -1/2 + y, 1/2 - z$ ; (iii)  $1 - x, 1/2 + y, 1/2 - z$ ; (iv)  $1 - x, -1/2 + y, 1/2 - z$ .]

**(1R,3S)-1,2,2-Trimethylcyclopentane-1,3-diammonium sulfate**

*Crystal data*

$C_8H_{20}N_2^{2+} \cdot SO_4^{2-}$

$M_r = 240.32$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 6.5631$  (7) Å

$b = 8.2864$  (9) Å

$c = 19.872$  (2) Å

$V = 1080.7$  (2) Å<sup>3</sup>

$Z = 4$

$F_{000} = 520$

$D_x = 1.477$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 5952 reflections

$\theta = 2.5$ – $28.2^\circ$

$\mu = 0.30$  mm<sup>-1</sup>

$T = 291$  (2) K

Block, colorless

$0.14 \times 0.12 \times 0.10$  mm

*Data collection*

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291$  (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2000)

2573 independent reflections

2530 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.057$

$\theta_{max} = 28.2^\circ$

$\theta_{min} = 2.1^\circ$

$h = -8 \rightarrow 8$

$T_{\min} = 0.961$ ,  $T_{\max} = 0.969$   
6729 measured reflections

$k = -10 \rightarrow 6$   
 $l = -26 \rightarrow 26$

### Refinement

Refinement on  $F^2$

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.035$

$$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.3153P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.092$

$$(\Delta/\sigma)_{\max} = 0.001$$

$S = 1.08$

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

2573 reflections

$$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$$

141 parameters

Extinction correction: none

Primary atom site location: structure-invariant direct methods

Absolute structure: Flack (1983), 1008 Friedel pairs

Secondary atom site location: difference Fourier map Flack parameter: 0.05 (7)

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2929 (3)	0.41806 (19)	0.40485 (7)	0.0187 (3)
C2	0.4177 (2)	0.5784 (2)	0.39285 (7)	0.0175 (3)
C3	0.2489 (2)	0.71107 (19)	0.38443 (8)	0.0193 (3)
H3	0.2431	0.7725	0.4265	0.023*
C4	0.0464 (3)	0.6245 (2)	0.37648 (9)	0.0231 (3)
H4A	0.0220	0.5949	0.3299	0.028*
H4B	-0.0657	0.6905	0.3924	0.028*
C5	0.0756 (3)	0.4757 (2)	0.42052 (9)	0.0243 (3)
H5A	-0.0234	0.3930	0.4093	0.029*
H5B	0.0617	0.5029	0.4678	0.029*
C6	0.3777 (3)	0.3036 (2)	0.45777 (9)	0.0282 (4)
H6A	0.3794	0.3566	0.5007	0.042*
H6B	0.5139	0.2727	0.4457	0.042*
H6C	0.2933	0.2092	0.4603	0.042*
C7	0.5424 (3)	0.6224 (2)	0.45556 (8)	0.0271 (4)

## supplementary materials

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H7A	0.6522	0.5469	0.4608	0.041*
H7B	0.4562	0.6186	0.4946	0.041*
H7C	0.5968	0.7293	0.4506	0.041*
C8	0.5608 (2)	0.5688 (2)	0.33204 (8)	0.0208 (3)
H8A	0.6351	0.6681	0.3280	0.031*
H8B	0.4822	0.5512	0.2919	0.031*
H8C	0.6546	0.4811	0.3381	0.031*
N1	0.2824 (2)	0.31718 (16)	0.34122 (7)	0.0212 (3)
H1A	0.4036	0.2727	0.3334	0.032*
H1B	0.2480	0.3798	0.3067	0.032*
H1C	0.1896	0.2398	0.3463	0.032*
N2	0.2841 (2)	0.82886 (17)	0.32852 (8)	0.0257 (3)
H2A	0.2823	0.7770	0.2893	0.039*
H2B	0.4046	0.8763	0.3341	0.039*
H2C	0.1863	0.9032	0.3290	0.039*
O1	0.0145 (2)	0.57816 (18)	0.12914 (7)	0.0317 (3)
O2	0.3575 (2)	0.4812 (2)	0.12373 (9)	0.0499 (4)
O3	0.1540 (3)	0.43956 (19)	0.22259 (7)	0.0467 (4)
O4	0.2805 (3)	0.70567 (17)	0.19494 (7)	0.0414 (4)
S1	0.20253 (6)	0.55228 (4)	0.167780 (18)	0.01945 (12)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0178 (7)	0.0197 (7)	0.0185 (6)	-0.0011 (7)	-0.0009 (5)	0.0010 (5)
C2	0.0129 (6)	0.0203 (7)	0.0192 (6)	0.0008 (6)	-0.0018 (5)	-0.0008 (5)
C3	0.0145 (7)	0.0191 (7)	0.0244 (7)	0.0008 (6)	0.0020 (6)	-0.0017 (5)
C4	0.0127 (7)	0.0245 (8)	0.0322 (8)	0.0008 (6)	0.0009 (6)	0.0030 (7)
C5	0.0162 (7)	0.0244 (8)	0.0322 (8)	-0.0001 (6)	0.0053 (6)	0.0036 (7)
C6	0.0307 (9)	0.0286 (9)	0.0253 (8)	0.0019 (8)	-0.0039 (7)	0.0077 (7)
C7	0.0226 (8)	0.0345 (9)	0.0243 (7)	-0.0029 (7)	-0.0058 (6)	-0.0038 (7)
C8	0.0152 (6)	0.0218 (7)	0.0256 (7)	-0.0003 (6)	0.0035 (6)	-0.0011 (7)
N1	0.0240 (7)	0.0184 (6)	0.0213 (6)	-0.0022 (6)	-0.0013 (6)	-0.0006 (5)
N2	0.0192 (7)	0.0184 (6)	0.0395 (8)	0.0022 (6)	0.0026 (7)	0.0049 (5)
O1	0.0241 (6)	0.0329 (7)	0.0381 (7)	0.0073 (6)	-0.0106 (5)	-0.0032 (6)
O2	0.0323 (8)	0.0544 (10)	0.0629 (10)	0.0159 (8)	0.0124 (7)	-0.0010 (8)
O3	0.0689 (11)	0.0422 (8)	0.0290 (6)	-0.0259 (9)	-0.0123 (7)	0.0151 (6)
O4	0.0549 (10)	0.0275 (7)	0.0417 (8)	-0.0168 (7)	-0.0111 (7)	-0.0010 (5)
S1	0.01899 (19)	0.01784 (18)	0.02151 (17)	-0.00102 (14)	-0.00342 (14)	0.00292 (13)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—N1	1.5173 (19)	C6—H6C	0.9600
C1—C6	1.522 (2)	C7—H7A	0.9600
C1—C5	1.536 (2)	C7—H7B	0.9600
C1—C2	1.579 (2)	C7—H7C	0.9600
C2—C8	1.532 (2)	C8—H8A	0.9600
C2—C7	1.535 (2)	C8—H8B	0.9600
C2—C3	1.570 (2)	C8—H8C	0.9600

C3—N2	1.497 (2)	N1—H1A	0.8900
C3—C4	1.519 (2)	N1—H1B	0.8900
C3—H3	0.9800	N1—H1C	0.8900
C4—C5	1.524 (2)	N2—H2A	0.8900
C4—H4A	0.9700	N2—H2B	0.8900
C4—H4B	0.9700	N2—H2C	0.8900
C5—H5A	0.9700	O1—S1	1.4693 (13)
C5—H5B	0.9700	O2—S1	1.4654 (16)
C6—H6A	0.9600	O3—S1	1.4697 (13)
C6—H6B	0.9600	O4—S1	1.4728 (14)
N1—C1—C6	104.42 (13)	C1—C6—H6C	109.5
N1—C1—C5	107.34 (13)	H6A—C6—H6C	109.5
C6—C1—C5	113.15 (14)	H6B—C6—H6C	109.5
N1—C1—C2	111.18 (12)	C2—C7—H7A	109.5
C6—C1—C2	116.06 (14)	C2—C7—H7B	109.5
C5—C1—C2	104.52 (13)	H7A—C7—H7B	109.5
C8—C2—C7	109.03 (13)	C2—C7—H7C	109.5
C8—C2—C3	112.63 (13)	H7A—C7—H7C	109.5
C7—C2—C3	107.24 (13)	H7B—C7—H7C	109.5
C8—C2—C1	113.15 (13)	C2—C8—H8A	109.5
C7—C2—C1	110.72 (13)	C2—C8—H8B	109.5
C3—C2—C1	103.84 (12)	H8A—C8—H8B	109.5
N2—C3—C4	111.46 (13)	C2—C8—H8C	109.5
N2—C3—C2	115.27 (13)	H8A—C8—H8C	109.5
C4—C3—C2	107.34 (13)	H8B—C8—H8C	109.5
N2—C3—H3	107.5	C1—N1—H1A	109.5
C4—C3—H3	107.5	C1—N1—H1B	109.5
C2—C3—H3	107.5	H1A—N1—H1B	109.5
C3—C4—C5	102.27 (13)	C1—N1—H1C	109.5
C3—C4—H4A	111.3	H1A—N1—H1C	109.5
C5—C4—H4A	111.3	H1B—N1—H1C	109.5
C3—C4—H4B	111.3	C3—N2—H2A	109.5
C5—C4—H4B	111.3	C3—N2—H2B	109.5
H4A—C4—H4B	109.2	H2A—N2—H2B	109.5
C4—C5—C1	104.57 (13)	C3—N2—H2C	109.5
C4—C5—H5A	110.8	H2A—N2—H2C	109.5
C1—C5—H5A	110.8	H2B—N2—H2C	109.5
C4—C5—H5B	110.8	O2—S1—O1	109.23 (10)
C1—C5—H5B	110.8	O2—S1—O3	109.73 (11)
H5A—C5—H5B	108.9	O1—S1—O3	107.35 (9)
C1—C6—H6A	109.5	O2—S1—O4	108.94 (11)
C1—C6—H6B	109.5	O1—S1—O4	110.95 (9)
H6A—C6—H6B	109.5	O3—S1—O4	110.62 (8)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O4 <sup>i</sup>	0.89	2.22	3.098 (2)	169
N1—H1B $\cdots$ O3	0.89	1.85	2.7011 (19)	160

## supplementary materials

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N1—H1C···O1 <sup>ii</sup>	0.89	1.96	2.840 (2)	172
N2—H2A···O4	0.89	1.97	2.844 (2)	169
N2—H2B···O2 <sup>iii</sup>	0.89	1.97	2.833 (2)	162
N2—H2C···O1 <sup>iv</sup>	0.89	2.13	2.969 (2)	157
N2—H2C···O3 <sup>iv</sup>	0.89	2.48	3.185 (2)	137
C7—H7C···O2 <sup>iii</sup>	0.96	2.57	3.428 (3)	148
C8—H8C···O4 <sup>i</sup>	0.96	2.41	3.229 (2)	143

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



Fig. 1

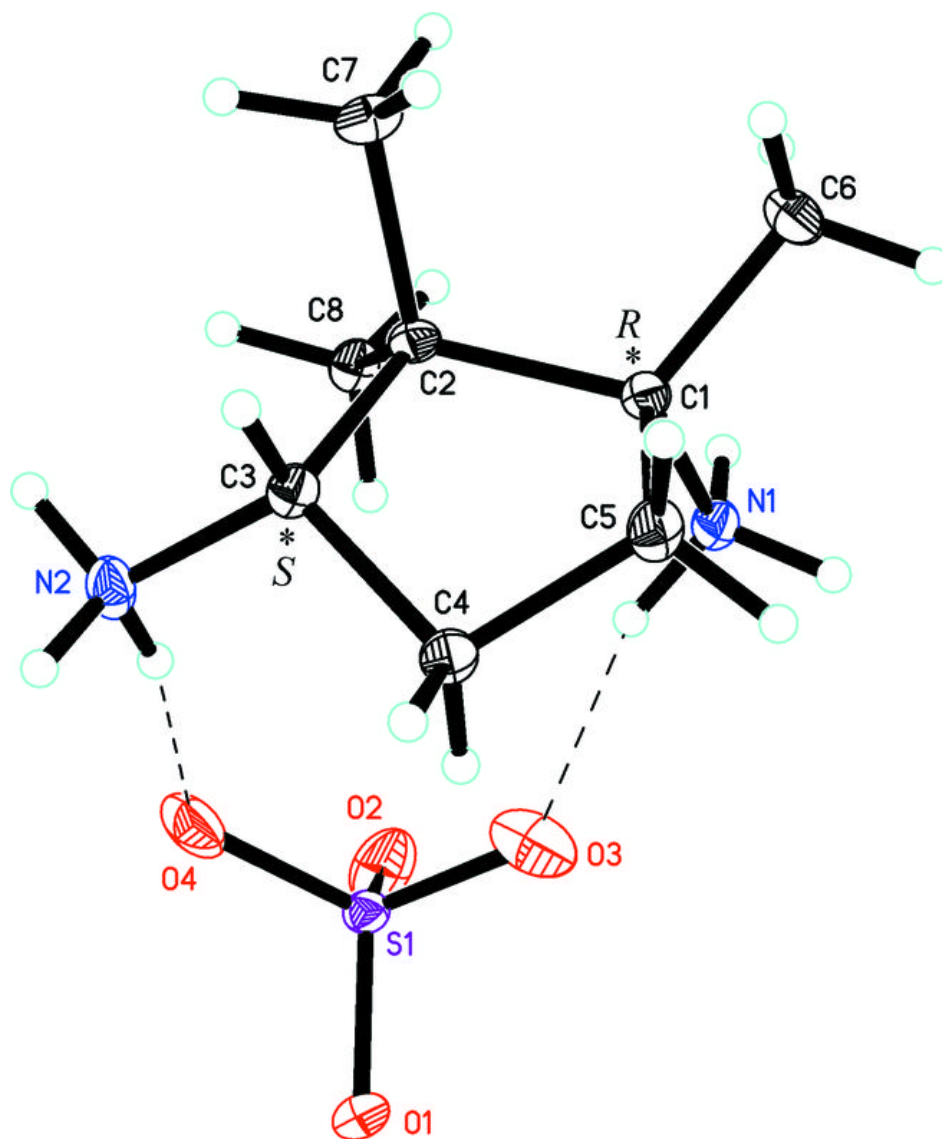


Fig. 2

