

## Bis[benzyl(methyl)ammonium] tetrasulfidotungstate(VI)

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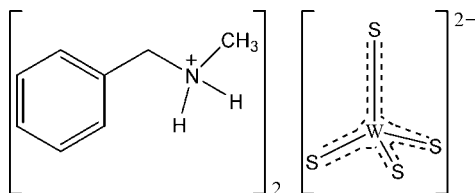
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.018;  $wR$  factor = 0.043; data-to-parameter ratio = 19.9.

The title compound,  $(\text{C}_8\text{H}_{12}\text{N})_2[\text{WS}_4]$ , was synthesized by the aqueous reaction of ammonium tetrasulfidotungstate(VI) with benzyl(methyl)amine in a 1:2 molar ratio. The compound is isotypic with the corresponding Mo analogue,  $(\text{C}_8\text{H}_{12}\text{N})_2[\text{MoS}_4]$ , and its structure consists of a slightly distorted tetrahedral  $[\text{WS}_4]^{2-}$  dianion and two crystallographically independent benzyl(methyl)ammonium cations, with all atoms located in general positions. The cations and anion are linked by weak  $\text{N}-\text{H}\cdots\text{S}$  and  $\text{C}-\text{H}\cdots\text{S}$  interactions, the strength and number of which can explain the observed  $\text{W}-\text{S}$  bond distances.

### Related literature

Previous reports give details of the structural characterization of several organic ammonium tetrasulfidotungstates containing organic cations derived from chiral amines (Srinivasan, Naik *et al.*, 2007), diamines (Srinivasan *et al.*, 2002; 2003a; Srinivasan, Näther *et al.*, 2006a), triamines (Srinivasan, Näther *et al.*, 2006b), cyclic amines (Srinivasan *et al.*, 2003b; Srinivasan, Naik *et al.*, 2006) and a tetraamine (Srinivasan *et al.*, 2005). The title compound is isotypic with the corresponding Mo analogue  $(\text{C}_8\text{H}_{12}\text{N})_2[\text{MoS}_4]$  (Srinivasan, Girkar & Raghavaiah 2007).



### Experimental

#### Crystal data

$(\text{C}_8\text{H}_{12}\text{N})_2[\text{WS}_4]$   
 $M_r = 556.46$

Triclinic,  $P\bar{1}$   
 $a = 7.2178$  (12) Å

$b = 10.7965$  (19) Å  
 $c = 14.900$  (3) Å  
 $\alpha = 111.057$  (2)°  
 $\beta = 90.539$  (2)°  
 $\gamma = 100.584$  (2)°  
 $V = 1061.6$  (3) Å<sup>3</sup>

$Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 5.83$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.28 \times 0.18 \times 0.06$  mm

#### Data collection

Bruker SMART APEX CCD  
diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2004)  
 $T_{\min} = 0.292$ ,  $T_{\max} = 0.711$

11136 measured reflections  
4189 independent reflections  
3976 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.043$   
 $S = 1.06$   
4189 reflections

210 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.61$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.44$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

W1—S1	2.1703 (8)	W1—S3	2.1962 (9)
W1—S2	2.1713 (9)	W1—S4	2.2083 (7)
S1—W1—S2	109.69 (3)	S1—W1—S4	109.63 (3)
S1—W1—S3	109.18 (3)	S2—W1—S4	108.89 (3)
S2—W1—S3	110.18 (4)	S3—W1—S4	109.26 (3)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H1B $\cdots$ S3 <sup>i</sup>	0.90	2.51	3.316 (3)	150
N1—H1B $\cdots$ S1 <sup>i</sup>	0.90	2.79	3.356 (2)	123
N1—H1A $\cdots$ S4	0.90	2.39	3.282 (3)	169
N2—H2A $\cdots$ S4	0.90	2.53	3.343 (3)	151
N2—H2B $\cdots$ S4 <sup>ii</sup>	0.90	2.58	3.290 (3)	136
N2—H2B $\cdots$ S2 <sup>ii</sup>	0.90	2.92	3.599 (3)	133
C7—H7B $\cdots$ S3	0.97	2.93	3.741 (3)	142
C15—H15A $\cdots$ S1 <sup>iii</sup>	0.97	2.95	3.648 (3)	130

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg 1999); 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: NC2077).

## References

- Brandenburg, K. (1999). *DIAMOND*. Release 2.1c. Crystal Impact GbR, Bonn, Germany.
- Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2001). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
- Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2002). *Acta Cryst.* **E58**, m622–m624.
- Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003a). *Acta Cryst.* **C59**, m124–m127.
- Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003b). *Acta Cryst.* **E59**, m681–m683.
- Srinivasan, B. R., Dhuri, S. N., Poisot, M., Näther, C. & Bensch, W. (2005). *Z. Anorg. Allg. Chem.* **631**, 1087–1094.
- Srinivasan, B. R., Girkar, S. V. & Raghavaiah, P. (2007). *Acta Cryst.* **E63**, m2737–m2738.
- Srinivasan, B. R., Naik, A. R., Näther, C. & Bensch, W. (2006). *Acta Cryst.* **E62**, m3491–m3493.
- Srinivasan, B. R., Naik, A. R., Näther, C. & Bensch, W. (2007). *Z. Anorg. Allg. Chem.* **633**, 582–588.
- Srinivasan, B. R., Näther, C., Dhuri, S. N. & Bensch, W. (2006a). *Monatsh. Chem.* **137**, 397–411.
- Srinivasan, B. R., Näther, C., Dhuri, S. N. & Bensch, W. (2006b). *Polyhedron*, **25**, 3269–3277.

**supplementary materials**

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## Bis[benzyl(methyl)ammonium] tetrasulfidotungstate(VI)

B. R. Srinivasan, S. V. Girkar and P. Raghavaiah

### Comment

As part of an ongoing research programme, we are investigating the synthesis and structural characterization of organic ammonium tetrasulfidometalates of the group VI metals Mo and W (Srinivasan, Naik *et al.*, 2007). In earlier work we have structurally characterized several  $[\text{WS}_4]^{2-}$  compounds derived from chiral amines (Srinivasan, Naik *et al.*, 2007), diamines (Srinivasan *et al.*, 2002; 2003a; Srinivasan *et al.*, 2006a), triamines (Srinivasan *et al.*, 2006b), cyclic amines (Srinivasan *et al.*, 2003b; Srinivasan *et al.*, 2006) and a tetraamine (Srinivasan *et al.*, 2005). All the organic ammonium tetrasulfidotungstates exhibit several weak hydrogen bonding interactions between the organic cations and  $[\text{WS}_4]^{2-}$  anions. We have also shown that in some organic  $[\text{WS}_4]^{2-}$  compounds the amines are partially protonated (Srinivasan *et al.*, 2006b). The secondary amine benzyl(methyl)amine used for the synthesis of the title compound is an isomer of the chiral primary amine  $\alpha$ -methylbenzylamine used in an earlier study (Srinivasan, Naik *et al.*, 2007).

The title compound is isostructural with the corresponding Mo analogue  $(\text{C}_8\text{H}_{12}\text{N})_2[\text{MoS}_4]$  (Srinivasan, Girkar & Raghavaiah 2007). The structure of (I) consists of a discrete tetrahedral  $[\text{WS}_4]^{2-}$  ion and two crystallographically independent benzyl(methyl)ammonium cations (Fig. 1) with all atoms located in general positions. The bond lengths and bond angles of the organic cations are in good agreement with the reported values for the isotopic Mo compound. The  $(\text{WS}_4)$  tetrahedron is slightly distorted with S—W—S angles between 108.89 (3) and 110.18 (4) ° (Table 1). The W—S bond lengths range from 2.1703 (8) to 2.2083 (7) Å with an average value of 2.1865 Å which is comparable to the bond lengths observed in the related chiral  $[\text{WS}_4]^{2-}$  compound synthesized from the isomeric chiral primary amine (Srinivasan, Naik *et al.*, 2007). The W1—S1 and W1—S2 bond distances are indistinguishable within experimental error and are shorter than the average Mo—S bond length while the other two W—S bonds are longer. The weak H-bonding interactions between the cations and anions can explain the observed short and long W—S bond distances. An analysis of the structure reveals that the organic cations and tetrasulfidotungstate anions are linked with the aid of several N—H $\cdots$ S and C—H $\cdots$ S hydrogen bonding interactions. Thus each  $[\text{WS}_4]^{2-}$  is hydrogen bonded to five different organic cations with the aid of six N—H $\cdots$ S bonds and two weak C—H $\cdots$ S interactions (Fig.2). An examination of the surroundings of the cations reveals that one organic cation (N1) is H-bonded to two different  $[\text{WS}_4]^{2-}$  ions while the second organic cation (N2) is surrounded by three different  $[\text{WS}_4]^{2-}$  ions. One H atom on each N atom functions as a singly shared donor with the other functioning as a bifurcated donor (Table 2). A benzylic H atom from each unique cation is involved in a weak C—H $\cdots$ S interaction. S4 atom which makes the longest W—S bond at 2.2083 (7) Å is involved in three N—H $\cdots$ S bonds, two of which are singly shared. S4 also makes the shortest singly shared N—H $\cdots$ S bond at 2.39 Å, which can explain the elongation of this bond. In contrast, S1 atom involved in the shortest W—S bond makes a bifurcated N—H $\cdots$ S bond at a longer S $\cdots$ H distance accompanied by a small NH—S angle. S1 also makes a very weak C—H $\cdots$ S contact. The observed difference  $\Delta$  between the longest and the shortest W—S bonds of 0.0380 Å in (I) is slightly longer than the  $\Delta$  value of 0.0356 Å in the tetrasulfidotungstate compound containing the *R*-form of the monoprotonated isomeric chiral primary amine  $\alpha$ -methylbenzylamine (Srinivasan, Naik *et al.*, 2007).

## Experimental

(NH<sub>4</sub>)<sub>2</sub>[WS<sub>4</sub>] (348 mg, 1 mmol) was dissolved in water (20 ml) containing a few drops of liquor ammonia. To this mixture benzyl(methyl)amine (0.6 ml) was added and the reaction mixture filtered and left in the refrigerator for crystallization. After two days crystals of the title compound separated. The product was filtered, washed with ice-cold water (2 ml), followed by 2-propanol (10 ml) and diethyl ether (10 ml) and dried. Yield: 71%.

## Refinement

The H atoms were positioned with idealized geometry (C—H = 0.93 (aromatic), 0.96 (methyl) and 0.97 (benzyl) Å and N—H = 0.90 Å) and were refined using a riding model, with  $U_{\text{iso}}(\text{H})$  fixed at  $1.5U_{\text{eq}}(\text{CH}_3)$  and  $1.2U_{\text{eq}}(\text{NH}_2)$ .

## Figures

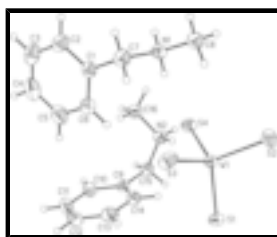


Fig. 1. The crystal structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

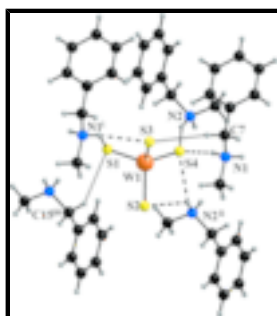


Fig. 2. A view of the surroundings of the [WS<sub>4</sub>]<sup>2-</sup> anion showing its linking to five different organic cations with the aid of six N—H···S and two C—H···S interactions. N—H···S and C—H···S interactions are shown as dashed lines and dotted lines respectively. Symmetry codes: (i)  $x + 1, y, z$  (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $-x, -y + 1, -z + 1$ ;

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### Crystal data

(C<sub>8</sub>H<sub>12</sub>N)<sub>2</sub>[WS<sub>4</sub>]

$M_r = 556.46$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 7.2178$  (12) Å

$b = 10.7965$  (19) Å

$c = 14.900$  (3) Å

$\alpha = 111.057$  (2)°

$\beta = 90.539$  (2)°

$Z = 2$

$F_{000} = 544$

$D_x = 1.741$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 9395 reflections

$\theta = 2.9$ – $26.1$ °

$\mu = 5.83$  mm<sup>-1</sup>

$T = 298$  (2) K

Plate, yellow

$\gamma = 100.584 (2)^\circ$   $0.28 \times 0.18 \times 0.06$  mm  
 $V = 1061.6 (3) \text{ \AA}^3$

*Data collection*

Bruker SMART Apex CCD diffractometer	4189 independent reflections
Radiation source: fine-focus sealed tube	3976 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.021$
$T = 298(2)$ K	$\theta_{\text{max}} = 26.1^\circ$
phi and $\omega$ scans	$\theta_{\text{min}} = 2.1^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.292$ , $T_{\text{max}} = 0.711$	$k = -13 \rightarrow 13$
11136 measured reflections	$l = -18 \rightarrow 18$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.018$	H-atom parameters constrained
$wR(F^2) = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.0392P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
4189 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
210 parameters	$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
	Extinction correction: none

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5898 (4)	0.4749 (3)	0.1050 (2)	0.0463 (7)
C2	0.7217 (5)	0.4217 (4)	0.0434 (3)	0.0606 (9)
H2	0.8281	0.4794	0.0360	0.073*

## supplementary materials

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C3	0.6967 (6)	0.2846 (4)	-0.0070 (3)	0.0747 (12)
H3	0.7846	0.2501	-0.0493	0.090*
C4	0.5427 (7)	0.1990 (4)	0.0051 (3)	0.0756 (11)
H4	0.5261	0.1062	-0.0287	0.091*
C5	0.4126 (6)	0.2505 (4)	0.0671 (3)	0.0753 (11)
H5	0.3089	0.1919	0.0758	0.090*
C6	0.4338 (5)	0.3877 (4)	0.1165 (2)	0.0613 (9)
H6	0.3437	0.4217	0.1575	0.074*
C7	0.6132 (5)	0.6251 (3)	0.1563 (2)	0.0519 (8)
H7A	0.7056	0.6709	0.1258	0.062*
H7B	0.4938	0.6516	0.1502	0.062*
C8	0.6955 (5)	0.8154 (3)	0.3147 (2)	0.0583 (8)
H8A	0.7747	0.8652	0.2826	0.087*
H8B	0.7516	0.8373	0.3786	0.087*
H8C	0.5731	0.8389	0.3186	0.087*
C9	0.1084 (4)	0.1210 (3)	0.2963 (2)	0.0394 (6)
C10	0.0900 (5)	0.0025 (3)	0.2165 (2)	0.0540 (8)
H10	0.1483	-0.0665	0.2186	0.065*
C11	-0.0147 (5)	-0.0135 (4)	0.1340 (3)	0.0688 (10)
H11	-0.0303	-0.0946	0.0813	0.083*
C12	-0.0958 (5)	0.0888 (4)	0.1290 (3)	0.0674 (10)
H12	-0.1651	0.0777	0.0727	0.081*
C13	-0.0749 (5)	0.2080 (4)	0.2071 (3)	0.0594 (9)
H13	-0.1279	0.2784	0.2034	0.071*
C14	0.0242 (4)	0.2233 (3)	0.2908 (2)	0.0494 (7)
H14	0.0347	0.3032	0.3442	0.059*
C15	0.2195 (5)	0.1388 (3)	0.3876 (2)	0.0495 (7)
H15A	0.1400	0.1605	0.4409	0.059*
H15B	0.2575	0.0545	0.3810	0.059*
C16	0.5271 (5)	0.2285 (4)	0.3352 (3)	0.0605 (9)
H16A	0.5625	0.1426	0.3222	0.091*
H16B	0.6375	0.2995	0.3580	0.091*
H16C	0.4705	0.2299	0.2771	0.091*
W1	0.164350 (13)	0.664901 (10)	0.381689 (7)	0.03309 (5)
N1	0.6756 (3)	0.6689 (2)	0.25987 (17)	0.0436 (5)
H1A	0.5917	0.6236	0.2871	0.052*
H1B	0.7876	0.6456	0.2649	0.052*
N2	0.3910 (3)	0.2489 (3)	0.40902 (18)	0.0510 (6)
H2A	0.3534	0.3271	0.4176	0.061*
H2B	0.4506	0.2582	0.4651	0.061*
S1	-0.10531 (10)	0.57374 (8)	0.41657 (6)	0.04382 (17)
S2	0.25800 (13)	0.86874 (8)	0.48700 (7)	0.0594 (2)
S3	0.13227 (12)	0.67014 (10)	0.23646 (6)	0.0540 (2)
S4	0.37736 (10)	0.54331 (7)	0.38502 (6)	0.04296 (16)

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

$U^{11}$

$U^{22}$

$U^{33}$

$U^{12}$

$U^{13}$

$U^{23}$

C1	0.0473 (17)	0.0562 (19)	0.0365 (15)	0.0147 (14)	-0.0022 (12)	0.0162 (14)
C2	0.054 (2)	0.076 (3)	0.058 (2)	0.0228 (18)	0.0114 (16)	0.0282 (19)
C3	0.089 (3)	0.088 (3)	0.055 (2)	0.049 (3)	0.012 (2)	0.020 (2)
C4	0.111 (4)	0.056 (2)	0.056 (2)	0.026 (2)	-0.011 (2)	0.0129 (18)
C5	0.085 (3)	0.065 (2)	0.065 (2)	-0.006 (2)	-0.005 (2)	0.021 (2)
C6	0.059 (2)	0.068 (2)	0.0486 (18)	0.0061 (18)	0.0056 (16)	0.0150 (17)
C7	0.0540 (19)	0.063 (2)	0.0458 (17)	0.0183 (16)	0.0010 (14)	0.0248 (15)
C8	0.056 (2)	0.0446 (18)	0.067 (2)	0.0056 (15)	0.0101 (16)	0.0139 (16)
C9	0.0366 (15)	0.0372 (15)	0.0441 (15)	0.0058 (12)	0.0052 (12)	0.0153 (12)
C10	0.0556 (19)	0.0400 (17)	0.061 (2)	0.0102 (14)	0.0048 (16)	0.0114 (15)
C11	0.075 (2)	0.060 (2)	0.051 (2)	0.0095 (19)	-0.0043 (17)	-0.0023 (17)
C12	0.056 (2)	0.089 (3)	0.053 (2)	0.014 (2)	-0.0092 (16)	0.021 (2)
C13	0.052 (2)	0.066 (2)	0.067 (2)	0.0199 (17)	0.0012 (16)	0.0292 (19)
C14	0.0451 (17)	0.0446 (17)	0.0546 (18)	0.0111 (14)	0.0044 (14)	0.0125 (14)
C15	0.0531 (18)	0.0531 (19)	0.0449 (17)	0.0108 (15)	0.0067 (14)	0.0210 (15)
C16	0.0456 (19)	0.069 (2)	0.067 (2)	0.0126 (17)	0.0075 (16)	0.0253 (18)
W1	0.02768 (7)	0.03355 (7)	0.03975 (7)	0.00685 (4)	0.00315 (4)	0.01511 (5)
N1	0.0389 (13)	0.0455 (14)	0.0473 (14)	0.0086 (11)	0.0024 (10)	0.0180 (11)
N2	0.0448 (14)	0.0594 (16)	0.0437 (14)	0.0114 (12)	-0.0039 (11)	0.0127 (12)
S1	0.0326 (4)	0.0491 (4)	0.0543 (4)	0.0068 (3)	0.0087 (3)	0.0250 (3)
S2	0.0653 (5)	0.0336 (4)	0.0685 (5)	0.0051 (4)	0.0000 (4)	0.0085 (4)
S3	0.0483 (4)	0.0789 (6)	0.0509 (4)	0.0229 (4)	0.0127 (3)	0.0378 (4)
S4	0.0338 (4)	0.0437 (4)	0.0560 (4)	0.0125 (3)	0.0033 (3)	0.0214 (3)

*Geometric parameters (Å, °)*

C1—C6	1.383 (5)	C10—H10	0.9300
C1—C2	1.385 (4)	C11—C12	1.365 (5)
C1—C7	1.500 (4)	C11—H11	0.9300
C2—C3	1.374 (5)	C12—C13	1.372 (5)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.366 (6)	C13—C14	1.373 (5)
C3—H3	0.9300	C13—H13	0.9300
C4—C5	1.372 (6)	C14—H14	0.9300
C4—H4	0.9300	C15—N2	1.491 (4)
C5—C6	1.375 (5)	C15—H15A	0.9700
C5—H5	0.9300	C15—H15B	0.9700
C6—H6	0.9300	C16—N2	1.466 (4)
C7—N1	1.480 (4)	C16—H16A	0.9600
C7—H7A	0.9700	C16—H16B	0.9600
C7—H7B	0.9700	C16—H16C	0.9600
C8—N1	1.474 (4)	W1—S1	2.1703 (8)
C8—H8A	0.9600	W1—S2	2.1713 (9)
C8—H8B	0.9600	W1—S3	2.1962 (9)
C8—H8C	0.9600	W1—S4	2.2083 (7)
C9—C14	1.380 (4)	N1—H1A	0.9000
C9—C10	1.382 (4)	N1—H1B	0.9000
C9—C15	1.506 (4)	N2—H2A	0.9000
C10—C11	1.376 (5)	N2—H2B	0.9000



## supplementary materials

C6—C1—C2	119.0 (3)	C11—C12—C13	119.9 (3)
C6—C1—C7	120.6 (3)	C11—C12—H12	120.1
C2—C1—C7	120.4 (3)	C13—C12—H12	120.1
C3—C2—C1	120.6 (4)	C12—C13—C14	120.1 (3)
C3—C2—H2	119.7	C12—C13—H13	120.0
C1—C2—H2	119.7	C14—C13—H13	120.0
C4—C3—C2	120.0 (4)	C13—C14—C9	120.5 (3)
C4—C3—H3	120.0	C13—C14—H14	119.7
C2—C3—H3	120.0	C9—C14—H14	119.7
C3—C4—C5	119.8 (4)	N2—C15—C9	111.3 (2)
C3—C4—H4	120.1	N2—C15—H15A	109.4
C5—C4—H4	120.1	C9—C15—H15A	109.4
C4—C5—C6	120.8 (4)	N2—C15—H15B	109.4
C4—C5—H5	119.6	C9—C15—H15B	109.4
C6—C5—H5	119.6	H15A—C15—H15B	108.0
C5—C6—C1	119.7 (3)	N2—C16—H16A	109.5
C5—C6—H6	120.1	N2—C16—H16B	109.5
C1—C6—H6	120.1	H16A—C16—H16B	109.5
N1—C7—C1	112.2 (2)	N2—C16—H16C	109.5
N1—C7—H7A	109.2	H16A—C16—H16C	109.5
C1—C7—H7A	109.2	H16B—C16—H16C	109.5
N1—C7—H7B	109.2	S1—W1—S2	109.69 (3)
C1—C7—H7B	109.2	S1—W1—S3	109.18 (3)
H7A—C7—H7B	107.9	S2—W1—S3	110.18 (4)
N1—C8—H8A	109.5	S1—W1—S4	109.63 (3)
N1—C8—H8B	109.5	S2—W1—S4	108.89 (3)
H8A—C8—H8B	109.5	S3—W1—S4	109.26 (3)
N1—C8—H8C	109.5	C8—N1—C7	114.6 (2)
H8A—C8—H8C	109.5	C8—N1—H1A	108.6
H8B—C8—H8C	109.5	C7—N1—H1A	108.6
C14—C9—C10	119.0 (3)	C8—N1—H1B	108.6
C14—C9—C15	120.5 (3)	C7—N1—H1B	108.6
C10—C9—C15	120.5 (3)	H1A—N1—H1B	107.6
C11—C10—C9	120.0 (3)	C16—N2—C15	115.5 (3)
C11—C10—H10	120.0	C16—N2—H2A	108.4
C9—C10—H10	120.0	C15—N2—H2A	108.4
C12—C11—C10	120.5 (3)	C16—N2—H2B	108.4
C12—C11—H11	119.8	C15—N2—H2B	108.4
C10—C11—H11	119.8	H2A—N2—H2B	107.5

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1B $\cdots$ S3 <sup>i</sup>	0.90	2.51	3.316 (3)	150
N1—H1B $\cdots$ S1 <sup>i</sup>	0.90	2.79	3.356 (2)	123
N1—H1A $\cdots$ S4	0.90	2.39	3.282 (3)	169
N2—H2A $\cdots$ S4	0.90	2.53	3.343 (3)	151
N2—H2B $\cdots$ S4 <sup>ii</sup>	0.90	2.58	3.290 (3)	136

N2—H2B···S2 <sup>ii</sup>	0.90	2.92	3.599 (3)	133
C7—H7B···S3	0.97	2.93	3.741 (3)	142
C15—H15A···S1 <sup>iii</sup>	0.97	2.95	3.648 (3)	130

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

Fig. 1

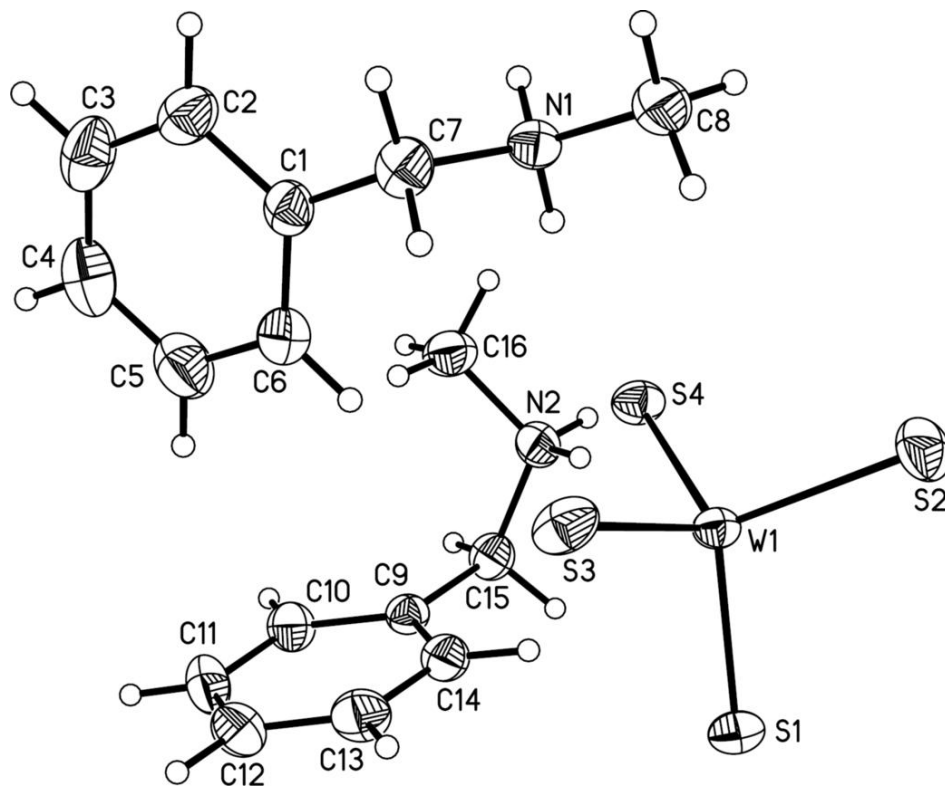


Fig. 2

