

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 2,2,6,6-Tetramethylpiperidinium pentachlorobenzenethiolate

Katarzyna Baranowska\* and Natalia Piwowarska

 Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 G. Narutowicz Street, 80952-PL Gdańsk, Poland  
 Correspondence e-mail: kasiab29@wp.pl

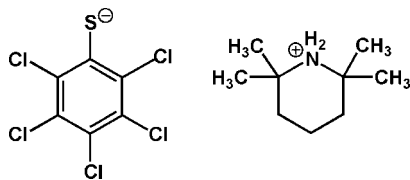
Received 4 July 2008; accepted 11 August 2008

 Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.097; data-to-parameter ratio = 11.3.

In the crystal structure of the title compound,  $\text{C}_9\text{H}_{20}\text{N}^+\cdot\text{C}_6\text{Cl}_5\text{S}^-$ , two cation–anion pairs are linked by  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds to produce a cyclic aggregate of  $R_4^2(8)$  type. The dimers are interconnected *via*  $\pi-\pi$  stacking [centroid–centroid distance =  $3.851(2)$  Å] and weak  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen-bonding interactions.

### Related literature

For the structures of similar salts and comparison of bond distances, see: Baranowska *et al.* (2008); Dołęga *et al.* (2008); Baranowska (2007); Pladzyk & Baranowska (2007); Baranowska, Chojnacki, Konitz *et al.* (2006); Baranowska, Chojnacki, Gosiewska & Wojnowski (2006); Baranowska *et al.* (2003). For the graph-set description of hydrogen-bonding patterns, see: Bernstein *et al.* (1995); Etter (1990). For synthesis techniques, see: Perrin & Armarego (1988).



### Experimental

#### Crystal data

$\text{C}_9\text{H}_{20}\text{N}^+\cdot\text{C}_6\text{Cl}_5\text{S}^-$   
 $M_r = 423.63$   
 Triclinic,  $P\bar{1}$   
 $a = 8.4230$  (5) Å  
 $b = 10.5081$  (4) Å  
 $c = 11.6142$  (6) Å  
 $\alpha = 110.946$  (4)°  
 $\beta = 102.614$  (4)°

$\gamma = 95.286$  (4)°  
 $V = 920.39$  (8) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.90$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 $0.21 \times 0.14 \times 0.09$  mm

#### Data collection

Oxford Diffraction KM4 CCD diffractometer

Absorption correction: analytical (*CrysAlis RED*; Oxford

Diffraction, 2006)  
 $T_{\min} = 0.779$ ,  $T_{\max} = 0.866$   
 5583 measured reflections

3161 independent reflections  
 2930 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.097$   
 $S = 1.21$   
 3161 reflections

279 parameters  
 All H-atom parameters refined  
 $\Delta\rho_{\max} = 0.67$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.44$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$   | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|----------|-------------|-------------|---------------|
| $\text{N1}-\text{H1B}\cdots\text{S1}^{\text{i}}$      | 0.87 (2) | 2.44 (2)    | 3.301 (2)   | 170 (2)       |
| $\text{N1}-\text{H1A}\cdots\text{S1}$                 | 0.90 (2) | 2.39 (2)    | 3.226 (2)   | 157 (2)       |
| $\text{C14}-\text{H14C}\cdots\text{Cl1}^{\text{ii}}$  | 0.91 (3) | 3.02 (2)    | 3.803 (2)   | 145 (2)       |
| $\text{C15}-\text{H15B}\cdots\text{Cl1}$              | 0.93 (2) | 2.88 (2)    | 3.748 (2)   | 156 (2)       |
| $\text{C13}-\text{H13B}\cdots\text{Cl3}^{\text{iii}}$ | 0.98 (2) | 3.02 (2)    | 3.905 (2)   | 151 (2)       |
| $\text{C13}-\text{H13C}\cdots\text{Cl4}^{\text{iv}}$  | 0.98 (2) | 3.08 (2)    | 3.782 (2)   | 129 (2)       |
| $\text{C9}-\text{H9B}\cdots\text{Cl4}^{\text{v}}$     | 0.95 (2) | 2.92 (2)    | 3.708 (2)   | 141 (2)       |
| $\text{C15}-\text{H15C}\cdots\text{Cl4}^{\text{v}}$   | 0.94 (2) | 2.94 (2)    | 3.646 (2)   | 133 (2)       |
| $\text{C8}-\text{H8B}\cdots\text{Cl5}^{\text{vi}}$    | 0.89 (3) | 2.87 (3)    | 3.748 (2)   | 169 (2)       |
| $\text{C10}-\text{H10A}\cdots\text{Cl5}^{\text{i}}$   | 0.97 (2) | 3.02 (2)    | 3.966 (2)   | 167 (2)       |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank Dr Anna Dołęga and Dr Jarosław Chojnacki for helpful discussions during the preparation of the manuscript.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2076).

### References

- Baranowska, K. (2007). *Acta Cryst.* **E63**, o2653–o2655.  
 Baranowska, K., Chojnacki, J., Becker, B. & Wojnowski, W. (2003). *Acta Cryst.* **E59**, o765–o766.  
 Baranowska, K., Chojnacki, J., Gosiewska, M. & Wojnowski, W. (2006). *Z. Anorg. Allg. Chem.* **632**, 1086–1090.  
 Baranowska, K., Chojnacki, J., Konitz, A., Wojnowski, W. & Becker, B. (2006). *Polyhedron*, **25**, 1555–1560.  
 Baranowska, K., Liadis, K. & Wojnowski, W. (2008). *Acta Cryst.* **E64**, o1329.  
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.  
 Dołęga, A., Pladzyk, A., Baranowska, K. & Wiczerzak, M. (2008). *Inorg. Chem. Commun.* **11**, 847–850.  
 Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.  
 Perrin, D. D. & Armarego, W. L. F. (1988). *Purification of Laboratory Chemicals*. Oxford: Pergamon Press.  
 Pladzyk, A. & Baranowska, K. (2007). *Acta Cryst.* **E63**, m1594.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2008). E64, o1781 [doi:10.1107/S1600536808025877]

## 2,2,6,6-Tetramethylpiperidinium pentachlorobenzenethiolate

Katarzyna Baranowska and Natalia Piwowarska

### S1. Comment

The crystal structure of the title compound shows an asymmetric unit consisting of one pentachlorobenzenethiolate anion and one 2,2,6,6-tetramethylpiperidinium cation. The ammonium thiolate forms a dimer  $[\text{C}_6\text{Cl}_5\text{S}^{(-)}\text{H}_2\text{N}^{(+)}\text{C}_5\text{H}_6\text{Me}_4]_2$  (Fig. 1) in which four charge-assisted  $^{(+)}\text{N}-\text{H}\cdots\text{S}^{(-)}$  hydrogen bonds form a stable core. This pattern of an eight-membered ring system with four donors and two acceptors is known as  $R_4^2(8)$ , using Etter's graph set analysis (Etter, 1990; Bernstein *et al.*, 1995). In the crystal the dimers pack as separate units bound together by van der Waals forces and weak  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonds (Fig. 2). Similar (thiol-amine)<sub>2</sub> ring formation has been observed in other ammonium salts (Baranowska *et al.*, 2008; Baranowska, 2007; Baranowska, Chojnacki, Konitz *et al.*, 2006; Baranowska, Chojnacki, Gosiewska & Wojnowski, 2006). The dimers are interconnected *via*  $\pi-\pi$  stacking interactions between  $Cg1$  and  $Cg2$ , where  $Cg1$  is the centroid of the C1–C6 ring and  $Cg2$  is the centroid of the C1–C6 ring at (1-x, -y, -z). The centroid-to-centroid (CC) distance is 3.851 (2) Å and the angle subtended by the plane normal to CC is 25.03°. Interactions of the  $\text{C}-\text{H}\cdots\text{Cl}$  type are weak with the shortest  $\text{H}\cdots\text{Cl}$  distance measuring to 2.86 Å.

The  $\text{N}\cdots\text{S}$  distances lie in the range 3.226 (2)–3.301 (2) Å and are therefore comparable with values observed in zinc and cobalt silanethiolates complexes (Dołęga *et al.*, 2008; Pladzyk & Baranowska, 2007) or aromatic thiolates (Baranowska, 2007; Baranowska *et al.* 2003).

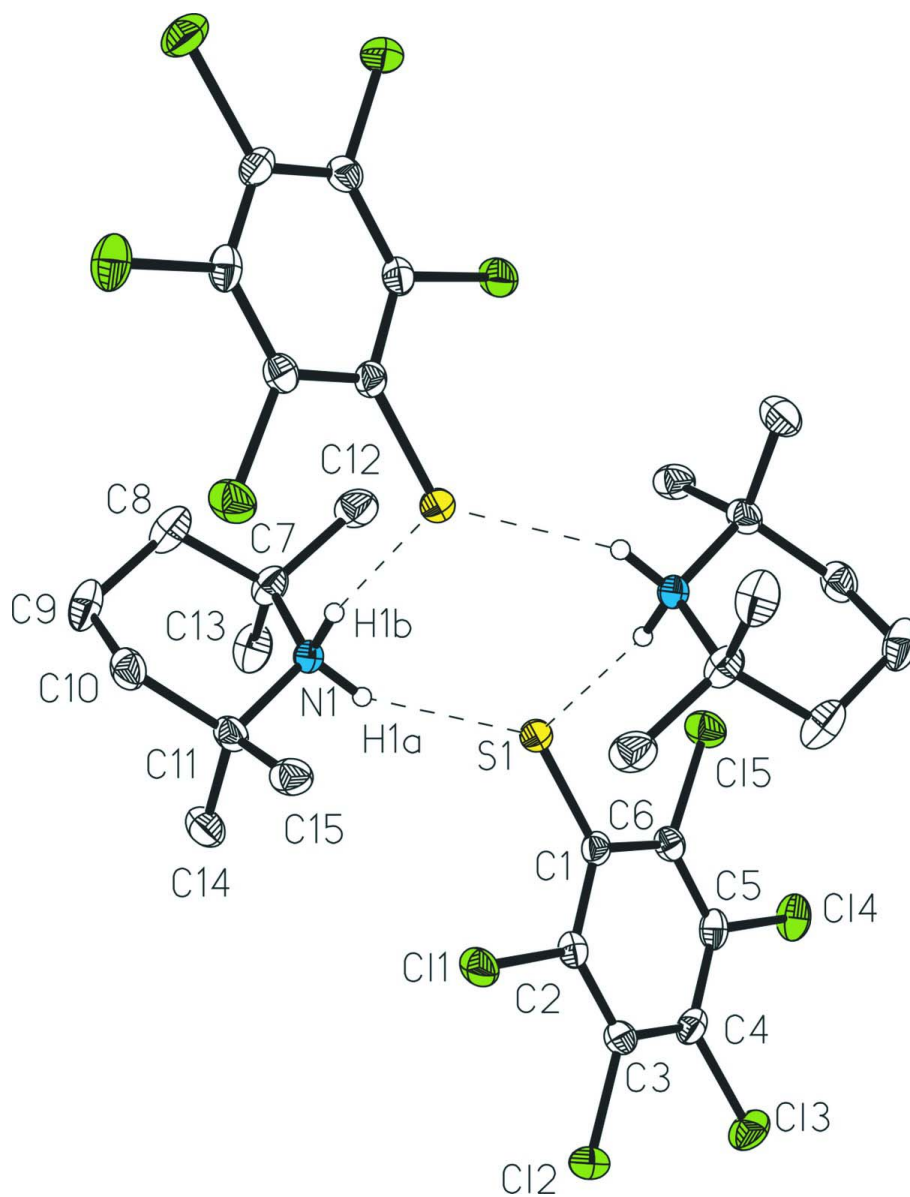
### S2. Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The solvents were purified and dried by standard methods (Perrin & Armarego, 1988).

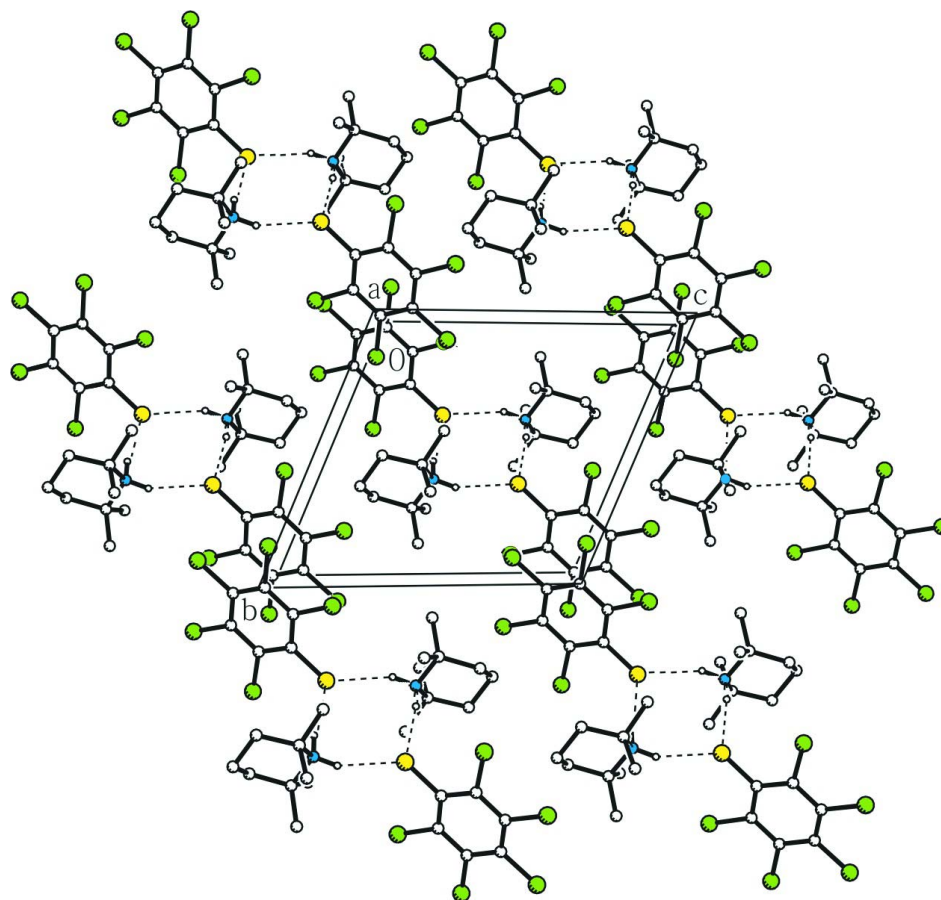
$\text{C}_6\text{Cl}_5\text{SH}$  (0.570 g, 2 mmol) was dissolved in tetrahydrofuran (*ca* 10 ml). Traces of impurities were removed by filtration under an argon atmosphere. Next, a portion of 2,2,6,6-tetramethylpiperidine (0.338 ml, 2 mmol) was added at room temperature. The color of the mixture changed to dark red. Slow crystallization from THF at 5° C yielded yellow crystals suitable for X-ray diffraction.

### S3. Refinement

All H atoms were located in the difference map and refined without constraints.

**Figure 1**

Structure of  $[\text{C}_6\text{Cl}_5\text{S}^{(-)}\text{H}_2\text{N}^{(+)}\text{C}_3\text{H}_6\text{Me}_4]_2$ , showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. C-bound H atoms have been omitted for clarity.

**Figure 2**

The crystal packing of (I), viewed approximately down the *a* axis.

### 2,2,6,6-Tetramethylpiperidinium pentachlorobenzenethiolate

#### Crystal data

$C_9H_{20}N^+ \cdot C_6Cl_5S^-$

$M_r = 423.63$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 8.4230$  (5) Å

$b = 10.5081$  (4) Å

$c = 11.6142$  (6) Å

$\alpha = 110.946$  (4)°

$\beta = 102.614$  (4)°

$\gamma = 95.286$  (4)°

$V = 920.39$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 436$

$D_x = 1.529$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6782 reflections

$\theta = 2.0\text{--}32.2^\circ$

$\mu = 0.90$  mm<sup>-1</sup>

$T = 120$  K

Prism, yellow

$0.21 \times 0.14 \times 0.09$  mm

#### Data collection

Oxford Diffraction KM4 CCD  
diffractometer

Graphite monochromator

Detector resolution: 8.1883 pixels mm<sup>-1</sup>

0.75° wide  $\omega$  scans

Absorption correction: analytical

(*CrysAlis RED*; Oxford Diffraction, 2006)

$T_{\min} = 0.779$ ,  $T_{\max} = 0.866$

5583 measured reflections

3161 independent reflections

2930 reflections with  $I > 2\sigma(I)$



$R_{\text{int}} = 0.019$   
 $\theta_{\text{max}} = 25.1^\circ$ ,  $\theta_{\text{min}} = 2.0^\circ$   
 $h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$   
 $l = -13 \rightarrow 10$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.097$   
 $S = 1.21$   
 3161 reflections  
 279 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.2069P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.67 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.44 \text{ e } \text{\AA}^{-3}$

### 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )

|     | $x$          | $y$          | $z$           | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| C11 | 0.93273 (6)  | 0.07455 (4)  | 0.24695 (4)   | 0.02718 (15)                     |
| C12 | 0.82093 (6)  | -0.14335 (4) | -0.03115 (4)  | 0.02729 (15)                     |
| C13 | 0.58390 (6)  | -0.08459 (5) | -0.24491 (4)  | 0.03127 (16)                     |
| C14 | 0.44756 (6)  | 0.19129 (5)  | -0.17487 (4)  | 0.02934 (15)                     |
| C15 | 0.57116 (6)  | 0.41671 (5)  | 0.09814 (4)   | 0.02804 (15)                     |
| S1  | 0.80012 (6)  | 0.36293 (4)  | 0.32284 (4)   | 0.02321 (15)                     |
| C1  | 0.7446 (2)   | 0.23869 (17) | 0.16726 (15)  | 0.0186 (4)                       |
| C2  | 0.7987 (2)   | 0.11030 (17) | 0.13157 (16)  | 0.0191 (4)                       |
| C3  | 0.7504 (2)   | 0.01128 (17) | 0.00666 (17)  | 0.0203 (4)                       |
| C4  | 0.6429 (2)   | 0.03617 (18) | -0.08959 (15) | 0.0211 (4)                       |
| C5  | 0.5855 (2)   | 0.16113 (18) | -0.05775 (16) | 0.0207 (4)                       |
| C6  | 0.6375 (2)   | 0.26039 (18) | 0.06694 (17)  | 0.0197 (4)                       |
| N1  | 0.89358 (18) | 0.38134 (15) | 0.61365 (13)  | 0.0176 (3)                       |
| C7  | 0.7556 (2)   | 0.43976 (19) | 0.66962 (16)  | 0.0238 (4)                       |
| C8  | 0.8123 (3)   | 0.4751 (2)   | 0.81401 (17)  | 0.0300 (4)                       |
| C9  | 0.8679 (2)   | 0.3550 (2)   | 0.84610 (18)  | 0.0309 (4)                       |
| C10 | 1.0115 (2)   | 0.31139 (19) | 0.79179 (17)  | 0.0246 (4)                       |
| C11 | 0.9685 (2)   | 0.26709 (17) | 0.64589 (16)  | 0.0208 (4)                       |
| C12 | 0.7388 (3)   | 0.5705 (2)   | 0.64296 (19)  | 0.0299 (4)                       |
| C13 | 0.5913 (2)   | 0.3374 (2)   | 0.60334 (19)  | 0.0309 (4)                       |
| C14 | 0.8482 (3)   | 0.12818 (19) | 0.57438 (19)  | 0.0281 (4)                       |
| C15 | 1.1256 (2)   | 0.25939 (19) | 0.60015 (18)  | 0.0252 (4)                       |

|      |           |           |             |            |
|------|-----------|-----------|-------------|------------|
| H14B | 0.758 (3) | 0.125 (2) | 0.611 (2)   | 0.030 (5)* |
| H13B | 0.566 (3) | 0.305 (2) | 0.510 (2)   | 0.029 (5)* |
| H15C | 1.177 (2) | 0.190 (2) | 0.6161 (19) | 0.025 (5)* |
| H13A | 0.511 (3) | 0.388 (3) | 0.627 (2)   | 0.039 (6)* |
| H13C | 0.586 (3) | 0.253 (3) | 0.622 (2)   | 0.036 (6)* |
| H14A | 0.802 (3) | 0.112 (2) | 0.486 (2)   | 0.026 (5)* |
| H15A | 1.208 (3) | 0.347 (2) | 0.6435 (19) | 0.022 (5)* |
| H15B | 1.102 (3) | 0.235 (2) | 0.513 (2)   | 0.037 (6)* |
| H14C | 0.908 (3) | 0.061 (2) | 0.580 (2)   | 0.034 (6)* |
| H12B | 0.838 (3) | 0.636 (3) | 0.679 (3)   | 0.049 (7)* |
| H10B | 1.046 (3) | 0.235 (2) | 0.808 (2)   | 0.031 (5)* |
| H10A | 1.105 (3) | 0.388 (2) | 0.8295 (19) | 0.026 (5)* |
| H12C | 0.703 (3) | 0.549 (2) | 0.552 (2)   | 0.029 (5)* |
| H9B  | 0.780 (3) | 0.277 (2) | 0.810 (2)   | 0.035 (6)* |
| H1B  | 0.974 (3) | 0.452 (2) | 0.640 (2)   | 0.024 (5)* |
| H12A | 0.661 (3) | 0.616 (2) | 0.682 (2)   | 0.032 (6)* |
| H1A  | 0.860 (3) | 0.349 (2) | 0.528 (2)   | 0.024 (5)* |
| H9A  | 0.896 (3) | 0.382 (2) | 0.935 (2)   | 0.032 (5)* |
| H8A  | 0.906 (3) | 0.553 (2) | 0.851 (2)   | 0.025 (5)* |
| H8B  | 0.728 (3) | 0.501 (2) | 0.846 (2)   | 0.040 (6)* |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$      | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|---------------|--------------|
| C11 | 0.0345 (3)  | 0.0226 (2)  | 0.0221 (2)  | 0.00649 (19) | -0.00126 (19) | 0.01083 (18) |
| C12 | 0.0355 (3)  | 0.0198 (2)  | 0.0260 (3)  | 0.00788 (19) | 0.0098 (2)    | 0.0066 (2)   |
| C13 | 0.0350 (3)  | 0.0329 (3)  | 0.0166 (2)  | 0.0010 (2)   | 0.00332 (19)  | 0.00236 (19) |
| C14 | 0.0234 (3)  | 0.0430 (3)  | 0.0236 (2)  | 0.0058 (2)   | 0.00059 (19)  | 0.0187 (2)   |
| C15 | 0.0284 (3)  | 0.0250 (3)  | 0.0323 (3)  | 0.01072 (19) | 0.0055 (2)    | 0.0130 (2)   |
| S1  | 0.0333 (3)  | 0.0174 (2)  | 0.0158 (2)  | 0.00052 (18) | 0.00399 (19)  | 0.00531 (18) |
| C1  | 0.0201 (8)  | 0.0188 (8)  | 0.0169 (8)  | -0.0004 (6)  | 0.0056 (7)    | 0.0075 (7)   |
| C2  | 0.0193 (8)  | 0.0206 (8)  | 0.0187 (8)  | 0.0019 (7)   | 0.0038 (7)    | 0.0105 (7)   |
| C3  | 0.0212 (9)  | 0.0178 (8)  | 0.0223 (9)  | 0.0012 (7)   | 0.0072 (7)    | 0.0081 (7)   |
| C4  | 0.0215 (9)  | 0.0241 (9)  | 0.0144 (8)  | -0.0020 (7)  | 0.0050 (7)    | 0.0052 (7)   |
| C5  | 0.0156 (8)  | 0.0294 (9)  | 0.0195 (8)  | 0.0016 (7)   | 0.0032 (7)    | 0.0139 (7)   |
| C6  | 0.0184 (8)  | 0.0200 (8)  | 0.0227 (8)  | 0.0023 (6)   | 0.0066 (7)    | 0.0104 (7)   |
| N1  | 0.0209 (8)  | 0.0174 (7)  | 0.0148 (7)  | 0.0040 (6)   | 0.0035 (6)    | 0.0072 (6)   |
| C7  | 0.0224 (9)  | 0.0317 (9)  | 0.0188 (8)  | 0.0106 (7)   | 0.0067 (7)    | 0.0094 (7)   |
| C8  | 0.0248 (10) | 0.0456 (12) | 0.0189 (9)  | 0.0122 (9)   | 0.0069 (8)    | 0.0097 (8)   |
| C9  | 0.0293 (10) | 0.0452 (12) | 0.0177 (9)  | 0.0010 (9)   | 0.0032 (8)    | 0.0150 (8)   |
| C10 | 0.0260 (10) | 0.0246 (9)  | 0.0227 (9)  | 0.0028 (8)   | 0.0004 (7)    | 0.0126 (7)   |
| C11 | 0.0239 (9)  | 0.0182 (8)  | 0.0209 (8)  | 0.0057 (7)   | 0.0025 (7)    | 0.0100 (7)   |
| C12 | 0.0333 (11) | 0.0302 (10) | 0.0270 (10) | 0.0163 (9)   | 0.0078 (9)    | 0.0098 (8)   |
| C13 | 0.0206 (10) | 0.0465 (12) | 0.0268 (10) | 0.0061 (9)   | 0.0032 (8)    | 0.0175 (9)   |
| C14 | 0.0321 (11) | 0.0211 (9)  | 0.0284 (10) | 0.0008 (8)   | 0.0012 (8)    | 0.0117 (8)   |
| C15 | 0.0267 (10) | 0.0222 (9)  | 0.0243 (10) | 0.0086 (8)   | 0.0036 (8)    | 0.0073 (8)   |

*Geometric parameters (Å, °)*

|            |             |               |             |
|------------|-------------|---------------|-------------|
| C11—C2     | 1.7286 (16) | C8—H8B        | 0.89 (3)    |
| C12—C3     | 1.7228 (18) | C9—C10        | 1.516 (3)   |
| C13—C4     | 1.7225 (16) | C9—H9B        | 0.95 (2)    |
| C14—C5     | 1.7283 (16) | C9—H9A        | 0.94 (2)    |
| C15—C6     | 1.7246 (18) | C10—C11       | 1.535 (2)   |
| S1—C1      | 1.7377 (16) | C10—H10B      | 0.94 (2)    |
| C1—C6      | 1.411 (2)   | C10—H10A      | 0.97 (2)    |
| C1—C2      | 1.413 (2)   | C11—C15       | 1.528 (3)   |
| C2—C3      | 1.392 (2)   | C11—C14       | 1.530 (2)   |
| C3—C4      | 1.396 (3)   | C12—H12B      | 0.94 (3)    |
| C4—C5      | 1.394 (3)   | C12—H12C      | 0.96 (2)    |
| C5—C6      | 1.391 (2)   | C12—H12A      | 0.95 (3)    |
| N1—C7      | 1.525 (2)   | C13—H13B      | 0.98 (2)    |
| N1—C11     | 1.529 (2)   | C13—H13A      | 0.92 (3)    |
| N1—H1B     | 0.87 (2)    | C13—H13C      | 0.98 (2)    |
| N1—H1A     | 0.90 (2)    | C14—H14B      | 0.95 (2)    |
| C7—C12     | 1.524 (3)   | C14—H14A      | 0.96 (2)    |
| C7—C13     | 1.528 (3)   | C14—H14C      | 0.91 (3)    |
| C7—C8      | 1.533 (2)   | C15—H15C      | 0.94 (2)    |
| C8—C9      | 1.524 (3)   | C15—H15A      | 0.99 (2)    |
| C8—H8A     | 0.98 (2)    | C15—H15B      | 0.93 (2)    |
|            |             |               |             |
| C6—C1—C2   | 115.27 (15) | C10—C9—H9A    | 111.4 (14)  |
| C6—C1—S1   | 120.91 (13) | C8—C9—H9A     | 108.9 (13)  |
| C2—C1—S1   | 123.81 (13) | H9B—C9—H9A    | 108.0 (19)  |
| C3—C2—C1   | 122.83 (15) | C9—C10—C11    | 112.65 (15) |
| C3—C2—C11  | 118.24 (13) | C9—C10—H10B   | 112.4 (14)  |
| C1—C2—C11  | 118.93 (13) | C11—C10—H10B  | 105.7 (13)  |
| C2—C3—C4   | 120.12 (16) | C9—C10—H10A   | 109.9 (12)  |
| C2—C3—C12  | 120.71 (13) | C11—C10—H10A  | 107.8 (12)  |
| C4—C3—C12  | 119.16 (14) | H10B—C10—H10A | 108.1 (18)  |
| C5—C4—C3   | 118.69 (16) | C15—C11—N1    | 105.70 (13) |
| C5—C4—C13  | 120.68 (13) | C15—C11—C14   | 109.75 (15) |
| C3—C4—C13  | 120.62 (14) | N1—C11—C14    | 110.28 (14) |
| C6—C5—C4   | 120.59 (16) | C15—C11—C10   | 110.55 (14) |
| C6—C5—C14  | 120.17 (14) | N1—C11—C10    | 107.83 (13) |
| C4—C5—C14  | 119.24 (13) | C14—C11—C10   | 112.49 (15) |
| C5—C6—C1   | 122.46 (16) | C7—C12—H12B   | 112.2 (16)  |
| C5—C6—C15  | 118.30 (13) | C7—C12—H12C   | 111.0 (13)  |
| C1—C6—C15  | 119.22 (13) | H12B—C12—H12C | 109 (2)     |
| C7—N1—C11  | 120.66 (13) | C7—C12—H12A   | 110.5 (14)  |
| C7—N1—H1B  | 104.8 (14)  | H12B—C12—H12A | 105 (2)     |
| C11—N1—H1B | 106.9 (14)  | H12C—C12—H12A | 108.8 (19)  |
| C7—N1—H1A  | 109.8 (13)  | C7—C13—H13B   | 111.6 (12)  |
| C11—N1—H1A | 106.0 (13)  | C7—C13—H13A   | 105.4 (15)  |
| H1B—N1—H1A | 108.1 (18)  | H13B—C13—H13A | 106 (2)     |

|            |             |               |            |
|------------|-------------|---------------|------------|
| C12—C7—N1  | 106.27 (15) | C7—C13—H13C   | 114.9 (13) |
| C12—C7—C13 | 108.56 (16) | H13B—C13—H13C | 105.8 (18) |
| N1—C7—C13  | 110.89 (15) | H13A—C13—H13C | 113 (2)    |
| C12—C7—C8  | 110.81 (16) | C11—C14—H14B  | 111.3 (13) |
| N1—C7—C8   | 106.89 (14) | C11—C14—H14A  | 111.4 (12) |
| C13—C7—C8  | 113.20 (16) | H14B—C14—H14A | 107.1 (18) |
| C9—C8—C7   | 113.09 (16) | C11—C14—H14C  | 106.6 (14) |
| C9—C8—H8A  | 108.4 (12)  | H14B—C14—H14C | 111 (2)    |
| C7—C8—H8A  | 107.6 (12)  | H14A—C14—H14C | 109.9 (19) |
| C9—C8—H8B  | 110.8 (15)  | C11—C15—H15C  | 110.0 (12) |
| C7—C8—H8B  | 107.1 (15)  | C11—C15—H15A  | 113.3 (12) |
| H8A—C8—H8B | 110 (2)     | H15C—C15—H15A | 107.1 (17) |
| C10—C9—C8  | 110.57 (16) | C11—C15—H15B  | 111.8 (14) |
| C10—C9—H9B | 107.8 (14)  | H15C—C15—H15B | 105.8 (19) |
| C8—C9—H9B  | 110.1 (14)  | H15A—C15—H15B | 108.5 (18) |

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i>                | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|-------------------------------|------------|--------------|--------------|----------------|
| N1—H1B...S1 <sup>i</sup>      | 0.87 (2)   | 2.44 (2)     | 3.301 (2)    | 170 (2)        |
| N1—H1A...S1                   | 0.90 (2)   | 2.39 (2)     | 3.226 (2)    | 157 (2)        |
| C14—H14C...C11 <sup>ii</sup>  | 0.91 (3)   | 3.02 (2)     | 3.803 (2)    | 145 (2)        |
| C15—H15B...C11                | 0.93 (2)   | 2.88 (2)     | 3.748 (2)    | 156 (2)        |
| C13—H13B...C13 <sup>iii</sup> | 0.98 (2)   | 3.02 (2)     | 3.905 (2)    | 151 (2)        |
| C13—H13C...C14 <sup>iv</sup>  | 0.98 (2)   | 3.08 (2)     | 3.782 (2)    | 129 (2)        |
| C9—H9B...C14 <sup>iv</sup>    | 0.95 (2)   | 2.92 (2)     | 3.708 (2)    | 141 (2)        |
| C15—H15C...C14 <sup>v</sup>   | 0.94 (2)   | 2.94 (2)     | 3.646 (2)    | 133 (2)        |
| C8—H8B...C15 <sup>vi</sup>    | 0.89 (3)   | 2.87 (3)     | 3.748 (2)    | 169 (2)        |
| C10—H10A...C15 <sup>i</sup>   | 0.97 (2)   | 3.02 (2)     | 3.966 (2)    | 167 (2)        |

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