Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Chlorothiazide dimethyl sulfoxide solvate

**Andrea Johnston,[a] Alastair J. Florence,[a]* Philippe Fernandes[a] and Alan R. Kennedy[b]**

[a]Solid-State Research Group, Strathclyde Institute of Pharmacy and Biomedical Sciences, The John Arbuthnott Building, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, and [b]WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland
Correspondence e-mail: alastair.florence@strath.ac.uk

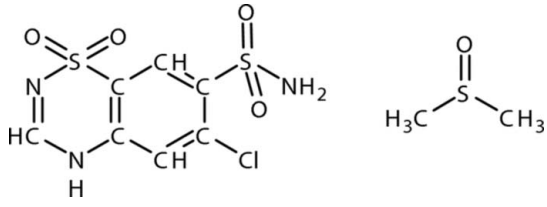
Received 29 March 2007; accepted 3 April 2007

Key indicators: single-crystal X-ray study; $T$ = 123 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.043; $wR$ factor = 0.112; data-to-parameter ratio = 15.7.

Chlorothiazide forms a 1:1 solvate with dimethyl sulfoxide (systematic name: 6-chloro-4*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide dimethyl sulfoxide solvate), $C_7H_6ClN_3O_4S_2{\cdot}C_2H_6OS$. The compound crystallizes with two molecules of solvent and two molecules of chlorothiazide in the asymmetric unit and displays an extensive network of hydrogen bonds.

## Related literature

For details on experimental methods used to obtain this form, see: Florence *et al.* (2003, 2006). For related literature on chlorothiazide, see: Dupont & Dideberg (1970), Shankland *et al.* (1997) and Johnston, Florence, Fernandes *et al.* (2007). Intermolecular interactions in polymorphs and solvates of the related thiazide diuretic hydrochlorothiazide have also been studied (Johnston, Florence, Shankland *et al.*, 2007).



## Experimental

### *Crystal data*

$C_7H_6ClN_3O_4S_2{\cdot}C_2H_6OS$
$M_r$ = 373.85
Triclinic, $P\overline{1}$
$a$ = 9.0965 (3) Å
$b$ = 11.2081 (4) Å
$c$ = 15.8916 (5) Å
$\alpha$ = 109.009 (2)°
$\beta$ = 103.384 (2)°
$\gamma$ = 96.246 (2)°
$V$ = 1460.07 (9) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.71 mm$^{-1}$
$T$ = 123 (2) K
0.25 × 0.25 × 0.15 mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
36041 measured reflections
6400 independent reflections
4748 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.057

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.112
$S$ = 1.04
6400 reflections
407 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.71 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.52 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H1N···O5 | 0.80 (3) | 1.92 (3) | 2.704 (3) | 168 (3) |
| N1—HN···N3$A^{i}$ | 0.83 (3) | 2.24 (4) | 3.055 (4) | 167 (3) |
| N1—H3N···O5$^{ii}$ | 0.80 (3) | 2.04 (3) | 2.821 (3) | 164 (3) |
| N2$A$—H4N···O5$A^{iii}$ | 0.78 (3) | 1.94 (3) | 2.714 (3) | 171 (3) |
| N1$A$—H5N···N3$^{iv}$ | 0.78 (3) | 2.27 (4) | 3.020 (3) | 162 (3) |
| N1$A$—H6N···O5$A^{v}$ | 0.85 (3) | 2.03 (3) | 2.865 (3) | 167 (3) |

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

Data collection: *COLLECT* (Nonius, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997; software used to prepare material for publication: *SHELXL97*.

The authors thank the Basic Technology Programme of the UK Research Councils for funding this work under the project Control and Prediction of the Organic Solid State (http://www.cposs.org.uk).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2266).

## References

Dupont, L. & Dideberg, O. (1970). *Acta Cryst.* B**26**, 1884–1885.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Florence, A. J., Baumgartner, B., Weston, C., Shankland, N., Kennedy, A. R., Shankland, K. & David, W. I. F. (2003). *J. Pharm. Sci.* **92**, 1930–1938.
Florence, A. J., Johnston, A., Fernandes, P., Shankland, N. & Shankland, K. (2006). *J. Appl. Cryst.* **39**, 922–924.
Johnston, A., Florence, A. J., Fernandes, P. & Kennedy, A. R. (2007). *Acta Cryst.* E**63**, o2422.
Johnston, A., Florence, A. J., Shankland, N., Kennedy, A. R., Shankland, K. & Price, S. L. (2007). *Cryst. Growth Des.* **7**, 705–712.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Shankland, K., David, W. I. F. & Sivia, D. S. (1997). *J. Mater. Chem.* **7**, 569–572.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

 doi:10.1107/S1600536807016406  

# supplementary materials

*Acta Cryst.* (2007). E**63**, o2423 [ **doi:10.1107/S1600536807016406** ]

# Chlorothiazide dimethyl sulfoxide solvate

**A. Johnston, A. J. Florence, P. Fernandes and A. R. Kennedy**

## Comment

The title compound, (I), was synthesized by the same method as the similar compound chlorothiazide *N*,*N*-dimethylacetamide solvate (1/2) (Johnston, Florence, Fernandes *et al.*, 2007). Here, we report the crystal structure of (I) determined by single-crystal X-ray diffraction (Fig. 1).

The molecules of (I) crystallize in space group $P\bar{1}$ with two chlorothiazide (CT) and two dimethyl sulfoxide (DMSO) molecules in the asymmetric unit. Bond lengths and angles in the chlorothiazide group of (I) are

comparable with those of the related compound chlorothiazide *N*,*N*-dimethylacetamide solvate (1/2) (Johnston, Florence, Fernandes *et al.*, 2007).

Hydrogen-bonded chains of CT molecules are formed via contacts 2 and 5 (Table 1) and connected to adjacent DMSO molecules *via* contacts 1, 3, 4 and 6 to form a layered structure of alternating CT and DMSO molecules (Fig. 2).

## Experimental

A single-crystal sample of the title compound, (I), was recrystallized from a saturated solution in dimethyl sulfoxide by isothermal solvent evaporation at 278 K.

## Refinement

H atoms bonded to N atoms were found in a difference synthesis and refined freely, but all other H atoms were constrained to idealised geometry using riding models, with C—H = 0.95–0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

## Figures

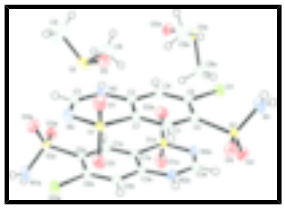


Fig. 1. The asymmetric unit of (I), showing 50% probablility displacement ellipsoids.

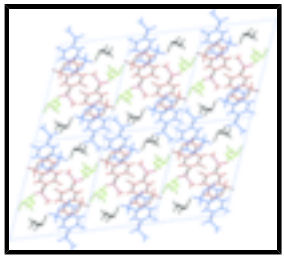


Fig. 2. A packing diagram for (I), showing alternating layers of CT and DMSO molecules, viewed down the b axis. Molecules are coloured by symmetry equivalence.

### 6-chloro-4*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide dimethyl sulfoxide solvate

*Crystal data*

| | |
|---|---|
| $C_7H_6ClN_3O_4S_2·C_2H_6OS$ | $Z = 4$ |
| $M_r = 373.85$ | $F_{000} = 768$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.701$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 9.0965$ (3) Å | Cell parameters from 6375 reflections |
| $b = 11.2081$ (4) Å | $\theta = 2.9$–$27.1°$ |
| $c = 15.8916$ (5) Å | $\mu = 0.71$ mm$^{-1}$ |
| $\alpha = 109.009$ (2)° | $T = 123$ (2) K |
| $\beta = 103.384$ (2)° | Cut block, colourless |
| $\gamma = 96.246$ (2)° | 0.25 × 0.25 × 0.15 mm |
| $V = 1460.07$ (9) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD area-detector diffractometer | 4748 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.057$ |
| Monochromator: graphite | $\theta_{max} = 27.1°$ |
| $T = 123(2)$ K | $\theta_{min} = 3.1°$ |
| φ and ω scans | $h = -11 \rightarrow 11$ |
| Absorption correction: none | $k = -14 \rightarrow 14$ |
| 36041 measured reflections | $l = -20 \rightarrow 20$ |
| 6400 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H atoms treated by a mixture of independent and constrained refinement |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 1.3342P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $wR(F^2) = 0.112$ | $\Delta\rho_{max} = 0.71$ e Å$^{-3}$ |
| $S = 1.04$ | $\Delta\rho_{min} = -0.52$ e Å$^{-3}$ |
| 6400 reflections | Extinction correction: none |

407 parameters
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.78822 (8) | 0.54314 (6) | 0.48340 (5) | 0.02664 (17) |
| Cl1A | 0.22271 (8) | −0.04500 (6) | 0.02658 (5) | 0.02603 (17) |
| S1 | 0.19851 (7) | 0.10617 (6) | 0.29501 (5) | 0.02128 (16) |
| S1A | 0.78675 (8) | 0.41554 (6) | 0.19570 (5) | 0.02323 (17) |
| S2 | 0.76779 (8) | 0.28008 (6) | 0.53626 (5) | 0.02136 (16) |
| S2A | 0.22252 (8) | 0.19926 (6) | −0.04620 (5) | 0.02154 (16) |
| O1 | 0.1121 (2) | 0.12083 (19) | 0.36173 (13) | 0.0280 (5) |
| O1A | 0.8685 (2) | 0.4035 (2) | 0.12706 (14) | 0.0349 (5) |
| O3 | 0.2377 (2) | −0.01677 (18) | 0.25809 (14) | 0.0315 (5) |
| O3A | 0.7356 (2) | 0.53353 (18) | 0.22984 (15) | 0.0365 (5) |
| O2 | 0.8963 (2) | 0.27955 (18) | 0.49818 (13) | 0.0257 (4) |
| O2A | 0.2797 (2) | 0.30466 (18) | −0.06949 (13) | 0.0270 (4) |
| O4 | 0.7018 (2) | 0.16690 (18) | 0.54795 (13) | 0.0270 (4) |
| O4A | 0.0953 (2) | 0.2041 (2) | −0.00693 (13) | 0.0289 (5) |
| N3 | 0.0993 (3) | 0.1405 (2) | 0.20961 (16) | 0.0241 (5) |
| N3A | 0.8968 (3) | 0.3918 (2) | 0.28270 (15) | 0.0242 (5) |
| N2 | 0.2675 (3) | 0.3372 (2) | 0.24384 (16) | 0.0209 (5) |
| N2A | 0.7405 (3) | 0.1942 (2) | 0.26051 (16) | 0.0211 (5) |
| N1 | 0.8120 (3) | 0.3972 (3) | 0.63228 (18) | 0.0299 (6) |
| N1A | 0.1847 (3) | 0.0712 (3) | −0.13469 (18) | 0.0278 (6) |
| C3 | 0.1405 (3) | 0.2460 (3) | 0.19625 (18) | 0.0227 (6) |
| H3 | 0.0724 | 0.2600 | 0.1468 | 0.027* |
| C3A | 0.8641 (3) | 0.2898 (3) | 0.30293 (18) | 0.0229 (6) |
| H3A | 0.9369 | 0.2828 | 0.3538 | 0.027* |
| C2 | 0.3815 (3) | 0.3307 (2) | 0.31655 (18) | 0.0190 (5) |
| C2A | 0.6220 (3) | 0.1890 (2) | 0.18582 (18) | 0.0182 (5) |
| C7 | 0.3671 (3) | 0.2252 (2) | 0.34459 (18) | 0.0190 (5) |

| | | | | |
|---|---|---|---|---|
| C7A | 0.6268 (3) | 0.2885 (2) | 0.15053 (18) | 0.0190 (5) |
| C1 | 0.4842 (3) | 0.2148 (2) | 0.41370 (18) | 0.0199 (6) |
| H1 | 0.4739 | 0.1415 | 0.4311 | 0.024* |
| C1A | 0.5055 (3) | 0.2868 (2) | 0.07812 (18) | 0.0206 (6) |
| H1A | 0.5092 | 0.3555 | 0.0556 | 0.025* |
| C5 | 0.6158 (3) | 0.3102 (2) | 0.45738 (18) | 0.0199 (6) |
| C5A | 0.3796 (3) | 0.1857 (2) | 0.03880 (18) | 0.0193 (5) |
| C6 | 0.6271 (3) | 0.4191 (2) | 0.43066 (19) | 0.0209 (6) |
| C6A | 0.3772 (3) | 0.0845 (2) | 0.07322 (18) | 0.0193 (5) |
| C4 | 0.5130 (3) | 0.4285 (2) | 0.36100 (18) | 0.0202 (6) |
| H4 | 0.5234 | 0.5013 | 0.3431 | 0.024* |
| C4A | 0.4955 (3) | 0.0863 (2) | 0.14576 (18) | 0.0211 (6) |
| H4A | 0.4911 | 0.0178 | 0.1685 | 0.025* |
| S3A | 0.81126 (9) | 0.94876 (7) | 0.38266 (5) | 0.02774 (18) |
| S3 | 0.27965 (11) | 0.58546 (7) | 0.12608 (5) | 0.0363 (2) |
| O5A | 0.7186 (2) | 0.97587 (18) | 0.29982 (13) | 0.0262 (4) |
| O5 | 0.3151 (2) | 0.56294 (19) | 0.21714 (14) | 0.0292 (5) |
| C8A | 0.9157 (3) | 0.8318 (3) | 0.3362 (2) | 0.0341 (7) |
| H8A | 0.8484 | 0.7661 | 0.2784 | 0.051* |
| H9A | 0.9523 | 0.7911 | 0.3810 | 0.051* |
| H10A | 1.0041 | 0.8733 | 0.3234 | 0.051* |
| C9A | 0.6747 (4) | 0.8466 (3) | 0.4064 (3) | 0.0450 (9) |
| H11A | 0.5953 | 0.8932 | 0.4249 | 0.068* |
| H12A | 0.7274 | 0.8207 | 0.4569 | 0.068* |
| H13A | 0.6264 | 0.7698 | 0.3506 | 0.068* |
| C8 | 0.4120 (4) | 0.7282 (4) | 0.1481 (3) | 0.0505 (10) |
| H8 | 0.4029 | 0.7971 | 0.2024 | 0.076* |
| H9 | 0.3889 | 0.7540 | 0.0940 | 0.076* |
| H10 | 0.5173 | 0.7122 | 0.1602 | 0.076* |
| C9 | 0.1108 (4) | 0.6518 (4) | 0.1194 (3) | 0.0667 (13) |
| H11 | 0.0234 | 0.5871 | 0.1133 | 0.100* |
| H12 | 0.0894 | 0.6777 | 0.0652 | 0.100* |
| H13 | 0.1263 | 0.7271 | 0.1758 | 0.100* |
| H1N | 0.286 (4) | 0.398 (3) | 0.230 (2) | 0.033 (9)* |
| H2N | 0.893 (4) | 0.450 (3) | 0.647 (2) | 0.033 (9)* |
| H3N | 0.771 (4) | 0.393 (3) | 0.671 (2) | 0.034 (10)* |
| H4N | 0.737 (3) | 0.137 (3) | 0.2779 (19) | 0.015 (7)* |
| H5N | 0.110 (4) | 0.023 (3) | −0.142 (2) | 0.034 (10)* |
| H6N | 0.218 (3) | 0.070 (3) | −0.180 (2) | 0.016 (7)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0221 (4) | 0.0211 (3) | 0.0306 (4) | −0.0037 (3) | 0.0022 (3) | 0.0076 (3) |
| Cl1A | 0.0214 (3) | 0.0224 (3) | 0.0289 (4) | −0.0054 (3) | 0.0015 (3) | 0.0092 (3) |
| S1 | 0.0168 (3) | 0.0201 (3) | 0.0228 (4) | −0.0013 (3) | 0.0014 (3) | 0.0070 (3) |
| S1A | 0.0189 (3) | 0.0203 (3) | 0.0263 (4) | −0.0031 (3) | 0.0010 (3) | 0.0091 (3) |
| S2 | 0.0173 (3) | 0.0231 (3) | 0.0218 (3) | 0.0016 (3) | 0.0023 (3) | 0.0088 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| S2A | 0.0176 (3) | 0.0250 (4) | 0.0207 (3) | 0.0028 (3) | 0.0023 (3) | 0.0091 (3) |
| O1 | 0.0211 (10) | 0.0343 (11) | 0.0279 (11) | −0.0017 (8) | 0.0057 (8) | 0.0136 (9) |
| O1A | 0.0268 (11) | 0.0451 (13) | 0.0325 (12) | −0.0064 (10) | 0.0055 (9) | 0.0200 (10) |
| O3 | 0.0284 (11) | 0.0214 (10) | 0.0351 (12) | −0.0002 (8) | 0.0002 (9) | 0.0059 (9) |
| O3A | 0.0334 (12) | 0.0166 (10) | 0.0472 (13) | −0.0003 (9) | −0.0024 (10) | 0.0071 (9) |
| O2 | 0.0196 (10) | 0.0315 (11) | 0.0273 (11) | 0.0065 (8) | 0.0064 (8) | 0.0122 (9) |
| O2A | 0.0268 (11) | 0.0277 (11) | 0.0263 (11) | 0.0024 (8) | 0.0019 (8) | 0.0143 (9) |
| O4 | 0.0218 (10) | 0.0277 (11) | 0.0308 (11) | 0.0024 (8) | 0.0007 (8) | 0.0153 (9) |
| O4A | 0.0236 (11) | 0.0397 (12) | 0.0264 (11) | 0.0099 (9) | 0.0073 (9) | 0.0146 (9) |
| N3 | 0.0201 (12) | 0.0270 (12) | 0.0209 (12) | −0.0008 (10) | 0.0007 (9) | 0.0084 (10) |
| N3A | 0.0196 (12) | 0.0273 (13) | 0.0215 (12) | 0.0003 (10) | 0.0006 (9) | 0.0084 (10) |
| N2 | 0.0216 (12) | 0.0206 (12) | 0.0214 (12) | 0.0030 (10) | 0.0045 (10) | 0.0104 (10) |
| N2A | 0.0224 (12) | 0.0209 (12) | 0.0215 (12) | 0.0042 (10) | 0.0043 (10) | 0.0111 (10) |
| N1 | 0.0252 (14) | 0.0360 (15) | 0.0227 (14) | −0.0042 (12) | 0.0053 (12) | 0.0078 (12) |
| N1A | 0.0253 (14) | 0.0313 (14) | 0.0202 (13) | −0.0058 (11) | 0.0050 (11) | 0.0055 (11) |
| C3 | 0.0208 (14) | 0.0291 (15) | 0.0196 (14) | 0.0077 (12) | 0.0052 (11) | 0.0102 (12) |
| C3A | 0.0186 (14) | 0.0289 (15) | 0.0188 (14) | 0.0052 (11) | 0.0028 (11) | 0.0072 (11) |
| C2 | 0.0184 (13) | 0.0211 (13) | 0.0195 (13) | 0.0060 (11) | 0.0073 (11) | 0.0079 (11) |
| C2A | 0.0164 (13) | 0.0195 (13) | 0.0195 (13) | 0.0039 (10) | 0.0066 (10) | 0.0068 (10) |
| C7 | 0.0181 (13) | 0.0186 (13) | 0.0199 (13) | 0.0034 (10) | 0.0060 (11) | 0.0060 (11) |
| C7A | 0.0169 (13) | 0.0172 (13) | 0.0197 (13) | −0.0001 (10) | 0.0034 (11) | 0.0050 (10) |
| C1 | 0.0181 (13) | 0.0204 (13) | 0.0221 (14) | 0.0027 (11) | 0.0064 (11) | 0.0088 (11) |
| C1A | 0.0236 (14) | 0.0183 (13) | 0.0212 (14) | 0.0039 (11) | 0.0066 (11) | 0.0088 (11) |
| C5 | 0.0180 (13) | 0.0223 (14) | 0.0184 (13) | 0.0033 (11) | 0.0044 (11) | 0.0067 (11) |
| C5A | 0.0183 (13) | 0.0201 (13) | 0.0187 (13) | 0.0039 (10) | 0.0043 (11) | 0.0066 (11) |
| C6 | 0.0160 (13) | 0.0176 (13) | 0.0247 (14) | −0.0016 (10) | 0.0049 (11) | 0.0043 (11) |
| C6A | 0.0165 (13) | 0.0160 (12) | 0.0216 (14) | −0.0007 (10) | 0.0042 (11) | 0.0040 (10) |
| C4 | 0.0205 (14) | 0.0176 (13) | 0.0245 (14) | 0.0032 (10) | 0.0084 (11) | 0.0090 (11) |
| C4A | 0.0221 (14) | 0.0189 (13) | 0.0235 (14) | 0.0034 (11) | 0.0069 (11) | 0.0090 (11) |
| S3A | 0.0363 (4) | 0.0231 (4) | 0.0237 (4) | 0.0067 (3) | 0.0045 (3) | 0.0110 (3) |
| S3 | 0.0579 (6) | 0.0253 (4) | 0.0265 (4) | 0.0114 (4) | 0.0091 (4) | 0.0116 (3) |
| O5A | 0.0290 (11) | 0.0280 (11) | 0.0263 (11) | 0.0083 (9) | 0.0067 (9) | 0.0161 (9) |
| O5 | 0.0310 (11) | 0.0316 (11) | 0.0303 (11) | 0.0071 (9) | 0.0087 (9) | 0.0178 (9) |
| C8A | 0.0271 (16) | 0.0289 (16) | 0.0469 (19) | 0.0074 (13) | 0.0046 (14) | 0.0178 (14) |
| C9A | 0.053 (2) | 0.052 (2) | 0.050 (2) | 0.0162 (18) | 0.0238 (18) | 0.0367 (18) |
| C8 | 0.041 (2) | 0.063 (2) | 0.073 (3) | 0.0148 (18) | 0.0268 (19) | 0.048 (2) |
| C9 | 0.029 (2) | 0.072 (3) | 0.114 (4) | 0.0059 (19) | 0.003 (2) | 0.067 (3) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C6 | 1.736 (3) | N1A—H5N | 0.78 (4) |
| Cl1A—C6A | 1.733 (3) | N1A—H6N | 0.84 (3) |
| S1—O1 | 1.439 (2) | N2A—H4N | 0.78 (3) |
| S1—N3 | 1.629 (3) | C1—C7 | 1.387 (4) |
| S1—C7 | 1.750 (3) | C1—C5 | 1.383 (4) |
| S1—O3 | 1.431 (2) | C2—C4 | 1.397 (4) |
| S2—O2 | 1.435 (2) | C2—C7 | 1.397 (3) |
| S2—N1 | 1.584 (3) | C4—C6 | 1.372 (4) |
| S2—C5 | 1.781 (3) | C5—C6 | 1.418 (4) |

| | | | |
|---|---|---|---|
| S2—O4 | 1.430 (2) | C1—H1 | 0.9500 |
| S1A—O1A | 1.436 (2) | C3—H3 | 0.9500 |
| S1A—O3A | 1.429 (2) | C4—H4 | 0.9500 |
| S1A—N3A | 1.625 (2) | C1A—C7A | 1.391 (4) |
| S1A—C7A | 1.749 (3) | C1A—C5A | 1.382 (4) |
| S2A—O2A | 1.430 (2) | C2A—C7A | 1.403 (3) |
| S2A—O4A | 1.434 (2) | C2A—C4A | 1.396 (4) |
| S2A—N1A | 1.584 (3) | C4A—C6A | 1.376 (4) |
| S2A—C5A | 1.782 (3) | C5A—C6A | 1.411 (3) |
| S3A—C8A | 1.770 (3) | C1A—H1A | 0.9500 |
| S3A—C9A | 1.785 (4) | C3A—H3A | 0.9500 |
| S3A—O5A | 1.529 (2) | C4A—H4A | 0.9500 |
| S3—O5 | 1.517 (2) | C8A—H10A | 0.9800 |
| S3—C8 | 1.776 (5) | C8A—H8A | 0.9800 |
| S3—C9 | 1.774 (4) | C8A—H9A | 0.9800 |
| N2—C3 | 1.337 (4) | C9A—H11A | 0.9800 |
| N2—C2 | 1.390 (4) | C9A—H12A | 0.9800 |
| N3—C3 | 1.299 (4) | C9A—H13A | 0.9800 |
| N1—H3N | 0.80 (3) | C8—H8 | 0.9800 |
| N1—H2N | 0.83 (4) | C8—H9 | 0.9800 |
| N2—H1N | 0.79 (4) | C8—H10 | 0.9800 |
| N2A—C3A | 1.335 (4) | C9—H11 | 0.9800 |
| N2A—C2A | 1.387 (4) | C9—H12 | 0.9800 |
| N3A—C3A | 1.307 (4) | C9—H13 | 0.9800 |
| O1—S1—O3 | 117.17 (13) | Cl1—C6—C5 | 120.9 (2) |
| O1—S1—N3 | 107.46 (13) | S1—C7—C1 | 119.00 (19) |
| O1—S1—C7 | 108.53 (13) | S1—C7—C2 | 120.4 (2) |
| O3—S1—N3 | 108.83 (13) | C1—C7—C2 | 120.6 (2) |
| O3—S1—C7 | 109.21 (12) | C7—C1—H1 | 120.00 |
| N3—S1—C7 | 104.96 (13) | C5—C1—H1 | 120.00 |
| O2—S2—O4 | 120.13 (13) | N3—C3—H3 | 116.00 |
| O2—S2—N1 | 108.54 (14) | N2—C3—H3 | 116.00 |
| O2—S2—C5 | 105.75 (12) | C2—C4—H4 | 120.00 |
| O4—S2—N1 | 108.97 (15) | C6—C4—H4 | 120.00 |
| O4—S2—C5 | 104.86 (12) | C5A—C1A—C7A | 120.4 (2) |
| N1—S2—C5 | 107.96 (14) | N2A—C2A—C4A | 120.7 (2) |
| O3A—S1A—N3A | 108.85 (13) | N2A—C2A—C7A | 120.2 (2) |
| O3A—S1A—C7A | 108.47 (13) | C4A—C2A—C7A | 119.1 (2) |
| N3A—S1A—C7A | 105.22 (13) | N2A—C3A—N3A | 127.7 (3) |
| O1A—S1A—O3A | 117.48 (14) | C2A—C4A—C6A | 119.8 (2) |
| O1A—S1A—N3A | 107.72 (13) | S2A—C5A—C6A | 124.1 (2) |
| O1A—S1A—C7A | 108.43 (13) | C1A—C5A—C6A | 118.7 (2) |
| O2A—S2A—O4A | 120.19 (13) | S2A—C5A—C1A | 117.00 (19) |
| O2A—S2A—N1A | 108.56 (15) | Cl1A—C6A—C4A | 117.83 (19) |
| O2A—S2A—C5A | 105.70 (12) | Cl1A—C6A—C5A | 120.8 (2) |
| N1A—S2A—C5A | 106.90 (14) | C4A—C6A—C5A | 121.3 (2) |
| O4A—S2A—N1A | 109.18 (14) | S1A—C7A—C1A | 118.89 (19) |
| O4A—S2A—C5A | 105.52 (12) | C1A—C7A—C2A | 120.6 (2) |
| C8A—S3A—C9A | 97.75 (17) | S1A—C7A—C2A | 120.5 (2) |

| | | | |
|---|---|---|---|
| O5A—S3A—C9A | 104.75 (16) | C7A—C1A—H1A | 120.00 |
| O5A—S3A—C8A | 105.48 (13) | C5A—C1A—H1A | 120.00 |
| O5—S3—C8 | 104.78 (17) | N3A—C3A—H3A | 116.00 |
| C8—S3—C9 | 97.3 (2) | N2A—C3A—H3A | 116.00 |
| O5—S3—C9 | 106.00 (17) | C2A—C4A—H4A | 120.00 |
| C2—N2—C3 | 123.8 (2) | C6A—C4A—H4A | 120.00 |
| S1—N3—C3 | 122.2 (2) | S3A—C8A—H9A | 109.00 |
| H2N—N1—H3N | 120 (3) | H8A—C8A—H10A | 109.00 |
| S2—N1—H2N | 118 (2) | S3A—C8A—H10A | 109.00 |
| S2—N1—H3N | 119 (2) | H8A—C8A—H9A | 109.00 |
| C2—N2—H1N | 115 (2) | S3A—C8A—H8A | 109.00 |
| C3—N2—H1N | 122 (2) | H9A—C8A—H10A | 110.00 |
| C2A—N2A—C3A | 124.1 (2) | S3A—C9A—H13A | 110.00 |
| S1A—N3A—C3A | 122.1 (2) | H11A—C9A—H13A | 109.00 |
| S2A—N1A—H6N | 120 (2) | H12A—C9A—H13A | 109.00 |
| S2A—N1A—H5N | 115 (2) | H11A—C9A—H12A | 109.00 |
| H5N—N1A—H6N | 120 (3) | S3A—C9A—H11A | 109.00 |
| C3A—N2A—H4N | 117 (2) | S3A—C9A—H12A | 109.00 |
| C2A—N2A—H4N | 119 (2) | S3—C8—H8 | 109.00 |
| C5—C1—C7 | 120.5 (2) | S3—C8—H9 | 109.00 |
| N2—C2—C4 | 120.2 (2) | S3—C8—H10 | 109.00 |
| N2—C2—C7 | 120.4 (2) | H8—C8—H9 | 110.00 |
| C4—C2—C7 | 119.4 (2) | H8—C8—H10 | 109.00 |
| N2—C3—N3 | 127.7 (3) | H9—C8—H10 | 110.00 |
| C2—C4—C6 | 119.8 (2) | S3—C9—H11 | 109.00 |
| S2—C5—C1 | 117.00 (19) | S3—C9—H12 | 109.00 |
| S2—C5—C6 | 124.2 (2) | S3—C9—H13 | 109.00 |
| C1—C5—C6 | 118.5 (2) | H11—C9—H12 | 109.00 |
| C4—C6—C5 | 121.2 (2) | H11—C9—H13 | 110.00 |
| Cl1—C6—C4 | 117.87 (19) | H12—C9—H13 | 110.00 |
| O1—S1—N3—C3 | 107.7 (3) | C3A—N2A—C2A—C7A | −0.4 (4) |
| O3—S1—N3—C3 | −124.5 (2) | C2A—N2A—C3A—N3A | −0.7 (5) |
| C7—S1—N3—C3 | −7.7 (3) | S1A—N3A—C3A—N2A | −1.9 (4) |
| O1—S1—C7—C1 | 72.2 (2) | C5—C1—C7—C2 | 1.4 (4) |
| O1—S1—C7—C2 | −106.2 (2) | C5—C1—C7—S1 | −176.9 (2) |
| O3—S1—C7—C1 | −56.6 (3) | C7—C1—C5—S2 | −173.6 (2) |
| O3—S1—C7—C2 | 125.0 (2) | C7—C1—C5—C6 | 0.8 (4) |
| N3—S1—C7—C1 | −173.2 (2) | C7—C2—C4—C6 | 0.8 (4) |
| N3—S1—C7—C2 | 8.5 (3) | N2—C2—C7—S1 | −5.2 (4) |
| O2—S2—C5—C1 | 117.5 (2) | N2—C2—C7—C1 | 176.5 (3) |
| O2—S2—C5—C6 | −56.5 (3) | C4—C2—C7—S1 | 176.1 (2) |
| O4—S2—C5—C1 | −10.4 (2) | N2—C2—C4—C6 | −177.9 (3) |
| O4—S2—C5—C6 | 175.6 (2) | C4—C2—C7—C1 | −2.2 (4) |
| N1—S2—C5—C1 | −126.5 (2) | C2—C4—C6—Cl1 | 179.9 (2) |
| N1—S2—C5—C6 | 59.6 (3) | C2—C4—C6—C5 | 1.3 (4) |
| C7A—S1A—N3A—C3A | 4.3 (3) | S2—C5—C6—C4 | 171.7 (2) |
| O1A—S1A—C7A—C1A | −69.2 (2) | C1—C5—C6—Cl1 | 179.4 (2) |
| O1A—S1A—C7A—C2A | 109.9 (2) | C1—C5—C6—C4 | −2.2 (4) |
| O3A—S1A—C7A—C1A | 59.4 (3) | S2—C5—C6—Cl1 | −6.8 (3) |

| | | | |
|---|---|---|---|
| O3A—S1A—C7A—C2A | −121.5 (2) | C7A—C1A—C5A—S2A | 174.5 (2) |
| O1A—S1A—N3A—C3A | −111.2 (3) | C7A—C1A—C5A—C6A | −0.3 (4) |
| O3A—S1A—N3A—C3A | 120.4 (2) | C5A—C1A—C7A—S1A | 177.9 (2) |
| N3A—S1A—C7A—C2A | −5.2 (3) | C5A—C1A—C7A—C2A | −1.2 (4) |
| N3A—S1A—C7A—C1A | 175.8 (2) | N2A—C2A—C4A—C6A | 178.4 (3) |
| O4A—S2A—C5A—C6A | 58.8 (3) | C7A—C2A—C4A—C6A | −0.6 (4) |
| O4A—S2A—C5A—C1A | −115.6 (2) | N2A—C2A—C7A—S1A | 3.6 (4) |
| O2A—S2A—C5A—C1A | 12.7 (2) | N2A—C2A—C7A—C1A | −177.3 (3) |
| N1A—S2A—C5A—C1A | 128.2 (2) | C4A—C2A—C7A—S1A | −177.4 (2) |
| N1A—S2A—C5A—C6A | −57.3 (3) | C4A—C2A—C7A—C1A | 1.6 (4) |
| O2A—S2A—C5A—C6A | −172.8 (2) | C2A—C4A—C6A—Cl1A | −179.7 (2) |
| C2—N2—C3—N3 | 1.8 (5) | C2A—C4A—C6A—C5A | −0.9 (4) |
| C3—N2—C2—C4 | 178.1 (3) | S2A—C5A—C6A—Cl1A | 5.8 (3) |
| C3—N2—C2—C7 | −0.6 (4) | S2A—C5A—C6A—C4A | −173.0 (2) |
| S1—N3—C3—N2 | 3.5 (4) | C1A—C5A—C6A—Cl1A | −179.9 (2) |
| C3A—N2A—C2A—C4A | −179.3 (3) | C1A—C5A—C6A—C4A | 1.3 (4) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H1N···O5 | 0.80 (3) | 1.92 (3) | 2.704 (3) | 168 (3) |
| N1—H2N···N3A$^{i}$ | 0.83 (3) | 2.24 (4) | 3.055 (4) | 167 (3) |
| N1—H3N···O5$^{ii}$ | 0.80 (3) | 2.04 (3) | 2.821 (3) | 164 (3) |
| N2A—H4N···O5A$^{iii}$ | 0.78 (3) | 1.94 (3) | 2.714 (3) | 171 (3) |
| N1A—H5N···N3$^{iv}$ | 0.78 (3) | 2.27 (4) | 3.020 (3) | 162 (3) |
| N1A—H6N···O5A$^{v}$ | 0.85 (3) | 2.03 (3) | 2.865 (3) | 167 (3) |

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*, *y*−1, *z*; (iv) −*x*, −*y*, −*z*; (v) −*x*+1, −*y*+1, −*z*.

**Fig. 1**

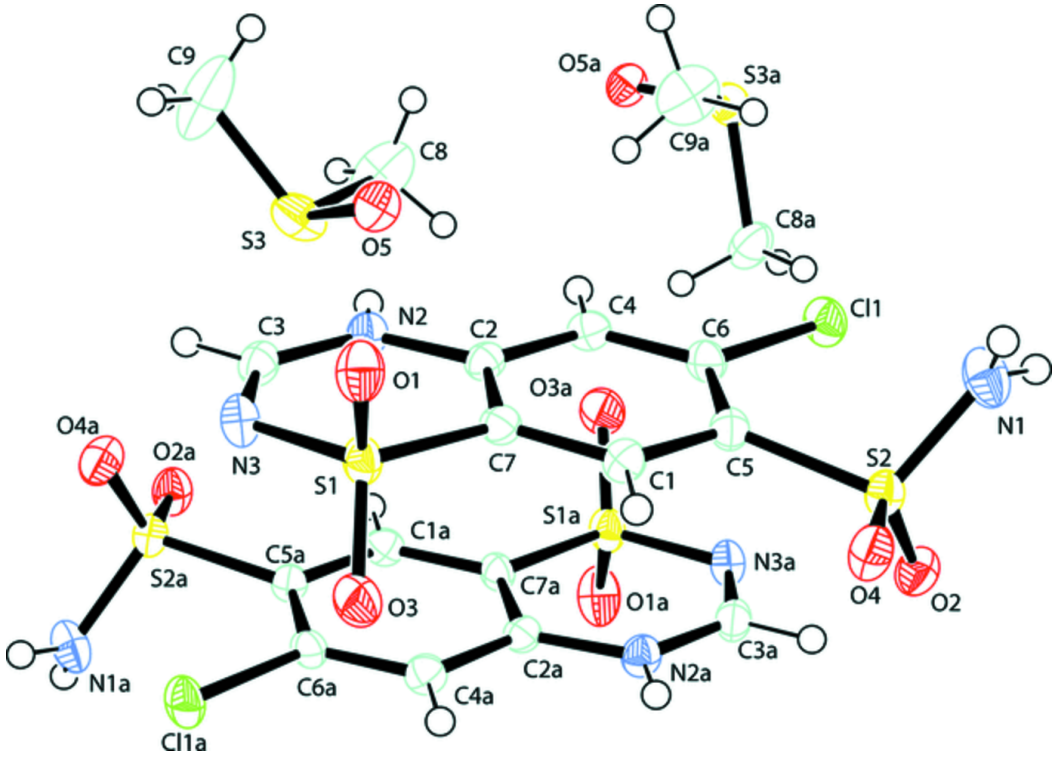

C9
C8
S3
O5
O5a
S3a
C9a
C8a
C3
N2
C2
C4
C6
Cl1
O1
O3a
N1
O4a
O2a
N3
S1
C7
C1
C5
S2
C1a
S1a
C5a
S2a
N3a
C7a
O1a
O4
O2
O3
N1a
C3a
C6a
C2a
N2a
C4a
Cl1a

**Fig. 2**