

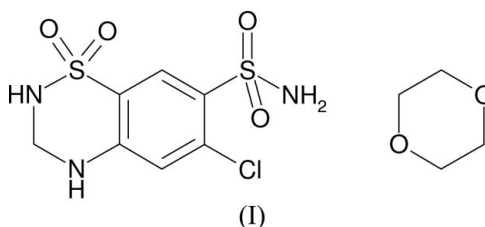
## Hydrochlorothiazide–1,4-dioxane (1/1)

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## Key indicators

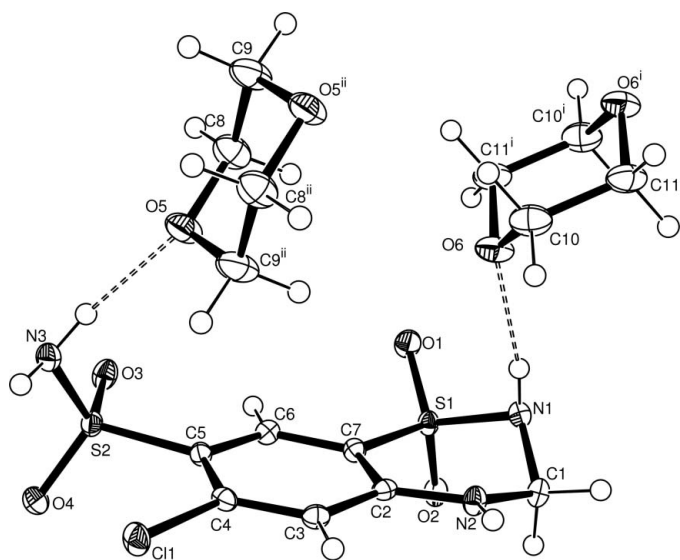
Single-crystal X-ray study  
 $T = 123$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.031  
 $wR$  factor = 0.078  
Data-to-parameter ratio = 15.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hydrochlorothiazide forms a 1:1 solvate with 1,4-dioxane,  $\text{C}_7\text{H}_8\text{ClN}_3\text{O}_4\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$  [systematic name: 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide–1,4-dioxane (1/1)]. The asymmetric unit comprises one molecule of hydrochlorothiazide and halves of two solvent molecules arranged around inversion centres. The structure contains a hydrogen-bonding network comprising three  $\text{N}-\text{H} \cdots \text{O}$  and one  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonds.Received 5 July 2005  
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Online 16 July 2005

## Comment

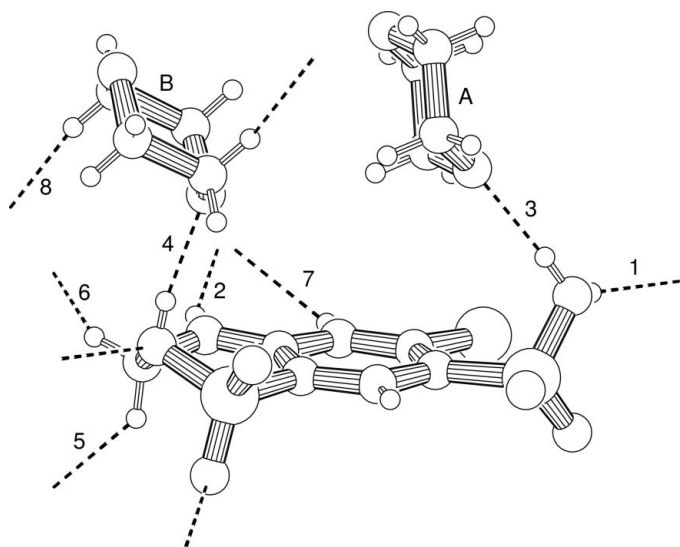
Hydrochlorothiazide (HCT) is a thiazide diuretic which is known to crystallize in at least one non-solvated form (Dupont & Dideberg, 1972). The title compound, (I), was produced during an automated parallel crystallization polymorph screen on HCT. The sample was identified as a novel form using multi-sample X-ray powder diffraction analysis of all recrystallized samples (Florence *et al.*, 2003). Subsequent manual recrystallization from a saturated 1:1 acetone/dioxane solution, by slow evaporation at 298 K, yielded samples of the HCT 1,4-dioxane solvate suitable for single-crystal X-ray analysis (Fig. 1).

In (I), the six-membered S1/N1/C1/N2/C2/C7 ring in HCT displays a half-chair conformation, atoms C1 and N1 having deviations of  $-0.134$  (2) and  $0.554$  (2) Å, respectively, from the least-squares plane through atoms C2–C7. The sulfonamide side chain adopts an N3–S2–C5–C4 torsion angle of  $57.55$  (18)°, such that atom O3 eclipses atom H6, and atoms O4 and N3 are staggered with respect to atom C11. In the non-solvated structure, this group is rotated by approximately 120° compared with that in (I), such that the amine group lies on the opposite side of the benzothiadiazine ring system. Both centrosymmetric solvent molecules adopt chair conformations, with puckering parameters (Cremer & Pople, 1975) for rings A and B of  $Q = 0.564$  (2) and  $0.566$  (2) Å,  $\theta = 2.11$  (1) and  $0.00^\circ$  and  $\varphi = 0$  and  $0^\circ$ , respectively.

The crystal structure is stabilized by a network of hydrogen bonds interconnecting (a) HCT molecules (Fig. 2, contacts 1 and 2), (b) HCT and solvent molecule A (contact 3), and (c) HCT and solvent molecule B (contact 4). Contact 1 forms an

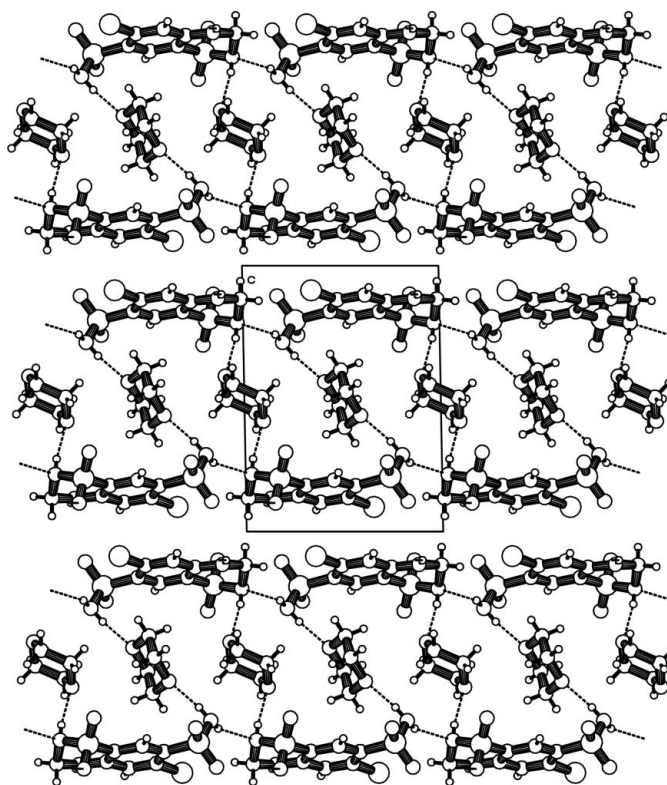

**Figure 1**

The asymmetric unit contents, expanded to complete the solvent molecules, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen-bond contacts. [Symmetry codes: (i)  $1-x, -y, 1-z$ ; (ii)  $-x, 1-y, 1-z$ ].


**Figure 2**

Intermolecular interactions in (I). Dashed lines indicate hydrogen bonds and unique contacts are labelled as follows: (1)  $N3 \cdots N1(-1+x, 1+y, z) = 3.097(3) \text{ \AA}$ ; (2)  $N2 \cdots O2(-1+x, y, z) = 3.032(2) \text{ \AA}$ ; (3)  $N3 \cdots O5 = 2.879(2) \text{ \AA}$ ; (4)  $N1 \cdots O6 = 2.848(2) \text{ \AA}$ ; (5)  $C1 \cdots O2(2-x, -y, -z) = 3.304(2) \text{ \AA}$ ; (6)  $C1 \cdots O4(x, -1+y, z) = 3.220(2) \text{ \AA}$ ; (7)  $C3 \cdots O2(-1+x, y, z) = 3.285(2) \text{ \AA}$ ; (8)  $C11 \cdots O3(x, -1+y, z) = 3.412(2) \text{ \AA}$ . Contacts calculated and illustrated using *PLATON* (Spek, 2003; program version 280604)

infinite chain of HCT molecules, which combine with contact 2 to form layers of HCT molecules in the *ab* plane. Each HCT layer is connected to parallel layers of 1,4-dioxane (via contacts 3 and 4) and HCT molecules. Hydrophobic interactions between layers of HCT include offset face-to-face (off)  $\pi$ - $\pi$  stacking between the ring formed by atoms C2-C7 [centroid-centroid distance =  $4.192(1) \text{ \AA}$ ]. Compound (I)


**Figure 3**

The crystal packing in the structure of (I); view down the *a* axis, showing the alternating layers of HCT and 1,4-dioxane molecules stacked along *c*. Hydrogen bonds are shown as dashed lines.

therefore adopts a stacked structure with alternating double layers of HCT, with single layers of solvent stacked in the *c* direction (Fig. 3). Three C—H...O contacts also exist between HCT molecules (Fig. 2, contacts 5–7), with a fourth connecting 1,4-dioxane molecule B to atom O3 of HCT (contact 8).

## Experimental

A single-crystal sample of the title compound was recrystallized from a 1:1 acetone/1,4-dioxane solution by slow evaporation at 298 K.

### Crystal data

$C_7H_8ClN_3O_4S_2 \cdot C_4H_8O_2$   
 $M_r = 385.84$   
 Triclinic, *P* $\bar{1}$   
 $a = 6.6684(2) \text{ \AA}$   
 $b = 9.8585(3) \text{ \AA}$   
 $c = 12.9149(4) \text{ \AA}$   
 $\alpha = 87.046(2)^\circ$   
 $\beta = 78.017(2)^\circ$   
 $\gamma = 70.872(2)^\circ$   
 $V = 784.55(4) \text{ \AA}^3$

$Z = 2$   
 $D_x = 1.633 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 3105 reflections  
 $\theta = 1.0\text{--}27.1^\circ$   
 $\mu = 0.54 \text{ mm}^{-1}$   
 $T = 123(2) \text{ K}$   
 Plate, colourless  
 $0.50 \times 0.20 \times 0.08 \text{ mm}$

### Data collection

Nonius KappaCCD diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: none  
 12343 measured reflections  
 3445 independent reflections  
 2879 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 27.1^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -12 \rightarrow 12$   
 $l = -16 \rightarrow 15$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.078$   
 $S = 1.03$   
 3445 reflections  
 224 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.4818P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O6	0.82 (2)	2.04 (2)	2.848 (2)	170 (2)
N2—H2N $\cdots$ O2 <sup>i</sup>	0.81 (2)	2.28 (3)	3.032 (2)	154 (2)
N3—H3N $\cdots$ N1 <sup>ii</sup>	0.81 (2)	2.35 (2)	3.097 (3)	155 (2)
N3—H4N $\cdots$ O5	0.87 (3)	2.02 (3)	2.879 (2)	170 (3)
C1—H1A $\cdots$ O2	0.99	2.60	2.980 (2)	103
C1—H1A $\cdots$ O2 <sup>iii</sup>	0.99	2.55	3.304 (2)	133
C1—H1B $\cdots$ O4 <sup>iv</sup>	0.99	2.41	3.220 (2)	139
C3—H3 $\cdots$ O2 <sup>i</sup>	0.95	2.56	3.285 (2)	133
C6—H6 $\cdots$ O3	0.95	2.38	2.800 (2)	107
C11—H11B $\cdots$ O3 <sup>iv</sup>	0.99	2.50	3.412 (2)	153

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

The amine H atoms were located in difference syntheses and were refined isotropically. All other H atoms were constrained to an

idealized geometry using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ; for  $\text{CH}_2$  groups,  $\text{C}-\text{H} = 0.99 \text{ \AA}$ , whilst for CH groups,  $\text{C}-\text{H} = 0.95 \text{ \AA}$ .

Data collection: *COLLECT* (Hooft, 1988) 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); software used to prepare material for publication: *SHELXL97*.

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## supporting information

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## Hydrochlorothiazide–1,4-dioxane (1/1)

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## 6-chloro-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide–1,4-dioxane (1/1)

*Crystal data*

$C_7H_8ClN_3O_4S_2 \cdot C_4H_8O_2$   
 $M_r = 385.84$   
 Triclinic,  $P\bar{1}$   
 Hall symbol:  $-P\ 1$   
 $a = 6.6684$  (2) Å  
 $b = 9.8585$  (3) Å  
 $c = 12.9149$  (4) Å  
 $\alpha = 87.046$  (2)°  
 $\beta = 78.017$  (2)°  
 $\gamma = 70.872$  (2)°  
 $V = 784.55$  (4) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 400$   
 $D_x = 1.633$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 3105 reflections  
 $\theta = 1.0$ – $27.1$ °  
 $\mu = 0.54$  mm<sup>-1</sup>  
 $T = 123$  K  
 Flattened (Plate?), colourless  
 $0.50 \times 0.20 \times 0.08$  mm

*Data collection*

Nonius KappaCCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$  and  $\varphi$  scans  
 12343 measured reflections  
 3445 independent reflections

2879 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.035$   
 $\theta_{max} = 27.1$ °,  $\theta_{min} = 1.6$ °  
 $h = -8 \rightarrow 8$   
 $k = -12 \rightarrow 12$   
 $l = -16 \rightarrow 15$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.078$   
 $S = 1.03$   
 3445 reflections  
 224 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  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.4818P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.43$  e Å<sup>-3</sup>

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.07843 (7)	0.65012 (5)	0.09254 (4)	0.01908 (12)
S1	0.88826 (7)	0.17340 (4)	0.20012 (4)	0.01332 (11)
S2	0.42002 (7)	0.73615 (4)	0.20612 (4)	0.01410 (11)
O1	0.9318 (2)	0.20556 (13)	0.29836 (11)	0.0206 (3)
O2	1.05861 (19)	0.14951 (13)	0.10752 (10)	0.0168 (3)
O3	0.5917 (2)	0.72299 (13)	0.26103 (11)	0.0193 (3)
O4	0.4063 (2)	0.82446 (13)	0.11418 (10)	0.0200 (3)
O5	0.1010 (2)	0.58970 (15)	0.43701 (11)	0.0260 (3)
O6	0.5231 (2)	0.09459 (16)	0.41565 (11)	0.0258 (3)
N1	0.8111 (3)	0.03091 (16)	0.21498 (13)	0.0151 (3)
N2	0.5155 (3)	0.12683 (16)	0.12386 (13)	0.0148 (3)
N3	0.1942 (3)	0.79977 (18)	0.28862 (14)	0.0173 (3)
C1	0.7164 (3)	0.01179 (18)	0.12586 (15)	0.0153 (4)
H1A	0.8206	0.0098	0.0586	0.018*
H1B	0.6886	-0.0813	0.1322	0.018*
C2	0.5001 (3)	0.26611 (18)	0.13433 (13)	0.0130 (4)
C3	0.3216 (3)	0.37838 (19)	0.11015 (14)	0.0140 (4)
H3	0.2157	0.3563	0.0814	0.017*
C4	0.2995 (3)	0.51923 (19)	0.12782 (14)	0.0136 (4)
C5	0.4490 (3)	0.55796 (18)	0.17218 (14)	0.0128 (4)
C6	0.6283 (3)	0.44909 (18)	0.19318 (14)	0.0140 (4)
H6	0.7334	0.4725	0.2218	0.017*
C7	0.6567 (3)	0.30640 (18)	0.17301 (14)	0.0129 (4)
C8	0.1831 (3)	0.5178 (2)	0.52605 (17)	0.0273 (5)
H8A	0.2506	0.5768	0.5576	0.033*
H8B	0.2958	0.4247	0.5025	0.033*
C9	0.0039 (4)	0.4925 (2)	0.60737 (16)	0.0296 (5)
H9A	0.0635	0.4404	0.6676	0.035*
H9B	-0.1035	0.5859	0.6345	0.035*
C10	0.3289 (3)	0.0572 (2)	0.44691 (17)	0.0271 (5)
H10A	0.2641	0.0582	0.3844	0.032*
H10B	0.2226	0.1290	0.4991	0.032*
C11	0.3771 (4)	-0.0892 (2)	0.49485 (16)	0.0267 (5)
H11A	0.2409	-0.1122	0.5177	0.032*
H11B	0.4753	-0.1620	0.4411	0.032*
H3N	0.095 (4)	0.837 (2)	0.2591 (18)	0.021 (6)*
H1N	0.730 (4)	0.039 (2)	0.2727 (18)	0.022 (6)*
H2N	0.416 (4)	0.108 (2)	0.1080 (17)	0.020 (6)*
H4N	0.172 (4)	0.741 (3)	0.339 (2)	0.039 (7)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0167 (2)	0.0153 (2)	0.0241 (3)	-0.00054 (17)	-0.00968 (19)	0.00146 (18)
S1	0.0128 (2)	0.0109 (2)	0.0167 (2)	-0.00285 (17)	-0.00548 (17)	0.00024 (17)
S2	0.0154 (2)	0.0108 (2)	0.0156 (2)	-0.00413 (17)	-0.00203 (18)	-0.00034 (17)
O1	0.0239 (7)	0.0184 (7)	0.0214 (7)	-0.0040 (6)	-0.0132 (6)	-0.0006 (6)
O2	0.0118 (6)	0.0151 (6)	0.0226 (7)	-0.0036 (5)	-0.0025 (5)	-0.0007 (5)
O3	0.0181 (7)	0.0162 (6)	0.0247 (7)	-0.0050 (5)	-0.0066 (6)	-0.0032 (5)
O4	0.0274 (7)	0.0154 (6)	0.0176 (7)	-0.0095 (6)	-0.0017 (6)	0.0035 (5)
O5	0.0361 (8)	0.0293 (8)	0.0194 (7)	-0.0191 (7)	-0.0085 (6)	0.0080 (6)
O6	0.0289 (8)	0.0357 (8)	0.0152 (7)	-0.0130 (7)	-0.0062 (6)	0.0033 (6)
N1	0.0156 (8)	0.0127 (7)	0.0168 (8)	-0.0046 (6)	-0.0033 (7)	0.0017 (6)
N2	0.0136 (8)	0.0129 (7)	0.0201 (8)	-0.0056 (6)	-0.0061 (7)	-0.0004 (6)
N3	0.0165 (8)	0.0144 (8)	0.0179 (8)	-0.0009 (7)	-0.0034 (7)	0.0010 (7)
C1	0.0142 (9)	0.0119 (8)	0.0195 (9)	-0.0036 (7)	-0.0031 (7)	-0.0018 (7)
C2	0.0138 (8)	0.0147 (9)	0.0101 (8)	-0.0048 (7)	-0.0011 (7)	-0.0008 (7)
C3	0.0134 (9)	0.0168 (9)	0.0130 (9)	-0.0060 (7)	-0.0038 (7)	0.0002 (7)
C4	0.0110 (8)	0.0145 (9)	0.0121 (9)	-0.0010 (7)	-0.0011 (7)	0.0022 (7)
C5	0.0136 (9)	0.0110 (8)	0.0131 (9)	-0.0038 (7)	-0.0019 (7)	0.0008 (7)
C6	0.0125 (8)	0.0152 (9)	0.0148 (9)	-0.0057 (7)	-0.0016 (7)	-0.0010 (7)
C7	0.0111 (8)	0.0124 (8)	0.0139 (9)	-0.0025 (7)	-0.0015 (7)	0.0003 (7)
C8	0.0301 (11)	0.0320 (12)	0.0257 (11)	-0.0151 (9)	-0.0116 (9)	0.0062 (9)
C9	0.0424 (13)	0.0379 (13)	0.0184 (10)	-0.0241 (11)	-0.0115 (10)	0.0070 (9)
C10	0.0215 (10)	0.0382 (12)	0.0208 (11)	-0.0070 (9)	-0.0073 (9)	0.0009 (9)
C11	0.0298 (11)	0.0380 (12)	0.0168 (10)	-0.0158 (10)	-0.0068 (9)	-0.0003 (9)

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

Cl1—C4	1.7372 (18)	C1—H1B	0.9900
S1—O1	1.4316 (13)	C2—C3	1.412 (2)
S1—O2	1.4373 (13)	C2—C7	1.416 (2)
S1—N1	1.6371 (15)	C3—C4	1.373 (2)
S1—C7	1.7541 (17)	C3—H3	0.9500
S2—O3	1.4357 (13)	C4—C5	1.406 (2)
S2—O4	1.4362 (13)	C5—C6	1.386 (2)
S2—N3	1.6060 (16)	C6—C7	1.388 (2)
S2—C5	1.7713 (17)	C6—H6	0.9500
O5—C8	1.431 (2)	C8—C9	1.497 (3)
O5—C9 <sup>i</sup>	1.435 (2)	C8—H8A	0.9900
O6—C10	1.434 (2)	C8—H8B	0.9900
O6—C11 <sup>ii</sup>	1.439 (2)	C9—O5 <sup>i</sup>	1.435 (2)
N1—C1	1.470 (2)	C9—H9A	0.9900
N1—H1N	0.82 (2)	C9—H9B	0.9900
N2—C2	1.355 (2)	C10—C11	1.502 (3)
N2—C1	1.448 (2)	C10—H10A	0.9900
N2—H2N	0.81 (2)	C10—H10B	0.9900
N3—H3N	0.81 (2)	C11—O6 <sup>ii</sup>	1.439 (2)



N3—H4N	0.87 (3)	C11—H11A	0.9900
C1—H1A	0.9900	C11—H11B	0.9900
O1—S1—O2	118.26 (8)	C3—C4—C11	117.42 (14)
O1—S1—N1	108.70 (8)	C5—C4—C11	120.55 (13)
O2—S1—N1	107.54 (8)	C6—C5—C4	117.82 (16)
O1—S1—C7	110.05 (8)	C6—C5—S2	117.75 (13)
O2—S1—C7	108.81 (8)	C4—C5—S2	124.42 (13)
N1—S1—C7	102.26 (8)	C5—C6—C7	120.92 (16)
O3—S2—O4	118.54 (8)	C5—C6—H6	119.5
O3—S2—N3	107.75 (9)	C7—C6—H6	119.5
O4—S2—N3	106.87 (9)	C6—C7—C2	121.50 (16)
O3—S2—C5	105.19 (8)	C6—C7—S1	118.84 (14)
O4—S2—C5	110.01 (8)	C2—C7—S1	119.63 (13)
N3—S2—C5	108.10 (8)	O5—C8—C9	110.31 (17)
C8—O5—C9 <sup>i</sup>	110.22 (15)	O5—C8—H8A	109.6
C10—O6—C11 <sup>ii</sup>	110.16 (15)	C9—C8—H8A	109.6
C1—N1—S1	111.21 (12)	O5—C8—H8B	109.6
C1—N1—H1N	114.2 (16)	C9—C8—H8B	109.6
S1—N1—H1N	107.2 (15)	H8A—C8—H8B	108.1
C2—N2—C1	121.31 (15)	O5 <sup>i</sup> —C9—C8	110.81 (17)
C2—N2—H2N	119.1 (15)	O5 <sup>i</sup> —C9—H9A	109.5
C1—N2—H2N	119.0 (15)	C8—C9—H9A	109.5
S2—N3—H3N	112.0 (16)	O5 <sup>i</sup> —C9—H9B	109.5
S2—N3—H4N	113.6 (17)	C8—C9—H9B	109.5
H3N—N3—H4N	116 (2)	H9A—C9—H9B	108.1
N2—C1—N1	111.09 (14)	O6—C10—C11	110.61 (17)
N2—C1—H1A	109.4	O6—C10—H10A	109.5
N1—C1—H1A	109.4	C11—C10—H10A	109.5
N2—C1—H1B	109.4	O6—C10—H10B	109.5
N1—C1—H1B	109.4	C11—C10—H10B	109.5
H1A—C1—H1B	108.0	H10A—C10—H10B	108.1
N2—C2—C3	121.02 (16)	O6 <sup>ii</sup> —C11—C10	110.62 (17)
N2—C2—C7	122.07 (16)	O6 <sup>ii</sup> —C11—H11A	109.5
C3—C2—C7	116.88 (15)	C10—C11—H11A	109.5
C4—C3—C2	120.68 (16)	O6 <sup>ii</sup> —C11—H11B	109.5
C4—C3—H3	119.7	C10—C11—H11B	109.5
C2—C3—H3	119.7	H11A—C11—H11B	108.1
C3—C4—C5	122.04 (16)		
O1—S1—N1—C1	166.87 (12)	N3—S2—C5—C4	57.55 (18)
O2—S1—N1—C1	-63.99 (13)	C4—C5—C6—C7	-1.3 (3)
C7—S1—N1—C1	50.51 (14)	S2—C5—C6—C7	177.15 (14)
C2—N2—C1—N1	47.3 (2)	C5—C6—C7—C2	-2.5 (3)
S1—N1—C1—N2	-66.28 (17)	C5—C6—C7—S1	179.43 (13)
C1—N2—C2—C3	166.39 (16)	N2—C2—C7—C6	-173.58 (17)
C1—N2—C2—C7	-15.7 (3)	C3—C2—C7—C6	4.4 (3)
N2—C2—C3—C4	175.51 (16)	N2—C2—C7—S1	4.4 (2)

C7—C2—C3—C4	-2.5 (3)	C3—C2—C7—S1	-177.61 (13)
C2—C3—C4—C5	-1.3 (3)	O1—S1—C7—C6	41.38 (17)
C2—C3—C4—C11	178.41 (13)	O2—S1—C7—C6	-89.67 (15)
C3—C4—C5—C6	3.2 (3)	N1—S1—C7—C6	156.76 (15)
C11—C4—C5—C6	-176.47 (13)	O1—S1—C7—C2	-136.70 (14)
C3—C4—C5—S2	-175.12 (14)	O2—S1—C7—C2	92.25 (15)
C11—C4—C5—S2	5.2 (2)	N1—S1—C7—C2	-21.32 (16)
O3—S2—C5—C6	-5.88 (16)	C9 <sup>i</sup> —O5—C8—C9	-57.3 (3)
O4—S2—C5—C6	122.85 (14)	O5—C8—C9—O5 <sup>i</sup>	57.7 (2)
N3—S2—C5—C6	-120.79 (15)	C11 <sup>ii</sup> —O6—C10—C11	-57.4 (2)
O3—S2—C5—C4	172.46 (15)	O6—C10—C11—O6 <sup>ii</sup>	57.7 (2)
O4—S2—C5—C4	-58.81 (17)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O6	0.82 (2)	2.04 (2)	2.848 (2)	170.4 (18)
N2—H2N $\cdots$ O2 <sup>iii</sup>	0.81 (2)	2.28 (3)	3.032 (2)	153.7 (18)
N3—H3N $\cdots$ N1 <sup>iv</sup>	0.81 (2)	2.35 (2)	3.097 (3)	154.5 (19)
N3—H4N $\cdots$ O5	0.87 (3)	2.02 (3)	2.879 (2)	170 (3)
C1—H1A $\cdots$ O2	0.99	2.60	2.980 (2)	103
C1—H1A $\cdots$ O2 <sup>v</sup>	0.99	2.55	3.304 (2)	133
C1—H1B $\cdots$ O4 <sup>vi</sup>	0.99	2.41	3.220 (2)	139
C3—H3 $\cdots$ O2 <sup>iii</sup>	0.95	2.56	3.285 (2)	133
C6—H6 $\cdots$ O3	0.95	2.38	2.800 (2)	107
C11—H11B $\cdots$ O3 <sup>vi</sup>	0.99	2.50	3.412 (2)	153

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