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# Hydrochlorothiazide *N*-methyl-2-pyrrolidone disolvate

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**Key indicators**

Single-crystal X-ray study
*T* = 123 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
*R* factor = 0.064
*wR* factor = 0.174
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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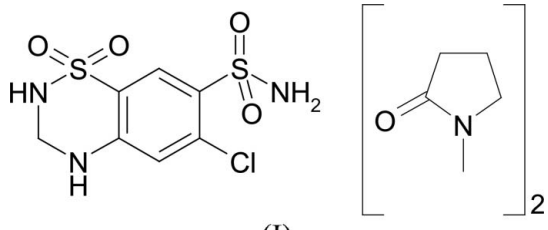
Hydrochlorothiazide forms a 1:2 solvate with *N*-methyl-pyrrolidone (systematic name: 6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide *N*-methyl-2-pyrrolidone disolvate), $C_7H_8ClN_3O_4S_2\cdot 2C_5H_9NO$. The compound crystallizes with one hydrochlorothiazide and two solvent molecules, one of which is disordered, in the asymmetric unit. The crystal structure is isostructural with the previously reported hydrochlorothiazide *N*,*N*-dimethyl-acetamide disolvate.

## Comment

Hydrochlorothiazide (HCT) is a thiazide diuretic which is known to crystallize in at least two non-solvated forms, form I (Dupont & Dideberg, 1972) and form II (Florence *et al.*, 2005). The title compound of this report, (I), was produced during an automated parallel crystallization study of HCT (Johnston, Florence, Shankland *et al.*, 2006). The sample was identified as a novel form using multi-sample foil transmission X-ray powder diffraction analysis (Florence *et al.*, 2003). Subsequent manual recrystallization from a saturated *N*-methyl-pyrrolidone (NMP) solution by slow evaporation at 298 K yielded samples of (I) suitable for single-crystal diffraction (Fig. 1).




(I)

It is notable that the crystal structure of (I) is isostructural with that of the previously reported HCT *N*,*N*-dimethyl-acetamide (DMA) disolvate (Johnston, Florence & Kennedy, 2006), with the same space group and very similar unit-cell parameters and packing arrangements. Adjacent HCT chains pack as layers in the *ab* plane and form an alternating stacked arrangement with layers of solvent molecules in the direction of the *c* axis (Fig. 2). The structures differ slightly in the extent of solvent disorder, with both solvent molecules disordered in the HCT–DMA disolvate, compared with a single molecule in (I). The structure also contains four N—H···O hydrogen bonds, with N1, N2 and N3 of HCT donating contacts to adjacent O atoms of NMP (Table 1).

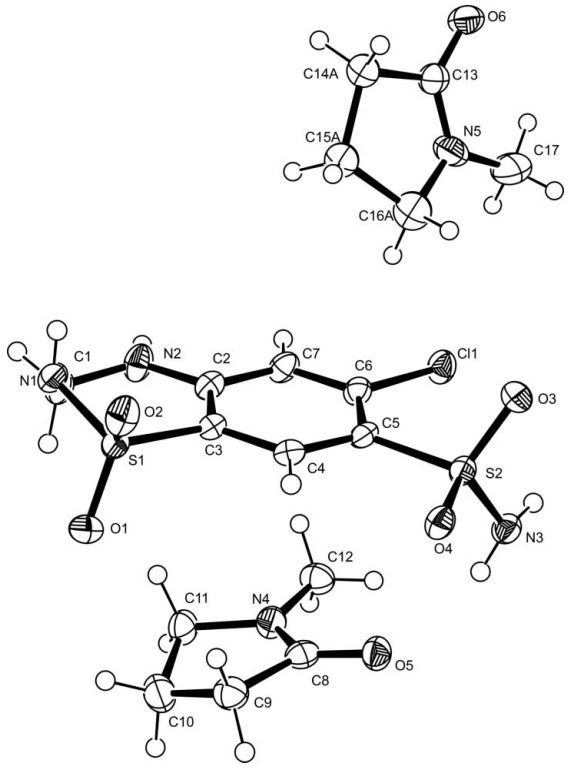



**Figure 1**
The asymmetric unit contents of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Minor disorder components have been omitted for clarity.

## Experimental

A single-crystal sample of the title compound was recrystallized from a saturated *N*-methylpyrrolidone solution by isothermal solvent evaporation at 298 K.

*Crystal data*

$C_7H_8ClN_3O_4S_2\cdot 2C_5H_9NO$
$M_r$ = 496.00
Monoclinic, $P2_1/c$
$a$ = 17.0756 (6) Å
$b$ = 7.4819 (3) Å
$c$ = 17.9978 (6) Å
$\beta$ = 105.211 (2)°
$V$ = 2218.81 (14) Å$^3$
$Z$ = 4
$D_x$ = 1.485 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu$ = 0.41 mm$^{-1}$
$T$ = 123 (2) K
Cut from prism, colourless
0.32 × 0.20 × 0.12 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: none
24804 measured reflections
4852 independent reflections
3673 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.093
$\theta_{max}$ = 27.1°

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.174
$S$ = 1.08
4852 reflections
296 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1041P)^2 + 0.892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.55 e Å$^{-3}$

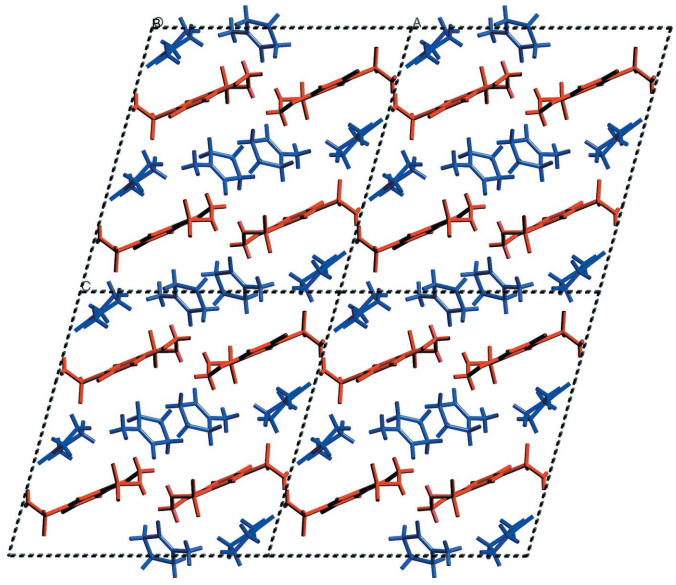



**Figure 2**
The crystal packing in the structure of (I), viewed down the *b* axis, showing the alternating layers of HCT and NMP molecules.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1N···O6$^{i}$ | 0.79 (5) | 2.01 (5) | 2.799 (4) | 177 (5) |
| N2—H2N···O6$^{ii}$ | 0.80 (4) | 2.35 (4) | 2.929 (4) | 130 (3) |
| N3—H3N···O5 | 0.84 (3) | 2.12 (4) | 2.891 (4) | 153 (4) |
| N3—H4N···O5$^{iii}$ | 0.86 (4) | 2.04 (4) | 2.884 (4) | 169 (3) |
| C1—H1*A*···O6$^{ii}$ | 0.99 | 2.58 | 3.075 (4) | 111 |
| C7—H7···O2$^{iv}$ | 0.95 | 2.33 | 3.249 (4) | 164 |
| C11—H11*B*···O3$^{v}$ | 0.99 | 2.52 | 3.423 (4) | 152 |

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, y+1, z$; (v) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Three C atoms (C14, C15 and C16) and the associated H atoms of one solvent molecule were treated as disordered over two sites. Isotropic refinement gave a refined occupancy of 0.52 (3):0.48 (3). All amine H atoms were found by difference synthesis and refined isotropically. All other H atoms were positioned geometrically at distances of 0.95 (CH), 0.98 ($CH_3$) or 0.99 Å ($CH_2$); a riding model was used during refinement, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl H atoms and $U_{iso}$(H) = 1.2$U_{eq}$(C) for all others.

Data collection: *COLLECT* (Nonius, 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: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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# supporting information

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## Hydrochlorothiazide *N*-methyl-2-pyrrolidone disolvate

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**6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide *N*-methyl-2-pyrrolidone disolvate**

*Crystal data*

$C_7H_8ClN_3O_4S_2·2C_5H_9NO$
$M_r = 496.00$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 17.0756$ (6) Å
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$c = 17.9978$ (6) Å
$\beta = 105.211$ (2)°
$V = 2218.81$ (14) Å$^3$
$Z = 4$
$F(000) = 1040$
$D_x = 1.485$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5023 reflections
$\theta = 1.0$–$27.1°$
$\mu = 0.41$ mm$^{-1}$
$T = 123$ K
Cut from prism, colourless
0.32 × 0.20 × 0.12 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
24804 measured reflections
4852 independent reflections
3673 reflections with $I > 2\sigma(I)$
$R_{int} = 0.093$
$\theta_{max} = 27.1°$, $\theta_{min} = 1.2°$
$h = -21 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.174$
$S = 1.08$
4852 reflections
296 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
$w = 1/[\sigma^2(F_o^2) + (0.1041P)^2 + 0.892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å$^{-3}$
$\Delta\rho_{min} = -0.55$ e Å$^{-3}$

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cl1 | 0.83783 (4) | 0.43550 (10) | 0.16447 (4) | 0.0287 (2) | |
| S1 | 0.65205 (4) | −0.18853 (10) | 0.27397 (4) | 0.0237 (2) | |
| S2 | 0.89965 (4) | 0.01810 (10) | 0.15514 (4) | 0.0210 (2) | |
| O1 | 0.69144 (13) | −0.2471 (3) | 0.35033 (12) | 0.0372 (6) | |
| O2 | 0.63256 (13) | −0.3193 (3) | 0.21369 (13) | 0.0310 (5) | |
| O3 | 0.88310 (12) | 0.0813 (3) | 0.07722 (11) | 0.0273 (5) | |
| O4 | 0.90847 (11) | −0.1695 (3) | 0.16923 (11) | 0.0247 (5) | |
| O5 | 0.98030 (12) | −0.0406 (3) | 0.35009 (12) | 0.0286 (5) | |
| O6 | 0.54188 (14) | 1.0488 (3) | −0.13077 (13) | 0.0361 (6) | |
| N1 | 0.56794 (15) | −0.0889 (3) | 0.27559 (16) | 0.0248 (5) | |
| N2 | 0.62120 (16) | 0.2066 (4) | 0.28470 (16) | 0.0304 (6) | |
| N3 | 0.97927 (15) | 0.1167 (4) | 0.20314 (16) | 0.0249 (5) | |
| N4 | 0.90110 (15) | 0.0930 (4) | 0.41855 (14) | 0.0288 (6) | |
| N5 | 0.63002 (18) | 0.9495 (4) | −0.02142 (15) | 0.0378 (7) | |
| C1 | 0.58148 (19) | 0.0752 (4) | 0.32033 (18) | 0.0289 (7) | |
| H1A | 0.5288 | 0.1229 | 0.3247 | 0.035* | |
| H1B | 0.6154 | 0.0494 | 0.3729 | 0.035* | |
| C2 | 0.68438 (17) | 0.1647 (4) | 0.25432 (16) | 0.0238 (6) | |
| C3 | 0.70834 (16) | −0.0145 (4) | 0.24753 (16) | 0.0214 (6) | |
| C4 | 0.77418 (16) | −0.0536 (4) | 0.21818 (16) | 0.0219 (6) | |
| H4 | 0.7905 | −0.1744 | 0.2158 | 0.026* | |
| C5 | 0.81629 (16) | 0.0808 (4) | 0.19233 (16) | 0.0210 (6) | |
| C6 | 0.79023 (16) | 0.2571 (4) | 0.19616 (16) | 0.0229 (6) | |
| C7 | 0.72558 (17) | 0.2987 (4) | 0.22588 (17) | 0.0256 (6) | |
| H7 | 0.7090 | 0.4197 | 0.2270 | 0.031* | |
| C8 | 0.93403 (18) | −0.0472 (4) | 0.39273 (17) | 0.0264 (7) | |
| C9 | 0.90442 (19) | −0.2160 (4) | 0.42372 (18) | 0.0309 (7) | |
| H9A | 0.9502 | −0.2975 | 0.4461 | 0.037* | |
| H9B | 0.8643 | −0.2798 | 0.3826 | 0.037* | |
| C10 | 0.8654 (2) | −0.1475 (5) | 0.48563 (19) | 0.0368 (8) | |
| H10A | 0.8162 | −0.2174 | 0.4857 | 0.044* | |
| H10B | 0.9040 | −0.1550 | 0.5373 | 0.044* | |
| C11 | 0.84395 (19) | 0.0454 (4) | 0.46353 (18) | 0.0314 (7) | |
| H11A | 0.7871 | 0.0562 | 0.4322 | 0.038* | |
| H11B | 0.8518 | 0.1220 | 0.5097 | 0.038* | |
| C12 | 0.91140 (19) | 0.2762 (4) | 0.39683 (18) | 0.0320 (7) | |
| H12A | 0.9503 | 0.2801 | 0.3654 | 0.048* | |
| H12B | 0.9317 | 0.3485 | 0.4433 | 0.048* | |
| H12C | 0.8591 | 0.3237 | 0.3671 | 0.048* | |
| C13 | 0.56205 (19) | 0.9407 (4) | −0.07679 (18) | 0.0295 (7) | |

| | | | | | |
|---|---|---|---|---|---|
| C14A | 0.5044 (7) | 0.7798 (12) | −0.0695 (6) | 0.032 (3)* | 0.52 (3) |
| H14A | 0.4508 | 0.8221 | −0.0653 | 0.039* | 0.52 (3) |
| H14B | 0.4969 | 0.6957 | −0.1132 | 0.039* | 0.52 (3) |
| C15A | 0.5546 (8) | 0.6956 (12) | 0.0066 (5) | 0.035 (2)* | 0.52 (3) |
| H15A | 0.5568 | 0.5641 | 0.0011 | 0.042* | 0.52 (3) |
| H15B | 0.5292 | 0.7227 | 0.0488 | 0.042* | 0.52 (3) |
| C16A | 0.6444 (5) | 0.7776 (18) | 0.0258 (6) | 0.045 (3)* | 0.52 (3) |
| H16A | 0.6656 | 0.8027 | 0.0814 | 0.054* | 0.52 (3) |
| H16B | 0.6823 | 0.6969 | 0.0089 | 0.054* | 0.52 (3) |
| C14B | 0.5226 (8) | 0.7851 (14) | −0.0571 (7) | 0.033 (3)* | 0.48 (3) |
| H14C | 0.5107 | 0.6995 | −0.1006 | 0.040* | 0.48 (3) |
| H14D | 0.4707 | 0.8193 | −0.0461 | 0.040* | 0.48 (3) |
| C15B | 0.5793 (10) | 0.6982 (14) | 0.0145 (6) | 0.045 (3)* | 0.48 (3) |
| H15C | 0.5501 | 0.6709 | 0.0539 | 0.055* | 0.48 (3) |
| H15D | 0.6037 | 0.5868 | 0.0008 | 0.055* | 0.48 (3) |
| C16B | 0.6381 (6) | 0.829 (2) | 0.0403 (7) | 0.048 (3)* | 0.48 (3) |
| H16C | 0.6930 | 0.7750 | 0.0543 | 0.058* | 0.48 (3) |
| H16D | 0.6292 | 0.8906 | 0.0860 | 0.058* | 0.48 (3) |
| C17 | 0.6911 (2) | 1.0796 (6) | −0.0191 (2) | 0.0549 (11) | |
| H17A | 0.7374 | 1.0236 | −0.0326 | 0.082* | |
| H17B | 0.7089 | 1.1299 | 0.0329 | 0.082* | |
| H17C | 0.6692 | 1.1751 | −0.0559 | 0.082* | |
| H1N | 0.538 (3) | −0.080 (6) | 0.234 (3) | 0.061 (14)* | |
| H2N | 0.613 (2) | 0.310 (5) | 0.290 (2) | 0.035 (10)* | |
| H3N | 0.994 (2) | 0.092 (5) | 0.250 (2) | 0.044 (11)* | |
| H4N | 0.986 (2) | 0.224 (5) | 0.189 (2) | 0.032 (9)* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0261 (4) | 0.0232 (4) | 0.0392 (4) | −0.0011 (3) | 0.0127 (3) | 0.0036 (3) |
| S1 | 0.0181 (4) | 0.0252 (4) | 0.0282 (4) | 0.0008 (3) | 0.0066 (3) | 0.0044 (3) |
| S2 | 0.0179 (4) | 0.0233 (4) | 0.0224 (4) | 0.0000 (3) | 0.0066 (3) | −0.0006 (3) |
| O1 | 0.0254 (11) | 0.0485 (14) | 0.0340 (12) | −0.0007 (11) | 0.0010 (9) | 0.0174 (11) |
| O2 | 0.0282 (11) | 0.0253 (11) | 0.0422 (12) | −0.0012 (9) | 0.0139 (10) | −0.0033 (9) |
| O3 | 0.0282 (11) | 0.0337 (12) | 0.0205 (10) | 0.0016 (9) | 0.0073 (9) | 0.0022 (9) |
| O4 | 0.0213 (10) | 0.0242 (11) | 0.0303 (11) | 0.0019 (8) | 0.0097 (9) | −0.0018 (9) |
| O5 | 0.0278 (11) | 0.0301 (11) | 0.0312 (11) | 0.0022 (9) | 0.0133 (10) | 0.0012 (9) |
| O6 | 0.0296 (12) | 0.0368 (13) | 0.0369 (13) | −0.0007 (10) | −0.0003 (10) | 0.0083 (10) |
| N1 | 0.0177 (12) | 0.0294 (14) | 0.0269 (13) | 0.0008 (10) | 0.0053 (11) | 0.0001 (11) |
| N2 | 0.0270 (14) | 0.0262 (15) | 0.0425 (16) | 0.0012 (11) | 0.0171 (12) | −0.0038 (12) |
| N3 | 0.0198 (12) | 0.0260 (14) | 0.0283 (14) | −0.0016 (11) | 0.0054 (11) | 0.0013 (12) |
| N4 | 0.0261 (13) | 0.0316 (14) | 0.0295 (14) | −0.0009 (11) | 0.0086 (11) | 0.0002 (11) |
| N5 | 0.0433 (17) | 0.0437 (17) | 0.0254 (14) | 0.0050 (13) | 0.0071 (13) | 0.0052 (12) |
| C1 | 0.0277 (15) | 0.0299 (16) | 0.0321 (16) | −0.0015 (13) | 0.0131 (13) | −0.0050 (13) |
| C2 | 0.0195 (14) | 0.0259 (15) | 0.0258 (14) | 0.0014 (12) | 0.0053 (11) | −0.0024 (12) |
| C7 | 0.0211 (14) | 0.0210 (14) | 0.0345 (16) | 0.0022 (12) | 0.0072 (12) | −0.0014 (12) |
| C6 | 0.0194 (13) | 0.0222 (14) | 0.0263 (14) | −0.0019 (12) | 0.0049 (11) | 0.0010 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C5 | 0.0142 (13) | 0.0253 (14) | 0.0220 (14) | 0.0015 (11) | 0.0021 (11) | −0.0014 (11) |
| C4 | 0.0200 (14) | 0.0214 (14) | 0.0224 (14) | 0.0023 (11) | 0.0022 (11) | 0.0009 (11) |
| C3 | 0.0162 (13) | 0.0245 (14) | 0.0224 (14) | 0.0007 (11) | 0.0032 (11) | 0.0014 (11) |
| C8 | 0.0231 (15) | 0.0296 (16) | 0.0228 (14) | 0.0004 (12) | −0.0004 (12) | −0.0029 (12) |
| C9 | 0.0304 (17) | 0.0294 (16) | 0.0312 (16) | −0.0015 (13) | 0.0049 (13) | 0.0010 (13) |
| C10 | 0.0380 (19) | 0.0414 (19) | 0.0326 (17) | −0.0058 (16) | 0.0122 (15) | 0.0032 (15) |
| C11 | 0.0298 (16) | 0.0400 (18) | 0.0276 (16) | 0.0007 (14) | 0.0134 (14) | −0.0020 (14) |
| C12 | 0.0336 (17) | 0.0277 (16) | 0.0326 (16) | −0.0013 (14) | 0.0047 (14) | 0.0022 (13) |
| C13 | 0.0286 (16) | 0.0328 (17) | 0.0278 (16) | 0.0057 (13) | 0.0086 (14) | −0.0026 (13) |
| C17 | 0.037 (2) | 0.074 (3) | 0.045 (2) | −0.010 (2) | −0.0049 (17) | 0.009 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C6 | 1.735 (3) | C4—H4 | 0.9500 |
| S1—O1 | 1.431 (2) | C8—C9 | 1.520 (4) |
| S1—O2 | 1.434 (2) | C9—C10 | 1.529 (4) |
| S1—N1 | 1.625 (3) | C9—H9A | 0.9900 |
| S1—C3 | 1.756 (3) | C9—H9B | 0.9900 |
| S2—O4 | 1.427 (2) | C10—C11 | 1.516 (5) |
| S2—O3 | 1.436 (2) | C10—H10A | 0.9900 |
| S2—N3 | 1.588 (3) | C10—H10B | 0.9900 |
| S2—C5 | 1.787 (3) | C11—H11A | 0.9900 |
| O5—C8 | 1.239 (4) | C11—H11B | 0.9900 |
| O6—C13 | 1.241 (4) | C12—H12A | 0.9800 |
| N1—C1 | 1.453 (4) | C12—H12B | 0.9800 |
| N1—H1N | 0.79 (4) | C12—H12C | 0.9800 |
| N2—C2 | 1.368 (4) | C13—C14B | 1.435 (11) |
| N2—C1 | 1.437 (4) | C13—C14A | 1.582 (11) |
| N2—H2N | 0.79 (4) | C14A—C15A | 1.547 (12) |
| N3—H3N | 0.84 (4) | C14A—H14A | 0.9900 |
| N3—H4N | 0.86 (4) | C14A—H14B | 0.9900 |
| N4—C8 | 1.330 (4) | C15A—C16A | 1.602 (14) |
| N4—C12 | 1.448 (4) | C15A—H15A | 0.9900 |
| N4—C11 | 1.466 (4) | C15A—H15B | 0.9900 |
| N5—C13 | 1.318 (4) | C16A—H16A | 0.9900 |
| N5—C16B | 1.411 (10) | C16A—H16B | 0.9900 |
| N5—C17 | 1.419 (5) | C14B—C15B | 1.538 (14) |
| N5—C16A | 1.525 (10) | C14B—H14C | 0.9900 |
| C1—H1A | 0.9900 | C14B—H14D | 0.9900 |
| C1—H1B | 0.9900 | C15B—C16B | 1.390 (14) |
| C2—C7 | 1.397 (4) | C15B—H15C | 0.9900 |
| C2—C3 | 1.416 (4) | C15B—H15D | 0.9900 |
| C7—C6 | 1.382 (4) | C16B—H16C | 0.9900 |
| C7—H7 | 0.9500 | C16B—H16D | 0.9900 |
| C6—C5 | 1.400 (4) | C17—H17A | 0.9800 |
| C5—C4 | 1.386 (4) | C17—H17B | 0.9800 |
| C4—C3 | 1.393 (4) | C17—H17C | 0.9800 |

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| O1—S1—O2 | 118.35 (14) | C9—C10—H10A | 110.9 |
| O1—S1—N1 | 108.55 (14) | C11—C10—H10B | 110.9 |
| O2—S1—N1 | 107.21 (13) | C9—C10—H10B | 110.9 |
| O1—S1—C3 | 109.54 (14) | H10A—C10—H10B | 108.9 |
| O2—S1—C3 | 109.62 (13) | N4—C11—C10 | 103.1 (2) |
| N1—S1—C3 | 102.34 (13) | N4—C11—H11A | 111.2 |
| O4—S2—O3 | 118.80 (12) | C10—C11—H11A | 111.2 |
| O4—S2—N3 | 108.95 (14) | N4—C11—H11B | 111.2 |
| O3—S2—N3 | 107.43 (14) | C10—C11—H11B | 111.2 |
| O4—S2—C5 | 104.41 (12) | H11A—C11—H11B | 109.1 |
| O3—S2—C5 | 107.89 (13) | N4—C12—H12A | 109.5 |
| N3—S2—C5 | 109.06 (13) | N4—C12—H12B | 109.5 |
| C1—N1—S1 | 112.6 (2) | H12A—C12—H12B | 109.5 |
| C1—N1—H1N | 115 (3) | N4—C12—H12C | 109.5 |
| S1—N1—H1N | 112 (3) | H12A—C12—H12C | 109.5 |
| C2—N2—C1 | 122.4 (3) | H12B—C12—H12C | 109.5 |
| C2—N2—H2N | 116 (3) | O6—C13—N5 | 124.6 (3) |
| C1—N2—H2N | 120 (3) | O6—C13—C14B | 132.1 (6) |
| S2—N3—H3N | 115 (3) | N5—C13—C14B | 103.4 (6) |
| S2—N3—H4N | 116 (2) | O6—C13—C14A | 120.7 (5) |
| H3N—N3—H4N | 118 (4) | N5—C13—C14A | 114.8 (5) |
| C8—N4—C12 | 124.0 (3) | C15A—C14A—C13 | 99.9 (7) |
| C8—N4—C11 | 113.9 (3) | C15A—C14A—H14A | 111.8 |
| C12—N4—C11 | 121.6 (3) | C13—C14A—H14A | 111.8 |
| C13—N5—C16B | 116.6 (5) | C15A—C14A—H14B | 111.8 |
| C13—N5—C17 | 123.5 (3) | C13—C14A—H14B | 111.8 |
| C16B—N5—C17 | 119.8 (5) | H14A—C14A—H14B | 109.5 |
| C13—N5—C16A | 111.1 (4) | C14A—C15A—C16A | 108.1 (7) |
| C17—N5—C16A | 123.5 (4) | C14A—C15A—H15A | 110.1 |
| N2—C1—N1 | 110.8 (2) | C16A—C15A—H15A | 110.1 |
| N2—C1—H1A | 109.5 | C14A—C15A—H15B | 110.1 |
| N1—C1—H1A | 109.5 | C16A—C15A—H15B | 110.1 |
| N2—C1—H1B | 109.5 | H15A—C15A—H15B | 108.4 |
| N1—C1—H1B | 109.5 | N5—C16A—C15A | 101.5 (6) |
| H1A—C1—H1B | 108.1 | N5—C16A—H16A | 111.5 |
| N2—C2—C7 | 120.5 (3) | C15A—C16A—H16A | 111.5 |
| N2—C2—C3 | 121.8 (3) | N5—C16A—H16B | 111.5 |
| C7—C2—C3 | 117.6 (2) | C15A—C16A—H16B | 111.5 |
| C6—C7—C2 | 120.7 (3) | H16A—C16A—H16B | 109.3 |
| C6—C7—H7 | 119.7 | C13—C14B—C15B | 108.5 (8) |
| C2—C7—H7 | 119.7 | C13—C14B—H14C | 110.0 |
| C7—C6—C5 | 121.8 (3) | C15B—C14B—H14C | 110.0 |
| C7—C6—Cl1 | 116.4 (2) | C13—C14B—H14D | 110.0 |
| C5—C6—Cl1 | 121.8 (2) | C15B—C14B—H14D | 110.0 |
| C4—C5—C6 | 117.9 (2) | H14C—C14B—H14D | 108.4 |
| C4—C5—S2 | 118.0 (2) | C16B—C15B—C14B | 102.9 (9) |
| C6—C5—S2 | 124.1 (2) | C16B—C15B—H15C | 111.2 |
| C5—C4—C3 | 121.1 (3) | C14B—C15B—H15C | 111.2 |

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| C5—C4—H4 | 119.4 | C16B—C15B—H15D | 111.2 |
| C3—C4—H4 | 119.4 | C14B—C15B—H15D | 111.2 |
| C4—C3—C2 | 120.7 (3) | H15C—C15B—H15D | 109.1 |
| C4—C3—S1 | 120.1 (2) | C15B—C16B—N5 | 105.9 (8) |
| C2—C3—S1 | 119.2 (2) | C15B—C16B—H16C | 110.6 |
| O5—C8—N4 | 125.6 (3) | N5—C16B—H16C | 110.6 |
| O5—C8—C9 | 126.0 (3) | C15B—C16B—H16D | 110.6 |
| N4—C8—C9 | 108.4 (3) | N5—C16B—H16D | 110.6 |
| C8—C9—C10 | 103.8 (3) | H16C—C16B—H16D | 108.7 |
| C8—C9—H9A | 111.0 | N5—C17—H17A | 109.5 |
| C10—C9—H9A | 111.0 | N5—C17—H17B | 109.5 |
| C8—C9—H9B | 111.0 | H17A—C17—H17B | 109.5 |
| C10—C9—H9B | 111.0 | N5—C17—H17C | 109.5 |
| H9A—C9—H9B | 109.0 | H17A—C17—H17C | 109.5 |
| C11—C10—C9 | 104.5 (2) | H17B—C17—H17C | 109.5 |
| C11—C10—H10A | 110.9 | | |

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|---|---|---|---|
| O1—S1—N1—C1 | 65.6 (2) | C12—N4—C8—O5 | 3.5 (5) |
| O2—S1—N1—C1 | −165.5 (2) | C11—N4—C8—O5 | 175.8 (3) |
| C3—S1—N1—C1 | −50.2 (2) | C12—N4—C8—C9 | −175.9 (3) |
| C2—N2—C1—N1 | −42.9 (4) | C11—N4—C8—C9 | −3.6 (3) |
| S1—N1—C1—N2 | 65.8 (3) | O5—C8—C9—C10 | 168.1 (3) |
| C1—N2—C2—C7 | −174.7 (3) | N4—C8—C9—C10 | −12.6 (3) |
| C1—N2—C2—C3 | 7.9 (5) | C8—C9—C10—C11 | 22.9 (3) |
| N2—C2—C7—C6 | 179.0 (3) | C8—N4—C11—C10 | 18.3 (3) |
| C3—C2—C7—C6 | −3.4 (4) | C12—N4—C11—C10 | −169.2 (3) |
| C2—C7—C6—C5 | 0.9 (4) | C9—C10—C11—N4 | −24.6 (3) |
| C2—C7—C6—Cl1 | −178.7 (2) | C16B—N5—C13—O6 | 172.2 (9) |
| C7—C6—C5—C4 | 1.1 (4) | C17—N5—C13—O6 | −3.6 (5) |
| Cl1—C6—C5—C4 | −179.3 (2) | C16A—N5—C13—O6 | −168.2 (6) |
| C7—C6—C5—S2 | −179.6 (2) | C16B—N5—C13—C14B | −7.4 (10) |
| Cl1—C6—C5—S2 | −0.1 (4) | C17—N5—C13—C14B | 176.8 (5) |
| O4—S2—C5—C4 | −6.0 (2) | C16A—N5—C13—C14B | 12.2 (8) |
| O3—S2—C5—C4 | 121.3 (2) | C16B—N5—C13—C14A | −6.7 (10) |
| N3—S2—C5—C4 | −122.4 (2) | C17—N5—C13—C14A | 177.5 (5) |
| O4—S2—C5—C6 | 174.8 (2) | C16A—N5—C13—C14A | 12.9 (8) |
| O3—S2—C5—C6 | −58.0 (3) | O6—C13—C14A—C15A | −177.5 (5) |
| N3—S2—C5—C6 | 58.4 (3) | N5—C13—C14A—C15A | 1.4 (7) |
| C6—C5—C4—C3 | −0.4 (4) | C14B—C13—C14A—C15A | 5 (3) |
| S2—C5—C4—C3 | −179.7 (2) | C13—C14A—C15A—C16A | −14.2 (10) |
| C5—C4—C3—C2 | −2.3 (4) | C13—N5—C16A—C15A | −20.6 (10) |
| C5—C4—C3—S1 | 175.8 (2) | C17—N5—C16A—C15A | 174.8 (5) |
| N2—C2—C3—C4 | −178.4 (3) | C14A—C15A—C16A—N5 | 21.0 (11) |
| C7—C2—C3—C4 | 4.2 (4) | O6—C13—C14B—C15B | 177.0 (6) |
| N2—C2—C3—S1 | 3.5 (4) | N5—C13—C14B—C15B | −3.5 (8) |
| C7—C2—C3—S1 | −173.9 (2) | C14A—C13—C14B—C15B | 180 (4) |
| O1—S1—C3—C4 | 83.6 (3) | C13—C14B—C15B—C16B | 12.5 (14) |
| O2—S1—C3—C4 | −47.8 (3) | C14B—C15B—C16B—N5 | −15.9 (16) |

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| N1—S1—C3—C4 | −161.3 (2) | C13—N5—C16B—C15B | 16.2 (17) |
| O1—S1—C3—C2 | −98.2 (3) | C17—N5—C16B—C15B | −167.9 (10) |
| O2—S1—C3—C2 | 130.4 (2) | C16A—N5—C16B—C15B | −61 (2) |
| N1—S1—C3—C2 | 16.8 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*N*···O6$^{i}$ | 0.79 (5) | 2.01 (5) | 2.799 (4) | 177 (5) |
| N2—H2*N*···O6$^{ii}$ | 0.80 (4) | 2.35 (4) | 2.929 (4) | 130 (3) |
| N3—H3*N*···O5 | 0.84 (3) | 2.12 (4) | 2.891 (4) | 153 (4) |
| N3—H4*N*···O5$^{iii}$ | 0.86 (4) | 2.04 (4) | 2.884 (4) | 169 (3) |
| C1—H1*A*···O6$^{ii}$ | 0.99 | 2.58 | 3.075 (4) | 111 |
| C7—H7···O2$^{iv}$ | 0.95 | 2.33 | 3.249 (4) | 164 |
| C11—H11*B*···O3$^{v}$ | 0.99 | 2.52 | 3.423 (4) | 152 |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+2, *y*+1/2, −*z*+1/2; (iv) *x*, *y*+1, *z*; (v) *x*, −*y*+1/2, *z*+1/2.