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Crystal structure of a mixed solvated form of amoxapine acetate

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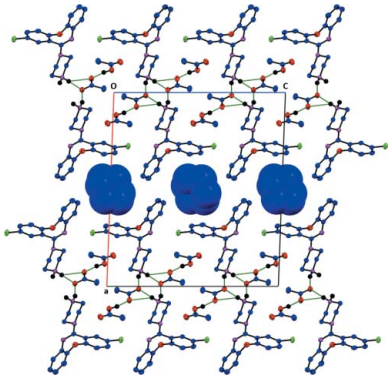
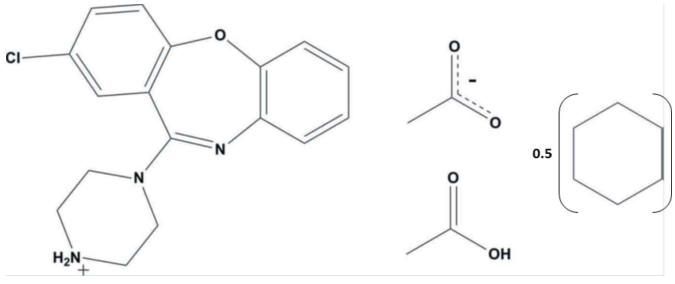
The mixed solvated salt 4-(2-chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)piperazin-1-ium acetate–acetic acid–cyclohexane (2/2/1), $C_{17}H_{17}ClN_3O^+\cdot C_2H_3O_2^-\cdot C_2H_4O_2\cdot 0.5C_6H_{12}$, crystallizes with one molecule of protonated amoxapine (AXPN), an acetate anion and a molecule of acetic acid together with half a molecule of cyclohexane. In the centrosymmetric crystal, both enantiomers of the protonated AXPN molecule stack alternatively along [001]. Acetate anions connect the AXPN cations through N—H···O hydrogen bonding in the [010] direction, creating a sheet lying parallel to (100). The acetic acid molecules are linked to the acetate anions *via* O—H···O hydrogen bonds within the sheets. Within the sheets there are also a number of C—H···O hydrogen bonds present. The cyclohexane solvent molecules occupy the space between the sheets.

1. Chemical context

2-Chloro-11-(piperazin-1-yl)dibenzo[*b*,*f*][1,4]oxazepine (Amoxapine, AXPN) is a benzodiazepine derivative and exhibits anti-depressant properties (Greenbla & Osterber, 1968) with one reported crystal structure (CSD refcode: AMOXAP; Cosulich & Lovell, 1977). AXPN acetate acetic acid cyclohexane was obtained as a part of a wider investigation that couples experimental crystallization techniques with computational methods in order to obtain a better understanding of the factors underpinning the solid-state structure and diversity of structurally related compounds, *i.e.* olanzapine, clozapine, loxapine and AXPN (Bhardwaj & Florence, 2013; Bhardwaj, Johnston *et al.*, 2013; Bhardwaj, Price *et al.*, 2013). The sample of AXPN acetate acetic acid cyclohexane was isolated during an experimental physical form screen of AXPN. The sample was identified as a novel form using multi-sample foil transmission X-ray powder diffraction analysis (Florence *et al.*, 2003). A suitable sample for single crystal X-ray diffraction analysis was obtained from slow evaporation of a saturated solution of AXPN in a 1:1 molar ratio of acetic acid and cyclohexane at room temperature.





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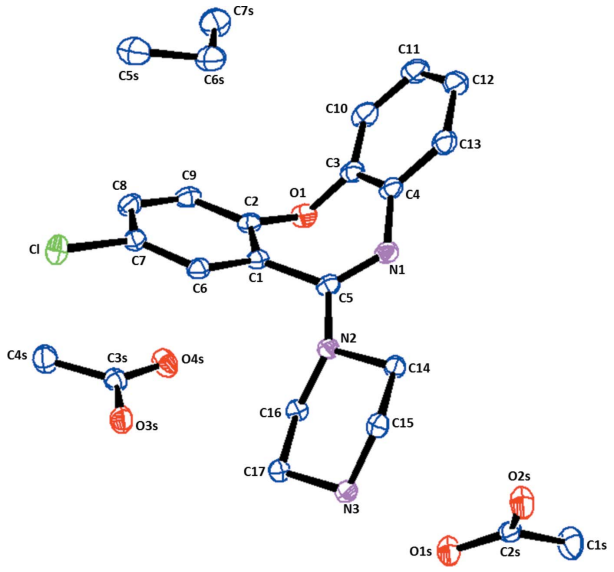

Figure 1
A view of the molecular structure of the asymmetric unit of the title molecular salt, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The title compound crystallizes with one molecule of protonated AXPN and an acetate anion each with a molecule of acetic acid and a half molecule of cyclohexane (which lies across a center of inversion) as solvent of crystallization in the asymmetric unit (Fig. 1). The dioxazepine ring of AXPN exists in a puckered conformation between the planes of the benzene rings [the benzene rings fused to the central ring make a dihedral angle of 58.63 (6)°], and the piperazine ring adopts a chair conformation, as observed in the AXPN free base (CSD refcode: AMOXAP; Cosulich and Lovell, 1977) and structurally related analogues (Bhardwaj & Florence, 2013; Bhardwaj, Johnston *et al.*, 2013; Bhardwaj, Price *et al.*, 2013).

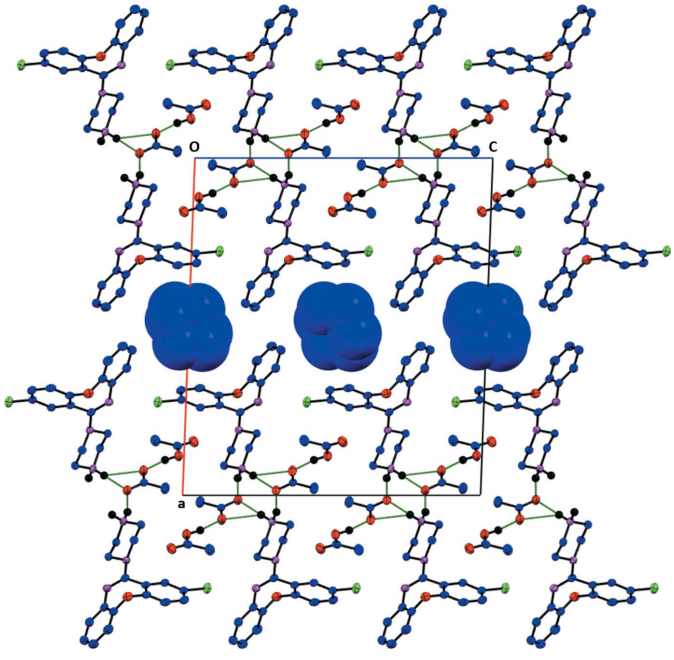

Figure 2
The crystal packing of the title molecular salt, viewed down the *b* axis. The cyclohexane molecules are shown as a blue space-fill model. Hydrogen bonds are shown as green lines (see Table 1 for details; atom colour code: C, N, O, Cl and H are blue, violet, red, green and black, respectively; H atoms not involved in hydrogen bonding have been omitted for clarity).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N3*···O1*S*	0.91 (2)	1.86 (2)	2.7664 (13)	175 (2)
O3*S*—H1*S*···O2*S*^{i}	0.94 (2)	1.61 (2)	2.5375 (13)	171 (2)
N3—H2*N3*···O1*S*^{ii}	0.94 (2)	1.82 (2)	2.7292 (14)	162 (1)
C1*S*—H1*S*1···O3*S*^{ii}	0.96	2.42	3.3778 (18)	172
C14—H14*A*···O1^{iii}	0.97	2.59	3.2448 (15)	125
C17—H17*A*···O4*S*^{iii}	0.97	2.32	3.2314 (15)	155

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

3. Supramolecular features

In the crystal, opposite enantiomers of protonated AXPN molecules stack along the *c*-axis direction. Each protonated

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{17}ClN_3O^+·C_2H_3O_2^-·C_2H_4O_2·0.5C_6H_{12}$
M_r	475.96
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	21.0726 (12), 6.0393 (3), 18.6087 (10)
β (°)	92.096 (2)
V (Å^3)	2366.6 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.55 × 0.22 × 0.11
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.647, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18828, 4860, 4177
R_{int}	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.082, 1.03
No. of reflections	4860
No. of parameters	312
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2010).

AXPN molecule forms two N—H···O hydrogen bonds with two acetate anions, which connect it to an adjacent protonated AXPN molecule along the *b* axis, creating a sheet-like structure parallel to (100); see Fig. 2 and Table 1. The acetic acid molecules act as hydrogen-bond donors to acetate anions and are present between the protonated AXPN molecules along the *c*-axis direction. There are also C—H···O hydrogen bonds present within the sheets (Table 1). These sheets stack along the *a* axis and the cyclohexane molecules occupy the space between the sheets (Fig. 2).

4. Synthesis and crystallization

Rod-shaped crystals were grown from a saturated solution of AXPN in a 1:1 molar ratio of acetic acid and cyclohexane by isothermal solvent evaporation at 298 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N- and O-bound H atoms were located in a difference Fourier map and freely refined. The C-bound H atoms were placed in calculated positions and refined as riding atoms: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and = 1.2U_{eq}(C) for other H atoms.

Acknowledgements

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008), *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004), *publCIF* (Westrip, 2010).

4-(2-Chlorodibenzo[*b*,*f*][1,4]oxazepin-11-yl)piperazin-1-ium acetate–acetic acid–cyclohexane (2/2/1)

Crystal data

$C_{17}H_{17}ClN_3O^+\cdot C_2H_3O_2^-\cdot C_2H_4O_2\cdot 0.5C_6H_{12}$
M_r = 475.96
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 21.0726 (12) Å
b = 6.0393 (3) Å
c = 18.6087 (10) Å
β = 92.096 (2)°
V = 2366.6 (2) Å^3
Z = 4
$F(000)$ = 1008
D_x = 1.336 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9940 reflections
θ = 2.9–26.4°
μ = 0.20 mm^{-1}
T = 150 K
Rod, colourless
0.55 × 0.22 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.647, T_{max} = 0.745
18828 measured reflections
4860 independent reflections
4177 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 26.4°, θ_{min} = 1.9°
h = −26→26
k = −6→7
l = −23→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.082
S = 1.03
4860 reflections
312 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
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
H2N3	0.0503 (7)	−0.014 (3)	0.3171 (8)	0.029 (4)*
H1N3	0.0584 (7)	0.167 (3)	0.2658 (9)	0.025 (4)*
H1S	0.1043 (10)	0.564 (4)	0.5635 (12)	0.064 (6)*
Cl	0.276361 (16)	0.39554 (6)	0.594267 (17)	0.02772 (10)
O1	0.30157 (4)	0.90957 (15)	0.32837 (5)	0.0225 (2)
O2S	0.07221 (4)	0.03016 (16)	0.13430 (5)	0.0259 (2)
O1S	0.01425 (4)	0.28471 (16)	0.18632 (5)	0.0234 (2)
N3	0.07793 (5)	0.09975 (18)	0.30430 (6)	0.0161 (2)
N2	0.19325 (5)	0.34168 (17)	0.31916 (5)	0.0160 (2)
N1	0.27645 (5)	0.48819 (18)	0.25813 (6)	0.0196 (2)
C4	0.33285 (6)	0.6088 (2)	0.25098 (7)	0.0198 (3)
C6	0.25997 (5)	0.4584 (2)	0.45099 (6)	0.0177 (2)
H6	0.2404	0.3204	0.4501	0.021*
C2S	0.03703 (5)	0.1974 (2)	0.13128 (6)	0.0175 (2)
C5	0.24619 (5)	0.4789 (2)	0.31684 (6)	0.0170 (2)
C2	0.29573 (5)	0.7852 (2)	0.39086 (7)	0.0183 (3)
C8	0.31125 (6)	0.7556 (2)	0.51865 (7)	0.0228 (3)
H8	0.3256	0.8140	0.5625	0.027*
C15	0.13972 (6)	0.0041 (2)	0.28291 (6)	0.0167 (2)
H15A	0.1326	−0.1006	0.2439	0.020*
H15B	0.1596	−0.0741	0.3233	0.020*
C1	0.26655 (5)	0.5783 (2)	0.38728 (7)	0.0168 (2)
C17	0.08763 (5)	0.2614 (2)	0.36432 (6)	0.0169 (2)
H17A	0.1044	0.1855	0.4068	0.020*
H17B	0.0473	0.3278	0.3757	0.020*
C7	0.28300 (6)	0.5483 (2)	0.51529 (7)	0.0200 (3)
C9	0.31772 (6)	0.8743 (2)	0.45570 (7)	0.0219 (3)
H9	0.3368	1.0133	0.4569	0.026*
C16	0.13360 (5)	0.4404 (2)	0.34257 (7)	0.0164 (2)
H16A	0.1145	0.5276	0.3037	0.020*
H16B	0.1425	0.5384	0.3830	0.020*
C10	0.39883 (6)	0.9372 (2)	0.26691 (7)	0.0264 (3)
H10	0.4059	1.0745	0.2884	0.032*
C3	0.34532 (6)	0.8156 (2)	0.28257 (7)	0.0208 (3)
C13	0.37702 (6)	0.5278 (2)	0.20305 (7)	0.0234 (3)

H13	0.3701	0.3911	0.1811	0.028*
C14	0.18287 (6)	0.1887 (2)	0.25899 (6)	0.0167 (2)
H14A	0.2231	0.1280	0.2446	0.020*
H14B	0.1634	0.2660	0.2182	0.020*
C12	0.43094 (6)	0.6479 (3)	0.18768 (7)	0.0275 (3)
H12	0.4600	0.5904	0.1562	0.033*
C1S	0.02027 (7)	0.2996 (3)	0.05945 (7)	0.0298 (3)
H1S1	−0.0177	0.2323	0.0396	0.045*
H1S2	0.0544	0.2763	0.0275	0.045*
H1S3	0.0134	0.4556	0.0653	0.045*
C11	0.44173 (6)	0.8535 (3)	0.21911 (8)	0.0297 (3)
H11	0.4776	0.9348	0.2082	0.036*
O4S	0.15853 (5)	0.90631 (17)	0.46941 (5)	0.0285 (2)
O3S	0.11677 (5)	0.61112 (17)	0.51804 (5)	0.0266 (2)
C4S	0.16200 (7)	0.8869 (2)	0.59805 (7)	0.0292 (3)
H4S1	0.1780	1.0354	0.5958	0.044*
H4S2	0.1937	0.7926	0.6202	0.044*
H4S3	0.1246	0.8849	0.6259	0.044*
C3S	0.14591 (6)	0.8053 (2)	0.52335 (7)	0.0212 (3)
C6S	0.44669 (7)	0.4352 (3)	0.45153 (8)	0.0347 (4)
H6S1	0.4659	0.3259	0.4209	0.042*
H6S2	0.4024	0.4505	0.4362	0.042*
C5S	0.45086 (7)	0.3553 (3)	0.52918 (9)	0.0363 (4)
H5S1	0.4317	0.2097	0.5322	0.044*
H5S2	0.4274	0.4555	0.5591	0.044*
C7S	0.48016 (7)	0.6561 (3)	0.44293 (9)	0.0370 (4)
H7S1	0.4580	0.7693	0.4691	0.044*
H7S2	0.4789	0.6974	0.3925	0.044*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.02984 (17)	0.0361 (2)	0.01704 (16)	0.00076 (14)	−0.00169 (12)	0.00358 (14)
O1	0.0221 (4)	0.0177 (4)	0.0275 (5)	−0.0006 (4)	−0.0010 (4)	0.0056 (4)
O2S	0.0311 (5)	0.0282 (5)	0.0183 (5)	0.0132 (4)	0.0001 (4)	0.0000 (4)
O1S	0.0258 (5)	0.0263 (5)	0.0179 (4)	0.0112 (4)	0.0001 (4)	0.0005 (4)
N3	0.0174 (5)	0.0156 (5)	0.0151 (5)	−0.0033 (4)	−0.0012 (4)	0.0029 (4)
N2	0.0154 (5)	0.0161 (5)	0.0165 (5)	−0.0018 (4)	0.0005 (4)	−0.0018 (4)
N1	0.0178 (5)	0.0222 (5)	0.0186 (5)	−0.0040 (4)	−0.0010 (4)	0.0033 (4)
C4	0.0183 (6)	0.0232 (7)	0.0175 (6)	−0.0036 (5)	−0.0034 (5)	0.0071 (5)
C6	0.0149 (5)	0.0185 (6)	0.0197 (6)	0.0015 (5)	−0.0005 (4)	−0.0006 (5)
C2S	0.0154 (5)	0.0197 (6)	0.0174 (6)	−0.0009 (5)	−0.0012 (4)	0.0017 (5)
C5	0.0164 (5)	0.0151 (6)	0.0192 (6)	−0.0001 (5)	−0.0024 (4)	0.0025 (5)
C2	0.0146 (5)	0.0179 (6)	0.0223 (6)	0.0017 (5)	−0.0010 (5)	0.0020 (5)
C8	0.0184 (6)	0.0274 (7)	0.0222 (6)	0.0019 (5)	−0.0036 (5)	−0.0073 (6)
C15	0.0201 (6)	0.0144 (6)	0.0155 (6)	0.0002 (5)	−0.0011 (4)	0.0011 (5)
C1	0.0133 (5)	0.0175 (6)	0.0196 (6)	0.0010 (4)	−0.0013 (4)	−0.0007 (5)
C17	0.0171 (5)	0.0184 (6)	0.0154 (6)	−0.0001 (5)	0.0010 (4)	0.0006 (5)

C7	0.0166 (6)	0.0259 (7)	0.0175 (6)	0.0040 (5)	−0.0005 (5)	0.0011 (5)
C9	0.0164 (6)	0.0192 (6)	0.0298 (7)	−0.0009 (5)	−0.0021 (5)	−0.0047 (5)
C16	0.0173 (6)	0.0141 (6)	0.0179 (6)	−0.0001 (4)	0.0003 (4)	−0.0003 (5)
C10	0.0266 (7)	0.0256 (7)	0.0264 (7)	−0.0086 (6)	−0.0048 (5)	0.0074 (6)
C3	0.0184 (6)	0.0235 (7)	0.0202 (6)	−0.0008 (5)	−0.0029 (5)	0.0074 (5)
C13	0.0228 (6)	0.0281 (7)	0.0193 (6)	−0.0038 (5)	−0.0009 (5)	0.0039 (6)
C14	0.0176 (5)	0.0173 (6)	0.0150 (6)	−0.0011 (5)	−0.0001 (4)	−0.0002 (5)
C12	0.0211 (6)	0.0394 (8)	0.0221 (7)	−0.0036 (6)	0.0017 (5)	0.0069 (6)
C1S	0.0350 (7)	0.0344 (8)	0.0197 (7)	0.0083 (6)	−0.0014 (6)	0.0068 (6)
C11	0.0221 (6)	0.0392 (8)	0.0278 (7)	−0.0122 (6)	−0.0008 (5)	0.0099 (6)
O4S	0.0308 (5)	0.0296 (5)	0.0254 (5)	0.0071 (4)	0.0062 (4)	0.0109 (4)
O3S	0.0309 (5)	0.0308 (5)	0.0182 (5)	−0.0071 (4)	0.0018 (4)	0.0010 (4)
C4S	0.0341 (7)	0.0292 (8)	0.0244 (7)	−0.0058 (6)	0.0035 (6)	−0.0020 (6)
C3S	0.0188 (6)	0.0233 (7)	0.0215 (6)	0.0054 (5)	0.0027 (5)	0.0031 (5)
C6S	0.0226 (7)	0.0481 (9)	0.0332 (8)	0.0057 (6)	−0.0017 (6)	−0.0085 (7)
C5S	0.0256 (7)	0.0440 (9)	0.0394 (9)	0.0011 (6)	0.0031 (6)	−0.0021 (7)
C7S	0.0302 (8)	0.0467 (9)	0.0341 (8)	0.0076 (7)	−0.0009 (6)	0.0030 (7)

Geometric parameters (Å, º)

Cl—C7	1.7450 (13)	C16—H16A	0.9700
O1—C2	1.3936 (15)	C16—H16B	0.9700
O1—C3	1.3985 (16)	C10—C3	1.3856 (18)
O2S—C2S	1.2529 (15)	C10—C11	1.387 (2)
O1S—C2S	1.2623 (15)	C10—H10	0.9300
N3—C15	1.4918 (15)	C13—C12	1.3866 (18)
N3—C17	1.4919 (16)	C13—H13	0.9300
N3—H2N3	0.938 (17)	C14—H14A	0.9700
N3—H1N3	0.908 (16)	C14—H14B	0.9700
N2—C5	1.3916 (15)	C12—C11	1.388 (2)
N2—C14	1.4618 (15)	C12—H12	0.9300
N2—C16	1.4716 (15)	C1S—H1S1	0.9600
N1—C5	1.2863 (16)	C1S—H1S2	0.9600
N1—C4	1.4044 (16)	C1S—H1S3	0.9600
C4—C13	1.4006 (19)	C11—H11	0.9300
C4—C3	1.4010 (19)	O4S—C3S	1.2125 (16)
C6—C7	1.3852 (17)	O3S—C3S	1.3256 (16)
C6—C1	1.4005 (17)	O3S—H1S	0.94 (2)
C6—H6	0.9300	C4S—C3S	1.5019 (19)
C2S—C1S	1.5027 (17)	C4S—H4S1	0.9600
C5—C1	1.4905 (17)	C4S—H4S2	0.9600
C2—C9	1.3854 (18)	C4S—H4S3	0.9600
C2—C1	1.3929 (17)	C6S—C7S	1.520 (2)
C8—C9	1.3845 (19)	C6S—C5S	1.523 (2)
C8—C7	1.3867 (19)	C6S—H6S1	0.9700
C8—H8	0.9300	C6S—H6S2	0.9700
C15—C14	1.5156 (16)	C5S—C7S^{i}	1.527 (2)
C15—H15A	0.9700	C5S—H5S1	0.9700

C15—H15B	0.9700	C5S—H5S2	0.9700
C17—C16	1.5164 (16)	C7S—C5S^{i}	1.527 (2)
C17—H17A	0.9700	C7S—H7S1	0.9700
C17—H17B	0.9700	C7S—H7S2	0.9700
C9—H9	0.9300		

C2—O1—C3	111.72 (9)	C3—C10—C11	119.77 (13)
C15—N3—C17	110.86 (9)	C3—C10—H10	120.1
C15—N3—H2N3	110.0 (10)	C11—C10—H10	120.1
C17—N3—H2N3	111.0 (10)	C10—C3—O1	118.21 (12)
C15—N3—H1N3	109.7 (9)	C10—C3—C4	121.72 (13)
C17—N3—H1N3	110.1 (10)	O1—C3—C4	119.99 (11)
H2N3—N3—H1N3	105.1 (13)	C12—C13—C4	121.16 (13)
C5—N2—C14	116.76 (10)	C12—C13—H13	119.4
C5—N2—C16	117.53 (10)	C4—C13—H13	119.4
C14—N2—C16	112.18 (9)	N2—C14—C15	108.33 (9)
C5—N1—C4	123.41 (11)	N2—C14—H14A	110.0
C13—C4—C3	117.37 (12)	C15—C14—H14A	110.0
C13—C4—N1	117.62 (12)	N2—C14—H14B	110.0
C3—C4—N1	124.68 (12)	C15—C14—H14B	110.0
C7—C6—C1	119.10 (12)	H14A—C14—H14B	108.4
C7—C6—H6	120.4	C13—C12—C11	120.26 (13)
C1—C6—H6	120.4	C13—C12—H12	119.9
O2S—C2S—O1S	122.84 (11)	C11—C12—H12	119.9
O2S—C2S—C1S	119.38 (11)	C2S—C1S—H1S1	109.5
O1S—C2S—C1S	117.79 (11)	C2S—C1S—H1S2	109.5
N1—C5—N2	118.38 (11)	H1S1—C1S—H1S2	109.5
N1—C5—C1	126.41 (11)	C2S—C1S—H1S3	109.5
N2—C5—C1	114.71 (10)	H1S1—C1S—H1S3	109.5
C9—C2—C1	121.55 (12)	H1S2—C1S—H1S3	109.5
C9—C2—O1	118.71 (11)	C10—C11—C12	119.73 (13)
C1—C2—O1	119.72 (11)	C10—C11—H11	120.1
C9—C8—C7	119.01 (12)	C12—C11—H11	120.1
C9—C8—H8	120.5	C3S—O3S—H1S	110.1 (14)
C7—C8—H8	120.5	C3S—C4S—H4S1	109.5
N3—C15—C14	109.42 (10)	C3S—C4S—H4S2	109.5
N3—C15—H15A	109.8	H4S1—C4S—H4S2	109.5
C14—C15—H15A	109.8	C3S—C4S—H4S3	109.5
N3—C15—H15B	109.8	H4S1—C4S—H4S3	109.5
C14—C15—H15B	109.8	H4S2—C4S—H4S3	109.5
H15A—C15—H15B	108.2	O4S—C3S—O3S	119.90 (12)
C2—C1—C6	118.71 (11)	O4S—C3S—C4S	123.51 (13)
C2—C1—C5	121.06 (11)	O3S—C3S—C4S	116.59 (11)
C6—C1—C5	120.13 (11)	C7S—C6S—C5S	111.54 (13)
N3—C17—C16	109.77 (9)	C7S—C6S—H6S1	109.3
N3—C17—H17A	109.7	C5S—C6S—H6S1	109.3
C16—C17—H17A	109.7	C7S—C6S—H6S2	109.3
N3—C17—H17B	109.7	C5S—C6S—H6S2	109.3

C16—C17—H17B	109.7	H6S1—C6S—H6S2	108.0
H17A—C17—H17B	108.2	C6S—C5S—C7S^{i}	110.96 (13)
C6—C7—C8	121.92 (12)	C6S—C5S—H5S1	109.4
C6—C7—Cl	118.96 (10)	C7S^{i}—C5S—H5S1	109.4
C8—C7—Cl	119.13 (10)	C6S—C5S—H5S2	109.4
C8—C9—C2	119.70 (12)	C7S^{i}—C5S—H5S2	109.4
C8—C9—H9	120.2	H5S1—C5S—H5S2	108.0
C2—C9—H9	120.2	C6S—C7S—C5S^{i}	111.37 (13)
N2—C16—C17	110.55 (10)	C6S—C7S—H7S1	109.4
N2—C16—H16A	109.5	C5S^{i}—C7S—H7S1	109.4
C17—C16—H16A	109.5	C6S—C7S—H7S2	109.4
N2—C16—H16B	109.5	C5S^{i}—C7S—H7S2	109.4
C17—C16—H16B	109.5	H7S1—C7S—H7S2	108.0
H16A—C16—H16B	108.1		

C5—N1—C4—C13	148.72 (12)	C9—C8—C7—Cl	178.58 (9)
C5—N1—C4—C3	−38.18 (18)	C7—C8—C9—C2	0.34 (18)
C4—N1—C5—N2	−175.55 (11)	C1—C2—C9—C8	0.53 (18)
C4—N1—C5—C1	−4.1 (2)	O1—C2—C9—C8	178.70 (11)
C14—N2—C5—N1	10.69 (16)	C5—N2—C16—C17	−162.34 (10)
C16—N2—C5—N1	−127.00 (12)	C14—N2—C16—C17	58.13 (12)
C14—N2—C5—C1	−161.70 (10)	N3—C17—C16—N2	−54.59 (12)
C16—N2—C5—C1	60.61 (14)	C11—C10—C3—O1	−177.05 (11)
C3—O1—C2—C9	111.88 (12)	C11—C10—C3—C4	−0.4 (2)
C3—O1—C2—C1	−69.92 (13)	C2—O1—C3—C10	−117.96 (12)
C17—N3—C15—C14	−59.51 (12)	C2—O1—C3—C4	65.30 (14)
C9—C2—C1—C6	−0.46 (17)	C13—C4—C3—C10	0.51 (18)
O1—C2—C1—C6	−178.62 (10)	N1—C4—C3—C10	−172.60 (12)
C9—C2—C1—C5	−176.70 (11)	C13—C4—C3—O1	177.14 (11)
O1—C2—C1—C5	5.14 (17)	N1—C4—C3—O1	4.02 (18)
C7—C6—C1—C2	−0.46 (17)	C3—C4—C13—C12	0.09 (18)
C7—C6—C1—C5	175.81 (11)	N1—C4—C13—C12	173.70 (12)
N1—C5—C1—C2	38.92 (18)	C5—N2—C14—C15	159.85 (10)
N2—C5—C1—C2	−149.41 (11)	C16—N2—C14—C15	−60.29 (12)
N1—C5—C1—C6	−137.27 (13)	N3—C15—C14—N2	60.12 (12)
N2—C5—C1—C6	34.41 (16)	C4—C13—C12—C11	−0.8 (2)
C15—N3—C17—C16	56.29 (12)	C3—C10—C11—C12	−0.4 (2)
C1—C6—C7—C8	1.35 (18)	C13—C12—C11—C10	1.0 (2)
C1—C6—C7—Cl	−178.52 (9)	C7S—C6S—C5S—C7S^{i}	−55.20 (19)
C9—C8—C7—C6	−1.29 (18)	C5S—C6S—C7S—C5S^{i}	55.42 (18)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*3···O1*S*	0.91 (2)	1.86 (2)	2.7664 (13)	175 (2)
O3*S*—H1*S*···O2*S*^{ii}	0.94 (2)	1.61 (2)	2.5375 (13)	171 (2)

N3—H2*N*3···O1*S*^{iii}	0.94 (2)	1.82 (2)	2.7292 (14)	162 (1)
C1*S*—H1*S*1···O3*S*^{iii}	0.96	2.42	3.3778 (18)	172
C14—H14*A*···O1^{iv}	0.97	2.59	3.2448 (15)	125
C17—H17*A*···O4*S*^{iv}	0.97	2.32	3.2314 (15)	155

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