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Methyl 2-{[(6*S**,7*R**,8*S**)-7-acetyl-8-(4-chlorophenyl)-4-cyano-6-hydroxy-1,6-dimethyl-5,6,7,8-tetrahydroisoquinolin-3-yl]sulfanyl}acetate

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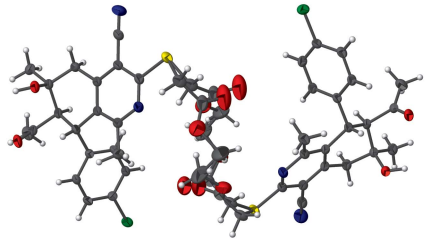
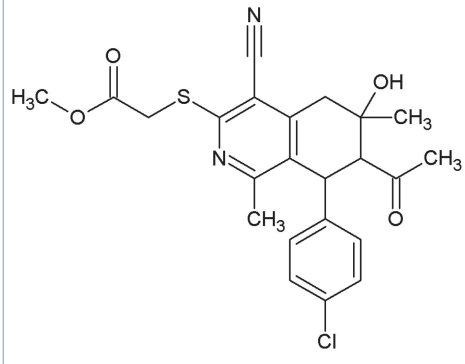
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{23}H_{23}ClN_2O_4S$, the 4-chlorophenyl ring is inclined to the pyridine ring of the isoquinoline group by 71.86 (13)°. In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds, forming inversion dimers, which stack along the *b*-axis direction. The methyl acetate group attached to the S atom is disordered over two sites in a 50:50 ratio, which appears to prevent close intermolecular contacts between the methyl groups.

3D view



Chemical scheme



Structure description

Many analogues of tetrahydroisoquinolines have been found to possess anti-tumor activity (Lane *et al.*, 2006; Aubry *et al.*, 2007). They also have the potential to treat Alzheimer's disease (Hu *et al.*, 2008) and are widely studied cytotoxic agents. Berberrubine, a protoberberine alkaloid, exhibits anti-tumor activity in animal models (Kim *et al.*, 1998). It has also been reported that noscapine, a plant alkaloid, binds to tubulin and induces apoptosis selectively in tumor cells to display anti-cancer activity in ovarian and T-cell lymphoma cancers (Aneja *et al.*, 2006). These examples demonstrate the utility of the tetrahydroisoquinoline core and why these types of compounds are of great interest. In this context, we report herein on the synthesis and crystal structure of the title compound.

The molecular structure of the title compound is illustrated in Fig. 1. The cyclohexene ring (C1–C6) of the tetrahydroisoquinoline moiety, has a slightly distorted half-chair conformation [puckering parameters Q = 0.524 (3) Å, θ = 127.1 (3)° and φ = 319.0 (4)°].

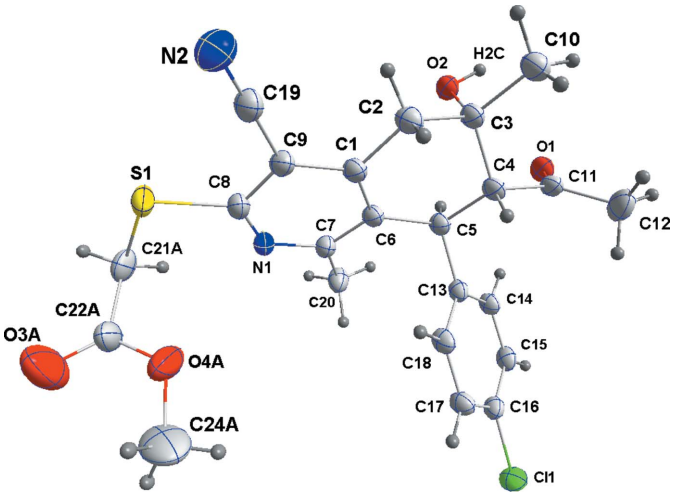


Figure 1
The molecular structure of the title compound, with the atom labelling and 50% probability ellipsoids. Only the major portion of the disorder is shown.

The dihedral angle between the plane of the chloro-substituted phenyl ring (C13–C18) and the pyridine ring (N1/C1/C6–C9) of the tetrahydroisoquinoline moiety is 71.86 (13)°. The methyl acetate group attached to atom S1 is disordered over two sites in a 50:50 ratio, which appears to prevent close intermolecular contacts between the methyl groups.

In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds, forming inversion dimers, which stack along the *b*-axis direction (Table 1 and Fig. 2).

Synthesis and crystallization

A mixture of 7-acetyl-8-(4-chlorophenyl)-1,6-dimethyl-6-hydroxy-3-thioxo-2,3,5,6,7,8-hexahydroisoquinoline-4-carbonitrile (3.87 g, 10 mmol), methyl chloroacetate (1.09 g, 10 mmol) and sodium acetate trihydrate (1.66 g,12 mmol) in ethanol (30 ml) was heated under reflux for one h. The precipitate that formed after cooling was collected and recrystallized from ethanol to give the title compound in the form of colourless needles (yield 83%, m.p. 422 K). IR: 3455 (OH), 2225(CN), 1740 (CO, ester), 1690 (CO, ketone) cm^{-1}.

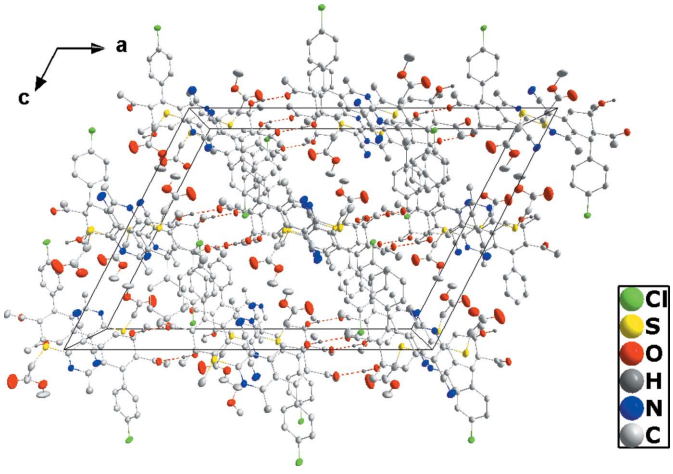


Figure 2
A view along the *b* axis of the crystal packing of the title compound, with the intermolecular O—H···O hydrogen bonds shown as dotted lines (see Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O1^{i}	0.92 (4)	2.00 (4)	2.918 (3)	174 (3)

Symmetry code: (i) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{23}ClN_2O_4S$
M_r	458.94
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	27.4679 (6), 9.5818 (2), 20.2584 (5)
β (°)	117.398 (1)
V (Å^3)	4733.78 (19)
Z	8
Radiation type	Cu *K*α
μ (mm^{-1})	2.51
Crystal size (mm)	0.33 × 0.16 × 0.09
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.65, 0.80
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38901, 4440, 4119
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.058, 0.166, 1.03
No. of reflections	4440
No. of parameters	308
No. of restraints	21
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.36, −0.63

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012) and *SHELXTL* Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The methyl acetate group attached to S1 is disordered over two sets of sites with equal occupancy although it appears that the methyl carbon atoms may be more highly disordered. Attempts to model additional disorder were unsuccessful so the two-component model was retained.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{23}H_{23}ClN_2O_4S$
M_r = 458.94
Monoclinic, $C2/c$
a = 27.4679 (6) Å
b = 9.5818 (2) Å
c = 20.2584 (5) Å
β = 117.398 (1)°
V = 4733.78 (19) Å^3
Z = 8
$F(000)$ = 1920
D_x = 1.288 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9777 reflections
θ = 3.3–69.9°
μ = 2.51 mm^{-1}
T = 150 K
Needles, colourless
0.33 × 0.16 × 0.09 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.65, T_{max} = 0.80
38901 measured reflections
4440 independent reflections
4119 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 70.0°, θ_{min} = 4.6°
h = −32→31
k = −11→11
l = −24→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.166
S = 1.03
4440 reflections
308 parameters
21 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0975P)^2 + 12.6727P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}
Extinction correction: (SHELXL2014; Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00050 (8)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.78857 (3)	0.87497 (8)	0.93943 (3)	0.0365 (2)	
S1	0.42650 (2)	0.67486 (7)	0.50425 (4)	0.0337 (2)	
O1	0.76188 (7)	0.7626 (2)	0.57782 (10)	0.0337 (4)	
O2	0.64464 (7)	0.74788 (19)	0.45364 (9)	0.0286 (4)	
H2O	0.6734 (14)	0.738 (4)	0.4426 (19)	0.043*	
N1	0.53338 (9)	0.6216 (2)	0.58959 (12)	0.0293 (5)	
N2	0.43952 (11)	0.9130 (3)	0.37729 (15)	0.0510 (7)	
C1	0.56952 (10)	0.8101 (3)	0.51663 (13)	0.0262 (5)	
C2	0.58663 (10)	0.9072 (3)	0.47298 (14)	0.0284 (5)	
H2A	0.5837	1.0045	0.4872	0.034*	
H2B	0.5610	0.8964	0.4194	0.034*	
C3	0.64480 (10)	0.8820 (3)	0.48486 (13)	0.0255 (5)	
C4	0.68291 (10)	0.8814 (3)	0.56997 (13)	0.0247 (5)	
H4	0.6772 (12)	0.972 (3)	0.5899 (16)	0.030*	
C5	0.66910 (9)	0.7603 (3)	0.60879 (13)	0.0240 (5)	
H5	0.6839 (12)	0.679 (3)	0.5982 (16)	0.029*	
C6	0.60761 (9)	0.7383 (3)	0.57919 (13)	0.0248 (5)	
C7	0.58742 (10)	0.6400 (3)	0.61211 (13)	0.0270 (5)	
C8	0.49729 (10)	0.6960 (3)	0.53286 (14)	0.0283 (5)	
C9	0.51353 (10)	0.7880 (3)	0.49294 (13)	0.0283 (5)	
C10	0.66028 (11)	0.9948 (3)	0.44489 (15)	0.0342 (6)	
H10A	0.6615	1.0856	0.4679	0.051*	
H10B	0.6329	0.9975	0.3924	0.051*	
H10C	0.6964	0.9739	0.4487	0.051*	
C11	0.74318 (10)	0.8721 (3)	0.58661 (13)	0.0269 (5)	
C12	0.77729 (12)	1.0014 (3)	0.61275 (17)	0.0421 (7)	
H12A	0.7592	1.0775	0.5776	0.063*	
H12B	0.8134	0.9840	0.6159	0.063*	
H12C	0.7816	1.0274	0.6619	0.063*	
C13	0.69897 (9)	0.7885 (2)	0.69231 (13)	0.0232 (5)	
C14	0.75137 (10)	0.7349 (3)	0.73590 (13)	0.0256 (5)	
H14	0.7680	0.6784	0.7134	0.031*	
C15	0.77968 (10)	0.7624 (3)	0.81162 (14)	0.0272 (5)	
H15	0.8155	0.7259	0.8408	0.033*	
C16	0.75476 (10)	0.8441 (3)	0.84376 (13)	0.0257 (5)	
C17	0.70294 (10)	0.8996 (3)	0.80178 (14)	0.0279 (5)	
H17	0.6864	0.9558	0.8246	0.033*	
C18	0.67548 (10)	0.8723 (3)	0.72617 (14)	0.0268 (5)	
H18	0.6401	0.9112	0.6970	0.032*	

C19	0.47278 (11)	0.8577 (3)	0.42859 (15)	0.0336 (6)	
C20	0.62335 (10)	0.5444 (3)	0.67411 (15)	0.0329 (6)	
H20A	0.6575	0.5270	0.6712	0.049*	
H20B	0.6042	0.4559	0.6697	0.049*	
H20C	0.6318	0.5880	0.7220	0.049*	
C21A	0.4275 (2)	0.5666 (5)	0.5770 (3)	0.0353 (10)	0.5
H21A	0.3959	0.5019	0.5557	0.042*	0.5
H21B	0.4614	0.5096	0.5978	0.042*	0.5
C22A	0.4252 (2)	0.6476 (7)	0.6387 (4)	0.0440 (10)	0.5
O3A	0.3854 (3)	0.6537 (9)	0.6501 (4)	0.0937 (17)	0.5
O4A	0.46776 (19)	0.7276 (5)	0.6735 (3)	0.0579 (9)	0.5
C23A	0.4722 (4)	0.8397 (11)	0.7324 (4)	0.092 (2)	0.5
H23A	0.5075	0.8828	0.7492	0.138*	0.5
H23B	0.4440	0.9076	0.7072	0.138*	0.5
H23C	0.4689	0.8036	0.7744	0.138*	0.5
C21B	0.4273 (2)	0.5115 (5)	0.5455 (3)	0.0353 (10)	0.5
H21C	0.3921	0.4638	0.5144	0.042*	0.5
H21D	0.4568	0.4540	0.5441	0.042*	0.5
C22B	0.4357 (2)	0.5140 (6)	0.6237 (3)	0.0440 (10)	0.5
O3B	0.4116 (3)	0.5907 (9)	0.6469 (4)	0.0937 (17)	0.5
O4B	0.46763 (19)	0.4116 (5)	0.6610 (2)	0.0579 (9)	0.5
C23B	0.4711 (4)	0.3458 (12)	0.7333 (4)	0.092 (2)	0.5
H23D	0.5000	0.2696	0.7500	0.138*	
H23E	0.4870	0.4173	0.7704	0.138*	0.5
H23F	0.4378	0.3130	0.7325	0.138*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0251 (3)	0.0529 (4)	0.0243 (3)	0.0036 (3)	0.0053 (3)	−0.0047 (3)
S1	0.0179 (3)	0.0439 (4)	0.0366 (4)	−0.0015 (2)	0.0102 (3)	0.0027 (3)
O1	0.0256 (9)	0.0424 (11)	0.0390 (10)	0.0002 (8)	0.0199 (8)	−0.0068 (8)
O2	0.0245 (9)	0.0355 (10)	0.0291 (9)	−0.0028 (7)	0.0152 (8)	−0.0067 (7)
N1	0.0214 (10)	0.0389 (12)	0.0276 (11)	−0.0021 (9)	0.0115 (9)	0.0007 (9)
N2	0.0360 (14)	0.0655 (18)	0.0425 (14)	0.0171 (13)	0.0103 (12)	0.0142 (13)
C1	0.0220 (12)	0.0352 (13)	0.0227 (11)	0.0026 (10)	0.0114 (10)	0.0004 (10)
C2	0.0240 (12)	0.0364 (13)	0.0259 (12)	0.0058 (10)	0.0124 (10)	0.0057 (10)
C3	0.0229 (12)	0.0315 (13)	0.0246 (12)	0.0004 (9)	0.0130 (10)	−0.0004 (9)
C4	0.0230 (12)	0.0301 (13)	0.0252 (12)	0.0011 (9)	0.0147 (10)	−0.0016 (9)
C5	0.0189 (11)	0.0302 (12)	0.0239 (12)	0.0027 (9)	0.0106 (10)	0.0002 (9)
C6	0.0202 (12)	0.0336 (13)	0.0216 (11)	0.0017 (9)	0.0105 (9)	−0.0006 (9)
C7	0.0209 (12)	0.0350 (13)	0.0241 (12)	−0.0007 (10)	0.0095 (10)	0.0000 (10)
C8	0.0203 (12)	0.0374 (14)	0.0272 (12)	−0.0003 (10)	0.0111 (10)	−0.0025 (10)
C9	0.0206 (12)	0.0398 (14)	0.0236 (12)	0.0046 (10)	0.0093 (10)	0.0008 (10)
C10	0.0330 (14)	0.0432 (15)	0.0293 (13)	−0.0016 (11)	0.0169 (11)	0.0046 (11)
C11	0.0231 (12)	0.0371 (14)	0.0228 (11)	−0.0024 (10)	0.0126 (10)	−0.0034 (10)
C12	0.0289 (14)	0.0488 (17)	0.0467 (16)	−0.0111 (12)	0.0157 (13)	−0.0122 (13)
C13	0.0184 (11)	0.0273 (11)	0.0239 (11)	0.0002 (9)	0.0096 (9)	0.0022 (9)

C14	0.0206 (11)	0.0302 (12)	0.0283 (13)	0.0040 (9)	0.0132 (10)	0.0012 (10)
C15	0.0170 (11)	0.0320 (12)	0.0298 (12)	0.0033 (9)	0.0085 (10)	0.0044 (10)
C16	0.0209 (12)	0.0302 (12)	0.0237 (12)	−0.0025 (9)	0.0085 (9)	0.0006 (9)
C17	0.0245 (12)	0.0343 (13)	0.0275 (12)	0.0043 (10)	0.0144 (10)	−0.0005 (10)
C18	0.0182 (11)	0.0359 (13)	0.0261 (12)	0.0062 (10)	0.0101 (10)	0.0034 (10)
C19	0.0233 (13)	0.0449 (15)	0.0328 (14)	0.0064 (11)	0.0130 (11)	0.0036 (12)
C20	0.0259 (13)	0.0378 (14)	0.0318 (13)	−0.0012 (11)	0.0105 (11)	0.0073 (11)
C21A	0.0260 (17)	0.030 (3)	0.043 (3)	−0.0075 (18)	0.010 (2)	−0.0018 (17)
C22A	0.034 (2)	0.057 (3)	0.046 (2)	−0.015 (2)	0.0227 (19)	−0.012 (2)
O3A	0.085 (4)	0.113 (5)	0.112 (4)	−0.025 (3)	0.070 (3)	−0.044 (3)
O4A	0.0497 (19)	0.073 (2)	0.0431 (17)	−0.0192 (18)	0.0142 (15)	−0.0105 (17)
C23A	0.074 (3)	0.166 (6)	0.028 (2)	0.021 (4)	0.017 (2)	0.008 (3)
C21B	0.0260 (17)	0.030 (3)	0.043 (3)	−0.0075 (18)	0.010 (2)	−0.0018 (17)
C22B	0.034 (2)	0.057 (3)	0.046 (2)	−0.015 (2)	0.0227 (19)	−0.012 (2)
O3B	0.085 (4)	0.113 (5)	0.112 (4)	−0.025 (3)	0.070 (3)	−0.044 (3)
O4B	0.0497 (19)	0.073 (2)	0.0431 (17)	−0.0192 (18)	0.0142 (15)	−0.0105 (17)
C23B	0.074 (3)	0.166 (6)	0.028 (2)	0.021 (4)	0.017 (2)	0.008 (3)

Geometric parameters (Å, º)

Cl1—C16	1.747 (2)	C12—H12B	0.9800
S1—C8	1.767 (3)	C12—H12C	0.9800
S1—C21B	1.770 (4)	C13—C18	1.392 (3)
S1—C21A	1.792 (4)	C13—C14	1.395 (3)
O1—C11	1.217 (3)	C14—C15	1.389 (4)
O2—C3	1.431 (3)	C14—H14	0.9500
O2—H2O	0.92 (4)	C15—C16	1.384 (4)
N1—C8	1.328 (3)	C15—H15	0.9500
N1—C7	1.349 (3)	C16—C17	1.385 (3)
N2—C19	1.150 (4)	C17—C18	1.386 (3)
C1—C6	1.398 (3)	C17—H17	0.9500
C1—C9	1.400 (3)	C18—H18	0.9500
C1—C2	1.500 (3)	C20—H20A	0.9800
C2—C3	1.521 (3)	C20—H20B	0.9800
C2—H2A	0.9900	C20—H20C	0.9800
C2—H2B	0.9900	C21A—C22A	1.496 (7)
C3—C10	1.524 (3)	C21A—H21A	0.9900
C3—C4	1.552 (3)	C21A—H21B	0.9900
C4—C11	1.533 (3)	C22A—O3A	1.219 (8)
C4—C5	1.544 (3)	C22A—O4A	1.300 (6)
C4—H4	1.00 (3)	O4A—C23A	1.569 (8)
C5—C6	1.525 (3)	C23A—H23A	0.9600
C5—C13	1.527 (3)	C23A—H23B	0.9600
C5—H5	0.95 (3)	C23A—H23C	0.9600
C6—C7	1.407 (3)	C21B—C22B	1.493 (7)
C7—C20	1.500 (3)	C21B—H21C	0.9900
C8—C9	1.401 (4)	C21B—H21D	0.9900
C9—C19	1.433 (4)	C22B—O3B	1.218 (8)

C10—H10A	0.9800	C22B—O4B	1.301 (6)
C10—H10B	0.9800	O4B—C23B	1.557 (7)
C10—H10C	0.9800	C23B—H23D	1.0152
C11—C12	1.496 (4)	C23B—H23E	0.9600
C12—H12A	0.9800	C23B—H23F	0.9601
C8—S1—C21B	100.0 (2)	C18—C13—C14	118.5 (2)
C8—S1—C21A	101.43 (19)	C18—C13—C5	120.9 (2)
C3—O2—H2O	112 (2)	C14—C13—C5	120.5 (2)
C8—N1—C7	119.3 (2)	C15—C14—C13	121.3 (2)
C6—C1—C9	118.8 (2)	C15—C14—H14	119.4
C6—C1—C2	122.2 (2)	C13—C14—H14	119.4
C9—C1—C2	119.0 (2)	C16—C15—C14	118.7 (2)
C1—C2—C3	113.5 (2)	C16—C15—H15	120.7
C1—C2—H2A	108.9	C14—C15—H15	120.7
C3—C2—H2A	108.9	C15—C16—C17	121.3 (2)
C1—C2—H2B	108.9	C15—C16—Cl1	119.50 (19)
C3—C2—H2B	108.9	C17—C16—Cl1	119.19 (19)
H2A—C2—H2B	107.7	C16—C17—C18	119.3 (2)
O2—C3—C2	106.4 (2)	C16—C17—H17	120.4
O2—C3—C10	110.3 (2)	C18—C17—H17	120.4
C2—C3—C10	109.4 (2)	C17—C18—C13	120.9 (2)
O2—C3—C4	110.56 (19)	C17—C18—H18	119.6
C2—C3—C4	107.39 (19)	C13—C18—H18	119.6
C10—C3—C4	112.5 (2)	N2—C19—C9	179.0 (3)
C11—C4—C5	109.7 (2)	C7—C20—H20A	109.5
C11—C4—C3	110.66 (18)	C7—C20—H20B	109.5
C5—C4—C3	111.7 (2)	H20A—C20—H20B	109.5
C11—C4—H4	108.4 (17)	C7—C20—H20C	109.5
C5—C4—H4	109.1 (17)	H20A—C20—H20C	109.5
C3—C4—H4	107.1 (16)	H20B—C20—H20C	109.5
C6—C5—C13	113.17 (19)	C22A—C21A—S1	113.3 (4)
C6—C5—C4	113.0 (2)	C22A—C21A—H21A	108.9
C13—C5—C4	107.37 (19)	S1—C21A—H21A	108.9
C6—C5—H5	108.1 (18)	C22A—C21A—H21B	108.9
C13—C5—H5	109.2 (18)	S1—C21A—H21B	108.9
C4—C5—H5	105.6 (18)	H21A—C21A—H21B	107.7
C1—C6—C7	117.7 (2)	O3A—C22A—O4A	122.0 (5)
C1—C6—C5	121.3 (2)	O3A—C22A—C21A	124.7 (5)
C7—C6—C5	120.9 (2)	O4A—C22A—C21A	112.7 (4)
N1—C7—C6	122.6 (2)	C22A—O4A—C23A	123.6 (5)
N1—C7—C20	113.7 (2)	O4A—C23A—H23A	106.1
C6—C7—C20	123.7 (2)	O4A—C23A—H23B	107.3
N1—C8—C9	121.9 (2)	H23A—C23A—H23B	109.5
N1—C8—S1	119.52 (19)	O4A—C23A—H23C	114.9
C9—C8—S1	118.54 (19)	H23A—C23A—H23C	109.5
C1—C9—C8	119.2 (2)	H23B—C23A—H23C	109.5
C1—C9—C19	121.1 (2)	C22B—C21B—S1	116.7 (4)

C8—C9—C19	119.7 (2)	C22B—C21B—H21C	108.1
C3—C10—H10A	109.5	S1—C21B—H21C	108.1
C3—C10—H10B	109.5	C22B—C21B—H21D	108.1
H10A—C10—H10B	109.5	S1—C21B—H21D	108.1
C3—C10—H10C	109.5	H21C—C21B—H21D	107.3
H10A—C10—H10C	109.5	O3B—C22B—O4B	124.9 (6)
H10B—C10—H10C	109.5	O3B—C22B—C21B	125.0 (6)
O1—C11—C12	121.9 (2)	O4B—C22B—C21B	109.8 (4)
O1—C11—C4	120.3 (2)	C22B—O4B—C23B	125.8 (5)
C12—C11—C4	117.8 (2)	O4B—C23B—H23D	107.7
C11—C12—H12A	109.5	O4B—C23B—H23E	104.8
C11—C12—H12B	109.5	H23D—C23B—H23E	104.4
H12A—C12—H12B	109.5	O4B—C23B—H23F	118.1
C11—C12—H12C	109.5	H23D—C23B—H23F	111.4
H12A—C12—H12C	109.5	H23E—C23B—H23F	109.5
H12B—C12—H12C	109.5		

C6—C1—C2—C3	20.3 (3)	C2—C1—C9—C8	179.1 (2)
C9—C1—C2—C3	−158.2 (2)	C6—C1—C9—C19	−179.2 (2)
C1—C2—C3—O2	66.7 (3)	C2—C1—C9—C19	−0.7 (4)
C1—C2—C3—C10	−174.1 (2)	N1—C8—C9—C1	−4.7 (4)
C1—C2—C3—C4	−51.7 (3)	S1—C8—C9—C1	177.55 (19)
O2—C3—C4—C11	70.3 (2)	N1—C8—C9—C19	175.1 (2)
C2—C3—C4—C11	−174.0 (2)	S1—C8—C9—C19	−2.6 (3)
C10—C3—C4—C11	−53.5 (3)	C5—C4—C11—O1	49.8 (3)
O2—C3—C4—C5	−52.3 (2)	C3—C4—C11—O1	−74.0 (3)
C2—C3—C4—C5	63.4 (3)	C5—C4—C11—C12	−130.9 (2)
C10—C3—C4—C5	−176.1 (2)	C3—C4—C11—C12	105.3 (3)
C11—C4—C5—C6	−164.64 (19)	C6—C5—C13—C18	−39.4 (3)
C3—C4—C5—C6	−41.5 (3)	C4—C5—C13—C18	86.0 (3)
C11—C4—C5—C13	69.9 (2)	C6—C5—C13—C14	142.9 (2)
C3—C4—C5—C13	−167.01 (19)	C4—C5—C13—C14	−91.7 (3)
C9—C1—C6—C7	4.3 (4)	C18—C13—C14—C15	0.7 (4)
C2—C1—C6—C7	−174.2 (2)	C5—C13—C14—C15	178.4 (2)
C9—C1—C6—C5	−178.6 (2)	C13—C14—C15—C16	0.4 (4)
C2—C1—C6—C5	3.0 (4)	C14—C15—C16—C17	−0.9 (4)
C13—C5—C6—C1	130.4 (2)	C14—C15—C16—Cl1	177.75 (19)
C4—C5—C6—C1	8.1 (3)	C15—C16—C17—C18	0.3 (4)
C13—C5—C6—C7	−52.5 (3)	Cl1—C16—C17—C18	−178.4 (2)
C4—C5—C6—C7	−174.8 (2)	C16—C17—C18—C13	0.9 (4)
C8—N1—C7—C6	1.8 (4)	C14—C13—C18—C17	−1.3 (4)
C8—N1—C7—C20	−177.2 (2)	C5—C13—C18—C17	−179.0 (2)
C1—C6—C7—N1	−5.7 (4)	C8—S1—C21A—C22A	93.2 (4)
C5—C6—C7—N1	177.1 (2)	S1—C21A—C22A—O3A	107.5 (9)
C1—C6—C7—C20	173.2 (2)	S1—C21A—C22A—O4A	−63.5 (7)
C5—C6—C7—C20	−4.0 (4)	O3A—C22A—O4A—C23A	−0.5 (12)
C7—N1—C8—C9	3.5 (4)	C21A—C22A—O4A—C23A	170.8 (6)
C7—N1—C8—S1	−178.79 (19)	C8—S1—C21B—C22B	87.6 (4)

C21B—S1—C8—N1	−18.7 (3)	S1—C21B—C22B—O3B	46.9 (8)
C21A—S1—C8—N1	8.5 (3)	S1—C21B—C22B—O4B	−140.4 (4)
C21B—S1—C8—C9	159.1 (3)	O3B—C22B—O4B—C23B	14.8 (11)
C21A—S1—C8—C9	−173.6 (3)	C21B—C22B—O4B—C23B	−157.9 (6)
C6—C1—C9—C8	0.6 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O1^{i}	0.92 (4)	2.00 (4)	2.918 (3)	174 (3)

Symmetry code: (i) −*x*+3/2, −*y*+3/2, −*z*+1.