Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Benzyl-7-chloro-9-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1*H*-pyrrolo-[3,4-*b*]quinoline

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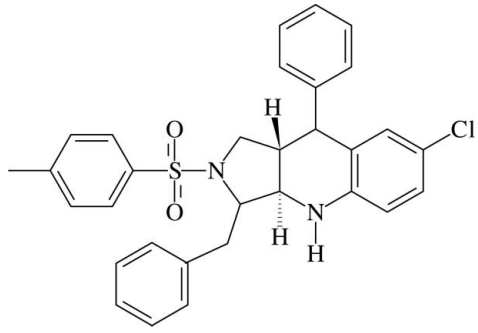
Received 27 October 2009; accepted 29 October 2009

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.090; data-to-parameter ratio = 23.7.

In the title compound, $C_{31}H_{29}ClN_2O_2S$, the pyrrolidine ring adopts an envelope conformation with the methine C atom adjacent to the NH group as the flap atom. The tetrahydropyridine ring has a half-chair conformation. The two rings are *trans*-fused. The chlorobenzene ring and the adjacent phenyl ring form a dihedral angle of 77.9 (1)°. The benzyl phenyl and the tosyl phenyl rings are oriented at a dihedral angle of 88.0 (1)°. In the crystal, molecules are linked into chains along the *a* axis by N—H···Cl and C—H···Cl hydrogen bonds and the adjacent chains are cross-linked *via* C—H···π interactions.

Related literature

For the caspase-3 inhibitory, vasorelaxing and antileukemic activities of pyrroloquinoline compounds, see: Kravchenko *et al.* (2005); Ferlin *et al.* (2002); Anderson *et al.* (1988). For related structures, see: Sudha *et al.* (2007, 2008*a*,*b*). For the crystal structure of the unchlorinated analogue, see: Chinnakali *et al.* (2009). For ring puckering parameters, see: Cremer & Pople (1975). For asymmetry parameters, see: Duax *et al.* (1976).



Experimental

Crystal data

$C_{31}H_{29}ClN_2O_2S$
M_r = 529.07
Orthorhombic, $P2_12_12_1$
a = 10.0106 (1) Å
b = 11.8612 (1) Å
c = 21.8256 (2) Å
V = 2591.52 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 100 K
0.28 × 0.25 × 0.15 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.930, T_{max} = 0.962
35839 measured reflections
8047 independent reflections
7259 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.090
S = 1.02
8047 reflections
339 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 3555 Friedel pairs
Flack parameter: 0.02 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1*N2*···Cl1^{i}	0.84 (2)	2.83 (2)	3.5947 (13)	153 (2)
C27—H27···Cl1^{i}	0.93	2.77	3.5980 (16)	149
C17—H17···*Cg*2^{ii}	0.93	2.70	3.5403 (16)	151
C29—H29···*Cg*1^{iii}	0.93	2.68	3.6014 (19)	170

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$. *Cg*1 and *Cg*2 are the centroids of the C19–C24 and C26–C31 rings, respectively.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

HKF thanks Universiti Sains Malaysia for the Research University Golden Goose grant No. 1001/PFIZIK/811012.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5197).

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supporting information

Acta Cryst. (2009). E**65**, o2973–o2974 [doi:10.1107/S1600536809045267]

3-Benzyl-7-chloro-9-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1*H*-pyrrolo[3,4-*b*]quinoline

K. Chinnakali, D. Sudha, M. Jayagobi, R. Raghunathan and Hoong-Kun Fun

S1. Comment

Pyrroloquinoline derivatives have been found to exhibit caspase-3 inhibitory (Kravchenko *et al.*, 2005), vasorelaxing (Ferlin *et al.*, 2002) and antileukemic (Anderson *et al.*, 1988) activities. Previously, we have reported crystal structures of some pyrroloquinoline derivatives (Sudha *et al.*, 2007,2008*a*,b). Now, herein the crystal structure of the title compound is reported.

The pyrrolidine ring adopts an envelope conformation with C10, the envelope flap, lying 0.695 (2) Å out of the plane formed by the rest of the atoms of the ring (r.m.s. deviation 0.019 Å). The asymmetry parameter (Duax *et al.*, 1976) ΔC_s[C10] = 5.3 (1)° and the puckering parameters (Cremer & Pople, 1975) q_2 = 0.464 (2) Å and φ = 102.7 (2)°. The tosyl group is attached to the pyrrolidine ring in a eqtorial position. The tetrahydropyridine ring adopts a half-chair conformation, with the local twofold rotation axis running through the midpoint of bonds C2—C10 and C4—C9 [asymmetry parameter ΔC_2[C2—C10] = 3.6 (2)°]. The phenyl ring attached to the tetrahydropyridine ring is in a biaxial position. The dihedral angle between the C4—C9 and C19—C24 rings is 77.9 (1)° and that between the C12—C17 and C26—C31 rings is 88.0 (1)°. Bond lengths and angles are comparable with those in the unchlorinated derivative, 3-benzyl-9-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1*H*-pyrrolo[3,4-*b*]quinoline (Chinnakali *et al.*, 2009).

The N2—H1N2···Cl1 and C27—H27···Cl1 hydrogen bonds (Table 1) form a pair of bifurcated acceptor bonds, generating a ring of graph-set motif $R^1_2(9)$. These hydrogen bonds link the molecules into a chain along the *a* axis (Fig. 2). The adjacent chains are crosslinked *via* C—H···π interactions involving the benzyl phenyl and the phenyl ring bound to the fused ring system.

A superposition of the non-H atoms (except the N-bound H atom) of the unchlorinated derivative (Chinnakali *et al.*, 2009) with those of the title molecule using *XP* in *SHELXTL* (Sheldrick, 2008), gave an r.m.s. deviation of 1.27 Å (Fig. 3). In the unchlorinated derivative, the benzyl phenyl ring is oriented in such a way to form an N—H···π interaction. But in the title molecule, the benzyl group is twisted away from the N—H group to make it available for participation in an N—H···Cl hydrogen bond.

S2. Experimental

$InCl_3$ (20 mol%) was added to a mixture of *S*-2-(*N*-cinnamyl-*N*-tosylamino)-3-phenyl propanal (1 mmol) and *p*-chloro-aniline (1 mmol) in acetonitrile (20 ml). The reaction mixture was stirred at room temperature for 1 min. On completion of the reaction, as indicated by TLC, the mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was chromatographed on silica gel using a hexane-ethyl acetate (8.5:1.5 *v*/*v*) mixture to obtain the title compound. The compound was recrystallized from ethyl acetate solution by slow evaporation.

S3. Refinement

The N-bound H atom was located in a difference map and refined freely [N—H = 0.84 (2) Å]. The remaining H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}). A rotating group model was used for methyl groups. Reflection 002 was partially obscured by the beam stop and was omitted.

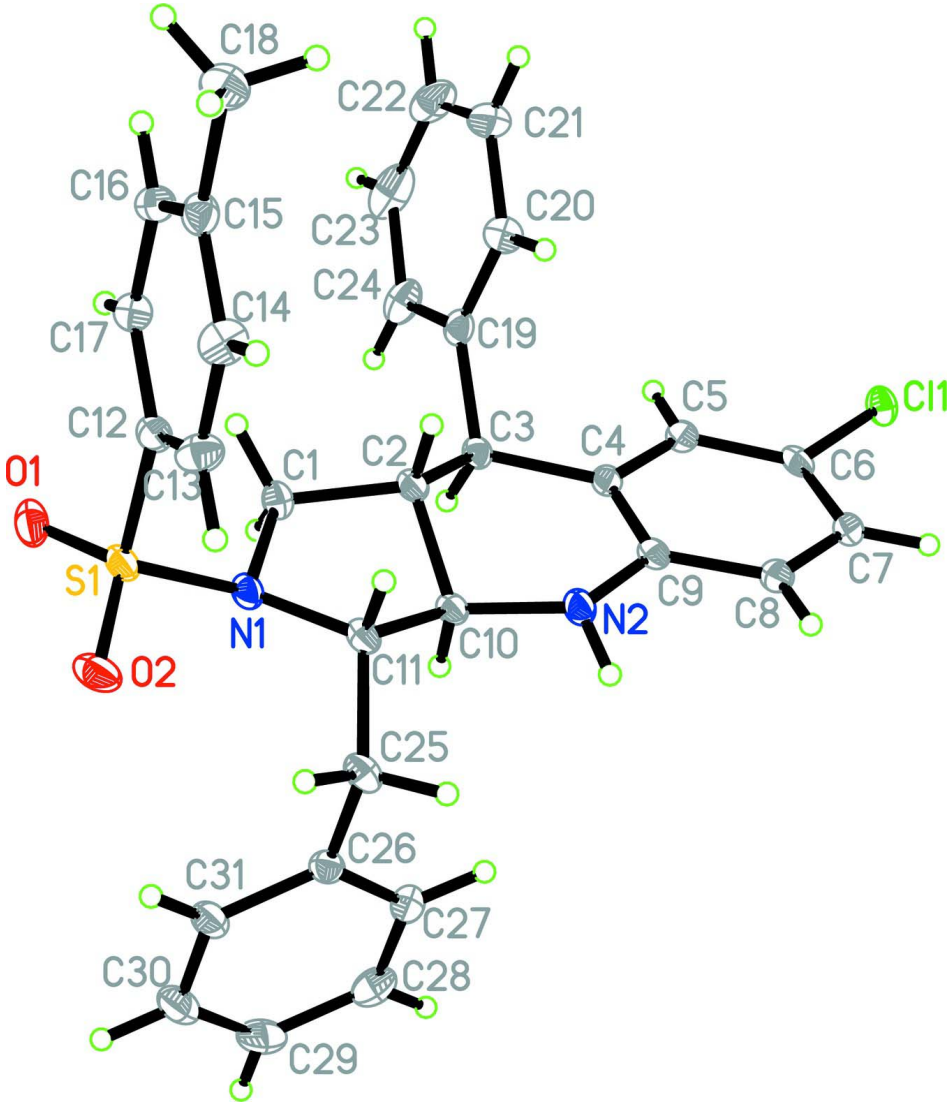

Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

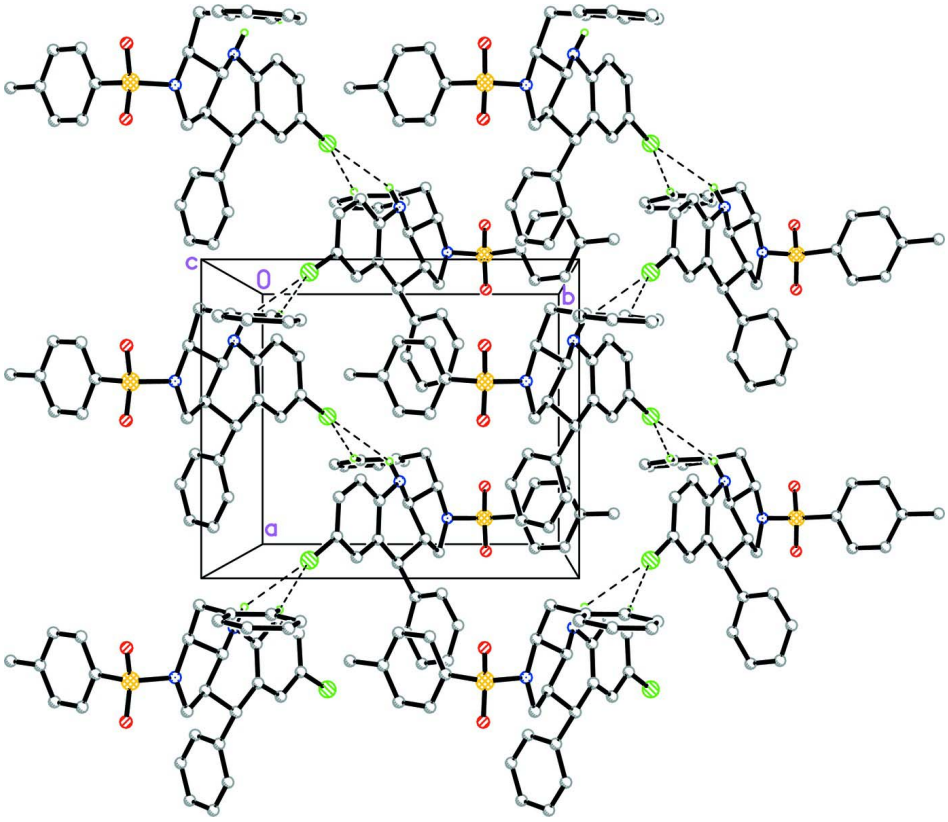

Figure 2

The crystal structure of (I), viewed along the *c* axis. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the interactions have been omitted.

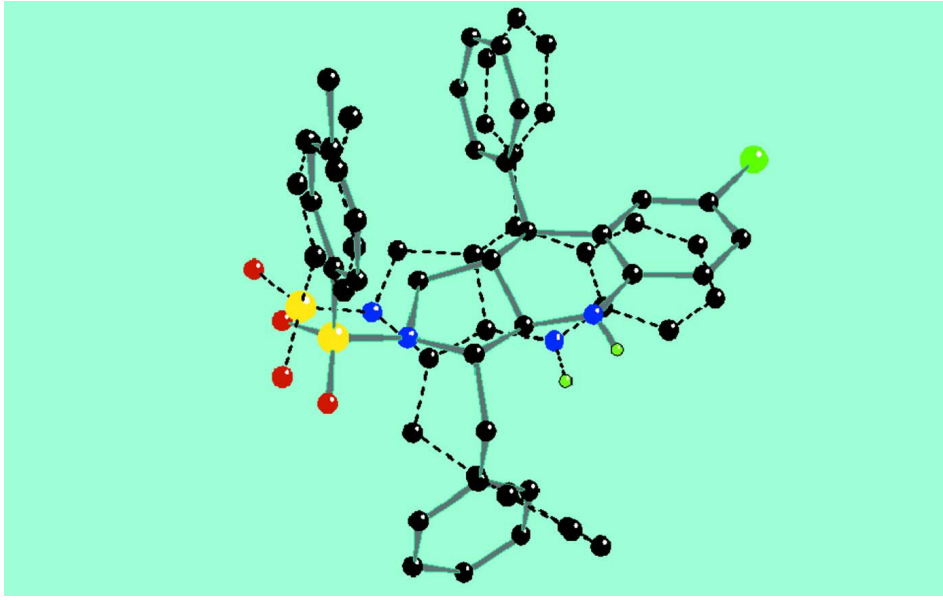

Figure 3

Fit of the title molecule (solid lines) with its unchlorinated analogue (dashed lines). C-bound H atoms have been omitted for clarity.

3-Benzyl-7-chloro-9-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1*H*- pyrrolo[3,4-*b*]quinoline

Crystal data

$C_{31}H_{29}ClN_2O_2S$
$M_r = 529.07$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 10.0106$ (1) Å
$b = 11.8612$ (1) Å
$c = 21.8256$ (2) Å
$V = 2591.52$ (4) Å^3
$Z = 4$
$F(000) = 1112$
$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9900 reflections
$\theta = 2.5$–$29.9°$
$\mu = 0.26$ mm^{-1}
$T = 100$ K
Block, colourless
0.28 × 0.25 × 0.15 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.930$, $T_{max} = 0.962$
35839 measured reflections
8047 independent reflections
7259 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 30.7°$, $\theta_{min} = 2.2°$
$h = -13 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -31 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.090$
$S = 1.02$
8047 reflections
339 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
$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.3209P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), 3555 Friedel pairs
Absolute structure parameter: 0.02 (4)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.99020 (3)	0.23630 (3)	0.611010 (16)	0.01750 (8)
S1	0.87572 (4)	0.74890 (3)	0.237629 (16)	0.01701 (8)
O1	1.00459 (12)	0.75400 (9)	0.20897 (5)	0.0229 (2)

O2	0.75758 (13)	0.75019 (10)	0.20046 (5)	0.0256 (2)
N1	0.87251 (14)	0.63195 (10)	0.27756 (6)	0.0150 (2)
N2	0.72707 (13)	0.48831 (11)	0.40955 (6)	0.0159 (2)
H1N2	0.654 (2)	0.4565 (17)	0.4026 (10)	0.027 (5)*
C1	0.99589 (16)	0.60584 (12)	0.31441 (7)	0.0160 (3)
H1A	1.0509	0.6725	0.3196	0.019*
H1B	1.0486	0.5472	0.2950	0.019*
C2	0.94008 (14)	0.56589 (12)	0.37568 (7)	0.0137 (3)
H2	0.9205	0.6320	0.4011	0.016*
C3	1.02378 (14)	0.48294 (12)	0.41319 (7)	0.0132 (3)
H3	1.0572	0.4246	0.3853	0.016*
C4	0.93338 (14)	0.42593 (12)	0.46062 (7)	0.0131 (3)
C5	0.99179 (15)	0.36541 (11)	0.50869 (7)	0.0142 (3)
H5	1.0843	0.3619	0.5118	0.017*
C6	0.91344 (15)	0.31068 (12)	0.55164 (7)	0.0141 (3)
C7	0.77481 (15)	0.31665 (12)	0.54938 (7)	0.0149 (3)
H7	0.7228	0.2811	0.5789	0.018*
C8	0.71615 (15)	0.37664 (13)	0.50226 (7)	0.0155 (3)
H8	0.6235	0.3817	0.5004	0.019*
C9	0.79311 (14)	0.43009 (12)	0.45709 (7)	0.0134 (3)
C10	0.80912 (14)	0.51222 (12)	0.35619 (7)	0.0133 (3)
H10	0.8266	0.4425	0.3335	0.016*
C11	0.75027 (16)	0.60125 (12)	0.31332 (7)	0.0147 (3)
H11	0.7237	0.6666	0.3379	0.018*
C12	0.86417 (16)	0.86286 (11)	0.28916 (7)	0.0159 (3)
C13	0.73961 (16)	0.90828 (13)	0.30416 (8)	0.0201 (3)
H13	0.6617	0.8776	0.2880	0.024*
C14	0.73412 (16)	0.99983 (13)	0.34358 (8)	0.0212 (3)
H14	0.6516	1.0306	0.3537	0.025*
C15	0.85024 (15)	1.04677 (12)	0.36832 (7)	0.0170 (3)
C16	0.97308 (15)	0.99944 (12)	0.35296 (7)	0.0175 (3)
H16	1.0509	1.0297	0.3694	0.021*
C17	0.98130 (15)	0.90773 (12)	0.31342 (7)	0.0157 (3)
H17	1.0638	0.8768	0.3033	0.019*
C18	0.84443 (18)	1.14674 (14)	0.41044 (8)	0.0236 (3)
H18A	0.9244	1.1907	0.4059	0.035*
H18B	0.8369	1.1212	0.4520	0.035*
H18C	0.7683	1.1922	0.4003	0.035*
C19	1.14346 (15)	0.53881 (12)	0.44351 (7)	0.0158 (3)
C20	1.12450 (17)	0.61970 (14)	0.48937 (7)	0.0217 (3)
H20	1.0382	0.6402	0.5006	0.026*
C21	1.2328 (2)	0.66992 (16)	0.51843 (9)	0.0292 (4)
H21	1.2188	0.7245	0.5483	0.035*
C22	1.36117 (19)	0.63871 (17)	0.50286 (9)	0.0324 (4)
H22	1.4338	0.6714	0.5227	0.039*
C23	1.38142 (17)	0.55904 (16)	0.45789 (10)	0.0318 (4)
H23	1.4680	0.5380	0.4474	0.038*
C24	1.27344 (16)	0.50968 (14)	0.42795 (8)	0.0221 (3)

H24	1.2885	0.4568	0.3973	0.027*
C25	0.62882 (16)	0.56231 (13)	0.27564 (7)	0.0171 (3)
H25A	0.5588	0.5405	0.3040	0.020*
H25B	0.5961	0.6264	0.2525	0.020*
C26	0.65082 (14)	0.46589 (12)	0.23147 (7)	0.0150 (3)
C27	0.65518 (16)	0.35343 (13)	0.25089 (7)	0.0192 (3)
H27	0.6466	0.3369	0.2924	0.023*
C28	0.67212 (16)	0.26635 (13)	0.20928 (8)	0.0237 (3)
H28	0.6760	0.1922	0.2230	0.028*
C29	0.68336 (18)	0.28986 (14)	0.14704 (8)	0.0253 (4)
H29	0.6945	0.2315	0.1190	0.030*
C30	0.67796 (17)	0.40097 (14)	0.12689 (8)	0.0239 (3)
H30	0.6850	0.4171	0.0853	0.029*
C31	0.66208 (16)	0.48796 (13)	0.16892 (7)	0.0189 (3)
H31	0.6589	0.5621	0.1551	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01853 (15)	0.02012 (16)	0.01386 (15)	0.00295 (13)	0.00000 (12)	0.00457 (12)
S1	0.02840 (18)	0.01221 (14)	0.01041 (15)	−0.00087 (15)	−0.00294 (13)	0.00055 (13)
O1	0.0372 (6)	0.0165 (5)	0.0151 (5)	−0.0010 (6)	0.0072 (5)	0.0006 (4)
O2	0.0404 (6)	0.0180 (5)	0.0185 (5)	−0.0022 (5)	−0.0136 (5)	0.0016 (5)
N1	0.0210 (6)	0.0123 (5)	0.0117 (6)	0.0001 (5)	−0.0011 (5)	0.0020 (4)
N2	0.0138 (6)	0.0219 (6)	0.0120 (6)	−0.0002 (5)	−0.0011 (5)	0.0026 (5)
C1	0.0179 (7)	0.0172 (6)	0.0130 (7)	0.0009 (6)	0.0002 (6)	0.0031 (5)
C2	0.0168 (6)	0.0134 (6)	0.0108 (7)	0.0004 (5)	−0.0010 (5)	0.0000 (5)
C3	0.0155 (6)	0.0127 (6)	0.0114 (6)	0.0007 (5)	0.0016 (5)	−0.0006 (5)
C4	0.0146 (6)	0.0124 (6)	0.0121 (7)	−0.0003 (5)	0.0012 (5)	−0.0013 (5)
C5	0.0144 (6)	0.0142 (6)	0.0139 (7)	0.0004 (5)	−0.0002 (5)	−0.0003 (5)
C6	0.0188 (7)	0.0140 (6)	0.0096 (7)	0.0020 (5)	−0.0031 (5)	−0.0001 (5)
C7	0.0164 (7)	0.0161 (6)	0.0121 (7)	−0.0012 (5)	0.0015 (5)	−0.0011 (5)
C8	0.0148 (6)	0.0174 (7)	0.0145 (7)	−0.0009 (5)	0.0002 (5)	−0.0015 (5)
C9	0.0155 (6)	0.0138 (6)	0.0109 (7)	0.0006 (5)	0.0003 (5)	−0.0021 (5)
C10	0.0162 (6)	0.0129 (6)	0.0109 (7)	0.0004 (5)	−0.0014 (5)	0.0002 (5)
C11	0.0187 (7)	0.0141 (6)	0.0112 (7)	0.0016 (5)	−0.0005 (6)	−0.0008 (5)
C12	0.0227 (7)	0.0122 (6)	0.0129 (7)	−0.0002 (5)	−0.0008 (6)	0.0000 (5)
C13	0.0178 (7)	0.0176 (7)	0.0250 (9)	−0.0002 (6)	−0.0048 (6)	−0.0004 (6)
C14	0.0179 (7)	0.0186 (7)	0.0272 (8)	0.0028 (6)	0.0003 (6)	−0.0009 (6)
C15	0.0203 (7)	0.0145 (6)	0.0163 (7)	0.0007 (5)	0.0030 (6)	0.0005 (5)
C16	0.0177 (7)	0.0174 (7)	0.0175 (7)	−0.0021 (5)	−0.0002 (5)	−0.0018 (6)
C17	0.0156 (7)	0.0145 (6)	0.0171 (7)	0.0020 (5)	−0.0002 (6)	−0.0001 (5)
C18	0.0277 (8)	0.0205 (7)	0.0225 (8)	0.0014 (6)	0.0042 (7)	−0.0066 (6)
C19	0.0164 (7)	0.0158 (6)	0.0152 (7)	−0.0012 (5)	−0.0012 (5)	0.0054 (5)
C20	0.0224 (8)	0.0236 (7)	0.0190 (8)	−0.0030 (7)	−0.0015 (6)	−0.0008 (6)
C21	0.0353 (10)	0.0311 (9)	0.0211 (9)	−0.0126 (8)	−0.0070 (7)	−0.0008 (7)
C22	0.0266 (9)	0.0339 (9)	0.0366 (11)	−0.0130 (8)	−0.0166 (8)	0.0158 (8)
C23	0.0153 (7)	0.0314 (9)	0.0486 (12)	0.0014 (7)	−0.0031 (8)	0.0182 (8)

C24	0.0174 (7)	0.0178 (7)	0.0311 (9)	0.0020 (6)	0.0026 (6)	0.0071 (6)
C25	0.0182 (7)	0.0201 (6)	0.0129 (7)	0.0040 (6)	−0.0020 (6)	0.0005 (5)
C26	0.0135 (6)	0.0176 (6)	0.0139 (7)	−0.0005 (5)	−0.0010 (5)	−0.0008 (5)
C27	0.0188 (7)	0.0206 (7)	0.0181 (8)	−0.0038 (6)	0.0006 (6)	0.0030 (6)
C28	0.0229 (7)	0.0157 (7)	0.0325 (9)	−0.0040 (6)	−0.0003 (7)	0.0000 (6)
C29	0.0283 (8)	0.0223 (7)	0.0253 (9)	−0.0029 (6)	−0.0037 (7)	−0.0103 (6)
C30	0.0297 (8)	0.0273 (8)	0.0148 (8)	−0.0015 (7)	−0.0033 (6)	−0.0037 (6)
C31	0.0234 (7)	0.0194 (7)	0.0141 (7)	−0.0009 (6)	−0.0039 (6)	0.0011 (6)

Geometric parameters (Å, º)

Cl1—C6	1.7459 (15)	C14—C15	1.397 (2)
S1—O2	1.4341 (12)	C14—H14	0.93
S1—O1	1.4349 (12)	C15—C16	1.393 (2)
S1—N1	1.6386 (12)	C15—C18	1.502 (2)
S1—C12	1.7623 (15)	C16—C17	1.391 (2)
N1—C11	1.496 (2)	C16—H16	0.93
N1—C1	1.506 (2)	C17—H17	0.93
N2—C9	1.4107 (19)	C18—H18A	0.96
N2—C10	1.4531 (19)	C18—H18B	0.96
N2—H1N2	0.84 (2)	C18—H18C	0.96
C1—C2	1.525 (2)	C19—C24	1.388 (2)
C1—H1A	0.97	C19—C20	1.399 (2)
C1—H1B	0.97	C20—C21	1.390 (2)
C2—C10	1.518 (2)	C20—H20	0.93
C2—C3	1.530 (2)	C21—C22	1.380 (3)
C2—H2	0.98	C21—H21	0.93
C3—C19	1.521 (2)	C22—C23	1.377 (3)
C3—C4	1.532 (2)	C22—H22	0.93
C3—H3	0.98	C23—C24	1.392 (3)
C4—C5	1.399 (2)	C23—H23	0.93
C4—C9	1.4072 (19)	C24—H24	0.93
C5—C6	1.384 (2)	C25—C26	1.512 (2)
C5—H5	0.93	C25—H25A	0.97
C6—C7	1.390 (2)	C25—H25B	0.97
C7—C8	1.382 (2)	C26—C31	1.394 (2)
C7—H7	0.93	C26—C27	1.400 (2)
C8—C9	1.403 (2)	C27—C28	1.386 (2)
C8—H8	0.93	C27—H27	0.93
C10—C11	1.529 (2)	C28—C29	1.391 (3)
C10—H10	0.98	C28—H28	0.93
C11—C25	1.539 (2)	C29—C30	1.390 (2)
C11—H11	0.98	C29—H29	0.93
C12—C17	1.392 (2)	C30—C31	1.390 (2)
C12—C13	1.397 (2)	C30—H30	0.93
C13—C14	1.386 (2)	C31—H31	0.93
C13—H13	0.93		

O2—S1—O1	119.63 (7)	C14—C13—C12	118.86 (15)
O2—S1—N1	107.08 (7)	C14—C13—H13	120.6
O1—S1—N1	106.57 (7)	C12—C13—H13	120.6
O2—S1—C12	107.38 (7)	C13—C14—C15	121.25 (15)
O1—S1—C12	107.75 (7)	C13—C14—H14	119.4
N1—S1—C12	107.97 (7)	C15—C14—H14	119.4
C11—N1—C1	110.00 (11)	C16—C15—C14	118.75 (14)
C11—N1—S1	119.97 (10)	C16—C15—C18	119.99 (14)
C1—N1—S1	116.23 (10)	C14—C15—C18	121.27 (14)
C9—N2—C10	114.84 (12)	C17—C16—C15	121.11 (14)
C9—N2—H1N2	108.8 (14)	C17—C16—H16	119.4
C10—N2—H1N2	115.8 (14)	C15—C16—H16	119.4
N1—C1—C2	103.40 (12)	C16—C17—C12	119.01 (14)
N1—C1—H1A	111.1	C16—C17—H17	120.5
C2—C1—H1A	111.1	C12—C17—H17	120.5
N1—C1—H1B	111.1	C15—C18—H18A	109.5
C2—C1—H1B	111.1	C15—C18—H18B	109.5
H1A—C1—H1B	109.0	H18A—C18—H18B	109.5
C10—C2—C1	101.60 (12)	C15—C18—H18C	109.5
C10—C2—C3	110.69 (11)	H18A—C18—H18C	109.5
C1—C2—C3	117.94 (12)	H18B—C18—H18C	109.5
C10—C2—H2	108.7	C24—C19—C20	118.21 (15)
C1—C2—H2	108.7	C24—C19—C3	121.56 (14)
C3—C2—H2	108.7	C20—C19—C3	120.21 (13)
C19—C3—C2	112.59 (11)	C21—C20—C19	120.94 (17)
C19—C3—C4	111.32 (12)	C21—C20—H20	119.5
C2—C3—C4	108.78 (12)	C19—C20—H20	119.5
C19—C3—H3	108.0	C22—C21—C20	119.93 (18)
C2—C3—H3	108.0	C22—C21—H21	120.0
C4—C3—H3	108.0	C20—C21—H21	120.0
C5—C4—C9	118.43 (13)	C23—C22—C21	119.78 (17)
C5—C4—C3	119.09 (13)	C23—C22—H22	120.1
C9—C4—C3	122.47 (13)	C21—C22—H22	120.1
C6—C5—C4	120.78 (14)	C22—C23—C24	120.57 (17)
C6—C5—H5	119.6	C22—C23—H23	119.7
C4—C5—H5	119.6	C24—C23—H23	119.7
C5—C6—C7	121.18 (14)	C19—C24—C23	120.54 (16)
C5—C6—Cl1	119.37 (11)	C19—C24—H24	119.7
C7—C6—Cl1	119.42 (12)	C23—C24—H24	119.7
C8—C7—C6	118.47 (14)	C26—C25—C11	116.91 (13)
C8—C7—H7	120.8	C26—C25—H25A	108.1
C6—C7—H7	120.8	C11—C25—H25A	108.1
C7—C8—C9	121.50 (14)	C26—C25—H25B	108.1
C7—C8—H8	119.2	C11—C25—H25B	108.1
C9—C8—H8	119.2	H25A—C25—H25B	107.3
C8—C9—C4	119.59 (14)	C31—C26—C27	118.21 (14)
C8—C9—N2	118.73 (13)	C31—C26—C25	119.60 (13)
C4—C9—N2	121.67 (13)	C27—C26—C25	122.14 (14)

N2—C10—C2	110.21 (12)	C28—C27—C26	121.02 (15)
N2—C10—C11	114.05 (12)	C28—C27—H27	119.5
C2—C10—C11	102.39 (11)	C26—C27—H27	119.5
N2—C10—H10	110.0	C27—C28—C29	120.02 (15)
C2—C10—H10	110.0	C27—C28—H28	120.0
C11—C10—H10	110.0	C29—C28—H28	120.0
N1—C11—C10	99.92 (12)	C30—C29—C28	119.71 (16)
N1—C11—C25	116.13 (12)	C30—C29—H29	120.1
C10—C11—C25	115.10 (12)	C28—C29—H29	120.1
N1—C11—H11	108.4	C31—C30—C29	119.96 (16)
C10—C11—H11	108.4	C31—C30—H30	120.0
C25—C11—H11	108.4	C29—C30—H30	120.0
C17—C12—C13	121.01 (13)	C30—C31—C26	121.07 (14)
C17—C12—S1	118.72 (12)	C30—C31—H31	119.5
C13—C12—S1	120.25 (12)	C26—C31—H31	119.5

O2—S1—N1—C11	−50.80 (12)	C2—C10—C11—N1	43.40 (13)
O1—S1—N1—C11	−179.92 (10)	N2—C10—C11—C25	−72.42 (16)
C12—S1—N1—C11	64.55 (12)	C2—C10—C11—C25	168.55 (12)
O2—S1—N1—C1	172.80 (10)	O2—S1—C12—C17	−155.56 (12)
O1—S1—N1—C1	43.67 (12)	O1—S1—C12—C17	−25.46 (14)
C12—S1—N1—C1	−71.85 (12)	N1—S1—C12—C17	89.29 (13)
C11—N1—C1—C2	−3.90 (14)	O2—S1—C12—C13	23.14 (15)
S1—N1—C1—C2	136.63 (10)	O1—S1—C12—C13	153.24 (12)
N1—C1—C2—C10	30.84 (14)	N1—S1—C12—C13	−92.01 (13)
N1—C1—C2—C3	151.97 (12)	C17—C12—C13—C14	0.4 (2)
C10—C2—C3—C19	−169.50 (12)	S1—C12—C13—C14	−178.31 (12)
C1—C2—C3—C19	74.18 (16)	C12—C13—C14—C15	−0.1 (2)
C10—C2—C3—C4	−45.62 (15)	C13—C14—C15—C16	−0.4 (2)
C1—C2—C3—C4	−161.95 (12)	C13—C14—C15—C18	179.29 (15)
C19—C3—C4—C5	−41.60 (17)	C14—C15—C16—C17	0.5 (2)
C2—C3—C4—C5	−166.23 (12)	C18—C15—C16—C17	−179.16 (14)
C19—C3—C4—C9	139.71 (14)	C15—C16—C17—C12	−0.2 (2)
C2—C3—C4—C9	15.08 (19)	C13—C12—C17—C16	−0.2 (2)
C9—C4—C5—C6	0.2 (2)	S1—C12—C17—C16	178.46 (11)
C3—C4—C5—C6	−178.56 (13)	C2—C3—C19—C24	−115.72 (15)
C4—C5—C6—C7	−1.8 (2)	C4—C3—C19—C24	121.83 (15)
C4—C5—C6—Cl1	−179.87 (11)	C2—C3—C19—C20	65.90 (17)
C5—C6—C7—C8	1.5 (2)	C4—C3—C19—C20	−56.56 (17)
Cl1—C6—C7—C8	179.53 (11)	C24—C19—C20—C21	0.2 (2)
C6—C7—C8—C9	0.5 (2)	C3—C19—C20—C21	178.68 (15)
C7—C8—C9—C4	−2.1 (2)	C19—C20—C21—C22	−1.1 (3)
C7—C8—C9—N2	178.85 (14)	C20—C21—C22—C23	1.0 (3)
C5—C4—C9—C8	1.7 (2)	C21—C22—C23—C24	0.0 (3)
C3—C4—C9—C8	−179.61 (12)	C20—C19—C24—C23	0.7 (2)
C5—C4—C9—N2	−179.25 (12)	C3—C19—C24—C23	−177.67 (14)
C3—C4—C9—N2	−0.5 (2)	C22—C23—C24—C19	−0.9 (2)
C10—N2—C9—C8	−162.78 (13)	N1—C11—C25—C26	54.31 (17)

C10—N2—C9—C4	18.1 (2)	C10—C11—C25—C26	−61.90 (18)
C9—N2—C10—C2	−49.72 (16)	C11—C25—C26—C31	−103.37 (17)
C9—N2—C10—C11	−164.22 (12)	C11—C25—C26—C27	79.21 (19)
C1—C2—C10—N2	−168.63 (12)	C31—C26—C27—C28	0.9 (2)
C3—C2—C10—N2	65.30 (15)	C25—C26—C27—C28	178.35 (14)
C1—C2—C10—C11	−46.93 (14)	C26—C27—C28—C29	−0.8 (2)
C3—C2—C10—C11	−172.99 (11)	C27—C28—C29—C30	0.2 (3)
C1—N1—C11—C10	−24.29 (13)	C28—C29—C30—C31	0.3 (3)
S1—N1—C11—C10	−163.12 (9)	C29—C30—C31—C26	−0.3 (3)
C1—N1—C11—C25	−148.72 (12)	C27—C26—C31—C30	−0.4 (2)
S1—N1—C11—C25	72.44 (15)	C25—C26—C31—C30	−177.87 (15)
N2—C10—C11—N1	162.44 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*2···Cl1^{i}	0.84 (2)	2.83 (2)	3.5947 (13)	153 (2)
C25—H25*B*···O2	0.97	2.46	3.0529 (19)	119
C27—H27···Cl1^{i}	0.93	2.77	3.5980 (16)	149
C17—H17···*Cg*2^{ii}	0.93	2.70	3.5403 (16)	151
C29—H29···*Cg*1^{iii}	0.93	2.68	3.6014 (19)	170

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