# organic compounds

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

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In the title compound, $C_{32}H_{32}N_2O_2S$, the pyrrolidine ring adopts a twist conformation while the tetrahydropyridine ring is in a distorted half-chair conformation. The two rings are *trans*-fused. The dihedral angle between the sulfonyl and benzyl phenyl rings is 72.54 (14)°. The molecular structure is stabilized by C—H···O hydrogen bonds, and N—H···$\pi$ interactions involving the benzyl phenyl ring. The screw-related molecules are linked into chains along the *b* axis by C—H···O hydrogen bonds and C—H···$\pi$ interactions. Adjacent inversion-related chains interact *via* C—H···$\pi$ interactions, forming a two-dimensional network parallel to the *bc* plane.

## Related literature

For the anticancer and photochemotherapeutic activity of pyrroloquinoline derivatives, see: Ferlin *et al.* (2005); Gasparotto *et al.* (2007); Barraja *et al.* (2003). For a related structure, see: Sudha *et al.* (2009). For ring puckering parameters, see: Cremer & Pople (1975). For asymmetry parameters, see: Duax *et al.* (1976).
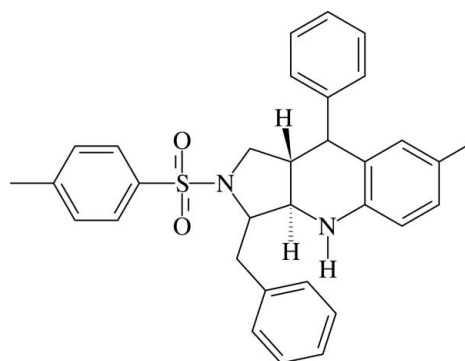
## Experimental

### Crystal data

| | |
|---|---|
| $C_{32}H_{32}N_2O_2S$ | $V = 2624.07$ (18) Å³ |
| $M_r = 508.66$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 9.0445$ (4) Å | $\mu = 0.16$ mm$^{-1}$ |
| $b = 10.6014$ (4) Å | $T = 100$ K |
| $c = 27.533$ (1) Å | $0.38 \times 0.20 \times 0.17$ mm |
| $\beta = 96.294$ (3)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 22823 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2005) | 5138 independent reflections |
| $T_{min} = 0.360$, $T_{max} = 0.974$ | 3615 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.078$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.178$ | |
| $S = 1.04$ | $\Delta\rho_{max} = 0.69$ e Å$^{-3}$ |
| 5138 reflections | $\Delta\rho_{min} = -0.51$ e Å$^{-3}$ |
| 340 parameters | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| C25—H25A···O2 | 0.97 | 2.56 | 3.182 (3) | 122 |
| C28—H28···O2[i] | 0.93 | 2.49 | 3.282 (4) | 143 |
| N2—H1N2···Cg3 | 0.87 (3) | 2.69 (3) | 3.461 (3) | 148 (2) |
| C3—H3···Cg3[i] | 0.98 | 2.93 | 3.852 (3) | 158 |
| C18—H18B···Cg2[ii] | 0.96 | 2.90 | 3.723 (4) | 145 |
| C21—H21···Cg1[iii] | 0.93 | 2.74 | 3.637 (3) | 162 |

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z$; (iii) $-x+2, -y, -z$. $Cg1$, $Cg2$ and $Cg3$ are the centroids of the C4–C9, C12–C17 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).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2561).

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# supporting information

## 3-Benzyl-7-methyl-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 synthesized and investigated as potential anticancer drugs (Ferlin *et al.*, 2005; Gasparotto *et al.*, 2007). Some of them have been found to exhibit photochemotherapeutic activity (Barraja *et al.*, 2003). As part of our studies on pyrroloquinoline derivatives, we report here the crystal structure of the title compound (I).

In the title molecule, the pyrrolidine ring adopts a twist conformation; the asymmetry parameters $\Delta C_2$[C2—C10] (Duax *et al.*, 1976) and the puckering parameters $q_2$ and $\varphi$ (Cremer & Pople, 1975) are 6.1 (3)°, 0.407 (3) Å and 85.0 (4)°, respectively. The tosyl group is attached to the pyrrolidine ring in a biaxial position. The tetrahydropyridine ring adopts a distorted half-chair conformation; the Q, $\theta$, $\varphi$ and $\Delta C_s$[C10] values for the above ring are 0.522 (3) Å, 129.4 (3)°, 93.1 (3)° and 101.3 (4)°, respectively. The phenyl group attached to the tetrahydropyridine ring is in a biaxial position. The C19—C24 phenyl ring forms dihedral angles of 80.98 (13) and 7.40 (14)°, respectively, with the C4—C9 and C12—C17 benzene rings. The C12—C17 and C26—C31 rings are oriented at a dihedral angle of 72.54 (14)°. The molecular structure is stabilized by C—H···O hydrogen bonds and N—H···$\pi$ interactions (Table 1).

Bond lengths and angles are comparable with those in 3-benzyl-9-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1*H*-pyrrolo-[3,4-*b*]quinoline, (II), (Sudha *et al.*, 2009). A superposition of the non-H atoms of the above molecule with those of the title molecule using *XP* in *SHELXTL* (Sheldrick, 2008), gave an r.m.s. deviation of 0.489 Å (Fig. 2). In both compounds, the pyrrolidine ring is *trans*-fused to the tetrahydropyridine ring but they differ in relative orientations of the phenyl rings.

In the solid state, screw-related molecules are linked into chains along the *b* axis by C—H···O hydrogen bonds and C—H···$\pi$ interactions involving the C26—C31 ring (Table 1). Adjacent inversion-related chains interact *via* C—H···$\pi$ interactions involving the C4—C9 and C12—C17 rings to form a two-dimensional network parallel to the *bc* plane (Fig.3).

A comparison of crystal packing in (I) and (II) shows that the presence of the methyl group at 7-position completely changes the packing mode. Without the methyl group, the molecules are linked into a chain along the *a* axis by intermolecular C—H···$\pi$ interactions. But the presence of the methyl group resulted in a two-dimensional network parallel to the *bc* plane, as discussed above.

### S2. Experimental

InCl₃ (20 mol%) was added to a mixture of 2-(*N*-cinnamyl-*N*-tosylamino)-3-phenyl propanal (1 mmol) and *p*-methyl 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 Na₂SO₄. 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 = 0.87 (3) 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.
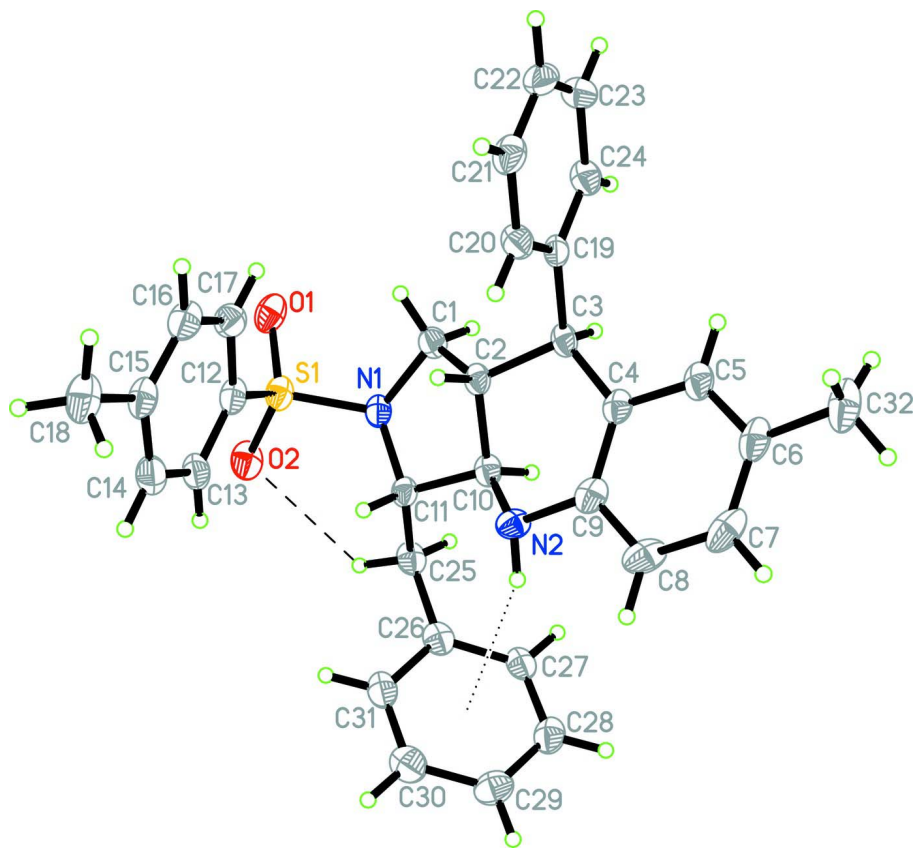


**Figure 1**

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a C—H···O hydrogen bond and the dotted line indicates an N—H···$\pi$ interaction.
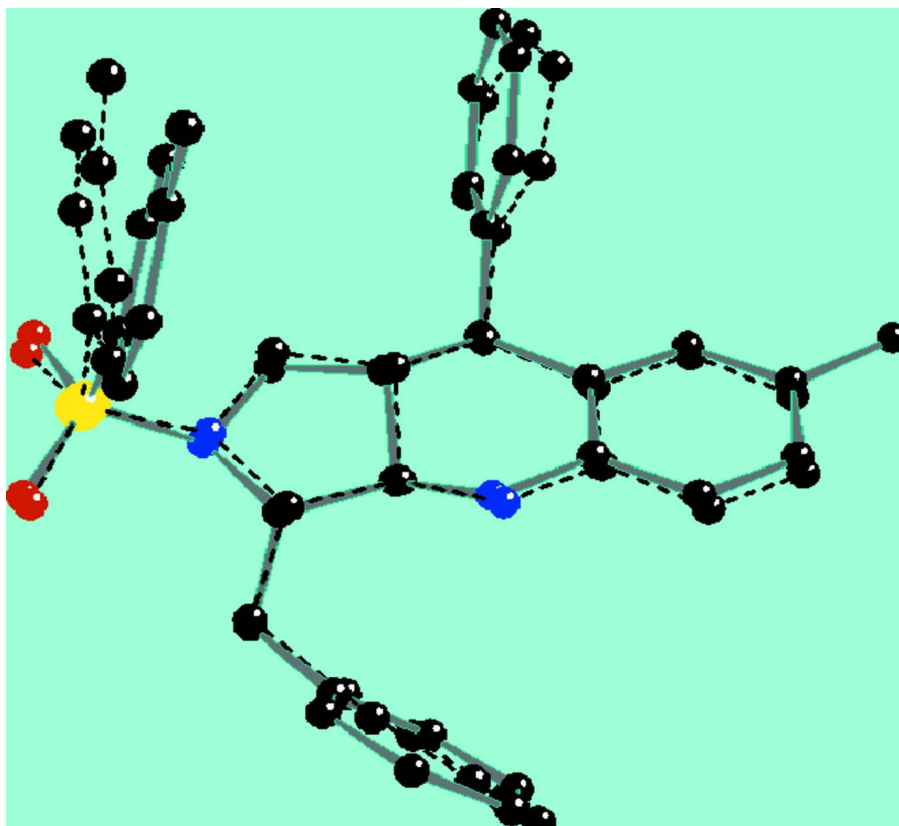
**Figure 2**
Fit of the title molecule (solid lines) with (II) (dashed lines). H atoms have been omitted for clarity.
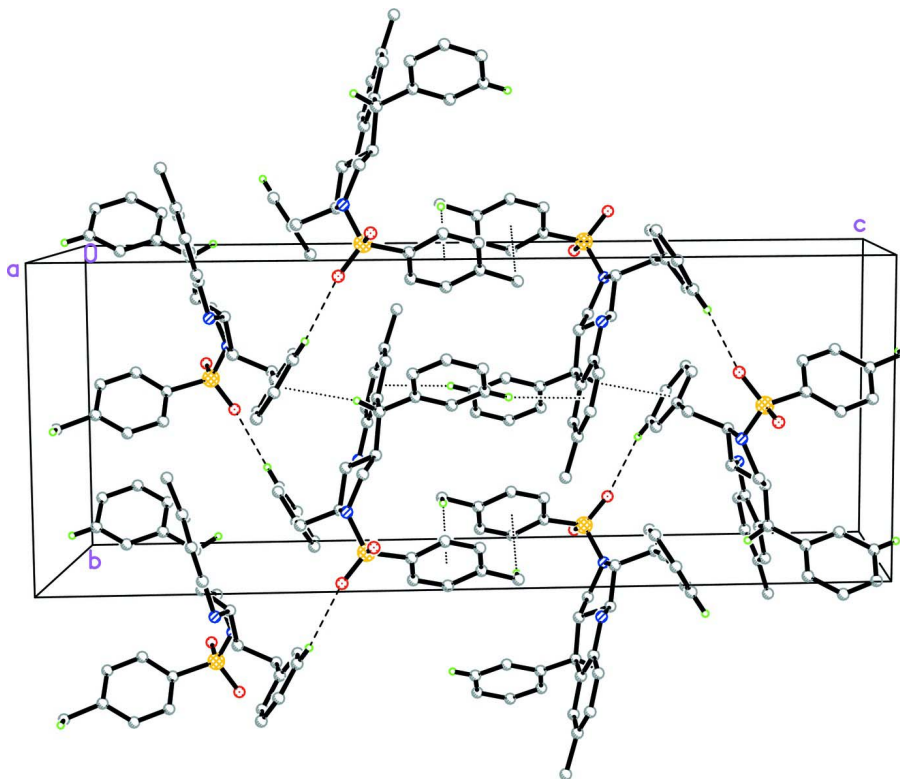
**Figure 3**

Crystal packing of the title compound. C—H⋯O hydrogen bonds are shown as dashed lines and C—H⋯π interactions are shown as dotted lines. For the sake of clarity, H atoms not involved in the interactions have been omitted.

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

*Crystal data*

| | |
|---|---|
| $C_{32}H_{32}N_2O_2S$ | $F(000) = 1080$ |
| $M_r = 508.66$ | $D_x = 1.288$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 5605 reflections |
| $a = 9.0445$ (4) Å | $\theta = 2.3–30.1°$ |
| $b = 10.6014$ (4) Å | $\mu = 0.16$ mm$^{-1}$ |
| $c = 27.533$ (1) Å | $T = 100$ K |
| $\beta = 96.294$ (3)° | Block, colourless |
| $V = 2624.07$ (18) Å$^3$ | $0.38 \times 0.20 \times 0.17$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 22823 measured reflections |
| | 5138 independent reflections |
| Radiation source: fine-focus sealed tube | 3615 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.078$ |
| $\varphi$ and $\omega$ scans | $\theta_{max} = 26.0°$, $\theta_{min} = 2.6°$ |
| Absorption correction: multi-scan | $h = -10 \rightarrow 11$ |
| (*SADABS*; Bruker, 2005) | $k = -13 \rightarrow 12$ |
| $T_{min} = 0.360$, $T_{max} = 0.974$ | $l = -33 \rightarrow 33$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.178$ | |
| $S = 1.04$ | H atoms treated by a mixture of independent and constrained refinement |
| 5138 reflections | |
| 340 parameters | $w = 1/[\sigma^2(F_o^2) + (0.1011P)^2 + 1.1335P]$ |
| 0 restraints | where $P = (F_o^2 + 2F_c^2)/3$ |
| Primary atom site location: structure-invariant direct methods | $(\Delta/\sigma)_{max} = 0.001$ |
| | $\Delta\rho_{max} = 0.69$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.51$ 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.62265 (8) | 0.48132 (7) | 0.13646 (2) | 0.0262 (2) |
| O1 | 0.4733 (2) | 0.4422 (2) | 0.12298 (7) | 0.0322 (5) |
| O2 | 0.6528 (2) | 0.58710 (19) | 0.16844 (7) | 0.0335 (5) |
| N1 | 0.7118 (3) | 0.3614 (2) | 0.16335 (8) | 0.0239 (5) |
| N2 | 1.0859 (3) | 0.2372 (2) | 0.15932 (8) | 0.0249 (5) |
| H1N2 | 1.156 (3) | 0.272 (3) | 0.1791 (11) | 0.022 (7)* |
| C1 | 0.6810 (3) | 0.2332 (3) | 0.14178 (10) | 0.0260 (6) |
| H1A | 0.6104 | 0.2378 | 0.1126 | 0.031* |
| H1B | 0.6422 | 0.1770 | 0.1651 | 0.031* |
| C2 | 0.8318 (3) | 0.1896 (2) | 0.12960 (8) | 0.0214 (6) |
| H2 | 0.8528 | 0.2304 | 0.0992 | 0.026* |
| C3 | 0.8577 (3) | 0.0474 (2) | 0.12508 (9) | 0.0217 (6) |
| H3 | 0.8140 | 0.0064 | 0.1520 | 0.026* |
| C4 | 1.0250 (3) | 0.0211 (3) | 0.13221 (8) | 0.0228 (6) |
| C5 | 1.0783 (3) | −0.0993 (3) | 0.12259 (9) | 0.0264 (6) |
| H5 | 1.0096 | −0.1616 | 0.1122 | 0.032* |
| C6 | 1.2275 (3) | −0.1305 (3) | 0.12773 (9) | 0.0305 (7) |
| C7 | 1.3287 (4) | −0.0369 (3) | 0.14395 (10) | 0.0362 (8) |
| H7 | 1.4300 | −0.0551 | 0.1478 | 0.043* |
| C8 | 1.2805 (3) | 0.0830 (3) | 0.15445 (10) | 0.0333 (7) |
| H8 | 1.3500 | 0.1441 | 0.1655 | 0.040* |
| C9 | 1.1304 (3) | 0.1136 (3) | 0.14877 (9) | 0.0258 (6) |
| C10 | 0.9342 (3) | 0.2446 (2) | 0.17126 (9) | 0.0223 (6) |
| H10 | 0.9251 | 0.1957 | 0.2010 | 0.027* |

| C11 | 0.8745 (3) | 0.3775 (2) | 0.17768 (9) | 0.0214 (6) |
| H11 | 0.9149 | 0.4339 | 0.1542 | 0.026* |
| C12 | 0.7040 (3) | 0.5160 (3) | 0.08227 (9) | 0.0262 (6) |
| C13 | 0.8142 (3) | 0.6074 (3) | 0.08287 (10) | 0.0296 (7) |
| H13 | 0.8492 | 0.6472 | 0.1120 | 0.036* |
| C14 | 0.8717 (4) | 0.6392 (3) | 0.03979 (10) | 0.0332 (7) |
| H14 | 0.9459 | 0.7000 | 0.0404 | 0.040* |
| C15 | 0.8201 (3) | 0.5815 (3) | −0.00429 (10) | 0.0293 (7) |
| C16 | 0.7127 (3) | 0.4883 (3) | −0.00385 (10) | 0.0307 (7) |
| H16 | 0.6792 | 0.4474 | −0.0329 | 0.037* |
| C17 | 0.6536 (3) | 0.4543 (3) | 0.03907 (10) | 0.0290 (6) |
| H17 | 0.5817 | 0.3914 | 0.0388 | 0.035* |
| C18 | 0.8756 (4) | 0.6232 (3) | −0.05135 (11) | 0.0381 (8) |
| H18A | 0.8361 | 0.5685 | −0.0774 | 0.057* |
| H18B | 0.9823 | 0.6194 | −0.0481 | 0.057* |
| H18C | 0.8439 | 0.7082 | −0.0586 | 0.057* |
| C19 | 0.7819 (3) | −0.0079 (2) | 0.07772 (9) | 0.0219 (6) |
| C20 | 0.8280 (3) | 0.0268 (3) | 0.03263 (9) | 0.0270 (6) |
| H20 | 0.9051 | 0.0844 | 0.0316 | 0.032* |
| C21 | 0.7597 (3) | −0.0241 (3) | −0.01055 (10) | 0.0305 (7) |
| H21 | 0.7916 | −0.0010 | −0.0403 | 0.037* |
| C22 | 0.6438 (3) | −0.1093 (3) | −0.00949 (11) | 0.0327 (7) |
| H22 | 0.5974 | −0.1428 | −0.0385 | 0.039* |
| C23 | 0.5976 (3) | −0.1444 (3) | 0.03477 (11) | 0.0329 (7) |
| H23 | 0.5202 | −0.2018 | 0.0357 | 0.040* |
| C24 | 0.6674 (3) | −0.0936 (3) | 0.07798 (10) | 0.0276 (6) |
| H24 | 0.6360 | −0.1180 | 0.1076 | 0.033* |
| C25 | 0.9111 (3) | 0.4321 (3) | 0.22950 (9) | 0.0261 (6) |
| H25A | 0.8648 | 0.5142 | 0.2315 | 0.031* |
| H25B | 0.8722 | 0.3769 | 0.2532 | 0.031* |
| C26 | 1.0768 (3) | 0.4441 (3) | 0.24082 (9) | 0.0257 (6) |
| C27 | 1.1623 (3) | 0.3525 (3) | 0.26768 (9) | 0.0263 (6) |
| H27 | 1.1146 | 0.2873 | 0.2823 | 0.032* |
| C28 | 1.3159 (4) | 0.3569 (3) | 0.27287 (9) | 0.0307 (7) |
| H28 | 1.3702 | 0.2939 | 0.2903 | 0.037* |
| C29 | 1.3898 (3) | 0.4552 (3) | 0.25217 (10) | 0.0332 (7) |
| H29 | 1.4932 | 0.4583 | 0.2556 | 0.040* |
| C30 | 1.3068 (4) | 0.5486 (3) | 0.22638 (10) | 0.0342 (7) |
| H30 | 1.3549 | 0.6153 | 0.2128 | 0.041* |
| C31 | 1.1532 (3) | 0.5429 (3) | 0.22085 (9) | 0.0293 (7) |
| H31 | 1.0993 | 0.6062 | 0.2035 | 0.035* |
| C32 | 1.2786 (4) | −0.2591 (3) | 0.11267 (11) | 0.0403 (8) |
| H32A | 1.2094 | −0.3220 | 0.1210 | 0.060* |
| H32B | 1.3752 | −0.2767 | 0.1294 | 0.060* |
| H32C | 1.2837 | −0.2603 | 0.0780 | 0.060* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0340 (4) | 0.0233 (4) | 0.0212 (3) | 0.0093 (3) | 0.0028 (3) | −0.0022 (3) |
| O1 | 0.0324 (12) | 0.0364 (12) | 0.0282 (10) | 0.0140 (9) | 0.0044 (8) | 0.0006 (9) |
| O2 | 0.0486 (13) | 0.0266 (11) | 0.0254 (10) | 0.0114 (9) | 0.0040 (9) | −0.0076 (8) |
| N1 | 0.0294 (13) | 0.0202 (12) | 0.0219 (11) | 0.0044 (9) | 0.0023 (9) | 0.0017 (9) |
| N2 | 0.0245 (13) | 0.0277 (13) | 0.0221 (11) | 0.0020 (10) | 0.0007 (10) | −0.0082 (10) |
| C1 | 0.0295 (16) | 0.0213 (15) | 0.0268 (14) | 0.0015 (12) | 0.0015 (11) | −0.0008 (11) |
| C2 | 0.0293 (15) | 0.0188 (14) | 0.0161 (12) | 0.0011 (11) | 0.0033 (11) | 0.0033 (10) |
| C3 | 0.0303 (16) | 0.0183 (14) | 0.0170 (12) | 0.0010 (11) | 0.0054 (10) | 0.0038 (10) |
| C4 | 0.0305 (16) | 0.0250 (15) | 0.0127 (11) | 0.0046 (12) | 0.0018 (10) | 0.0019 (10) |
| C5 | 0.0384 (17) | 0.0252 (15) | 0.0153 (12) | 0.0051 (12) | 0.0015 (11) | 0.0047 (10) |
| C6 | 0.0436 (19) | 0.0342 (17) | 0.0134 (12) | 0.0147 (14) | 0.0012 (12) | 0.0039 (11) |
| C7 | 0.0331 (18) | 0.054 (2) | 0.0205 (13) | 0.0201 (15) | −0.0019 (12) | −0.0069 (13) |
| C8 | 0.0294 (17) | 0.048 (2) | 0.0214 (13) | 0.0040 (14) | −0.0010 (12) | −0.0121 (13) |
| C9 | 0.0318 (16) | 0.0328 (16) | 0.0125 (11) | 0.0063 (12) | 0.0013 (11) | −0.0017 (11) |
| C10 | 0.0297 (16) | 0.0212 (14) | 0.0163 (12) | 0.0029 (11) | 0.0035 (10) | 0.0008 (10) |
| C11 | 0.0271 (15) | 0.0193 (14) | 0.0177 (12) | 0.0027 (11) | 0.0015 (10) | 0.0010 (10) |
| C12 | 0.0345 (17) | 0.0234 (15) | 0.0206 (12) | 0.0089 (12) | 0.0023 (11) | 0.0016 (11) |
| C13 | 0.0454 (19) | 0.0191 (14) | 0.0231 (13) | 0.0035 (13) | −0.0016 (12) | 0.0006 (11) |
| C14 | 0.0408 (19) | 0.0254 (16) | 0.0326 (15) | 0.0012 (13) | 0.0004 (13) | 0.0060 (12) |
| C15 | 0.0352 (17) | 0.0258 (16) | 0.0269 (14) | 0.0114 (13) | 0.0029 (12) | 0.0032 (11) |
| C16 | 0.0402 (18) | 0.0306 (16) | 0.0206 (13) | 0.0107 (13) | −0.0001 (12) | −0.0049 (11) |
| C17 | 0.0324 (17) | 0.0258 (16) | 0.0281 (14) | 0.0046 (12) | −0.0006 (12) | −0.0029 (11) |
| C18 | 0.048 (2) | 0.0374 (18) | 0.0297 (15) | 0.0112 (15) | 0.0075 (14) | 0.0067 (13) |
| C19 | 0.0264 (15) | 0.0167 (13) | 0.0223 (12) | 0.0039 (11) | 0.0013 (11) | 0.0025 (10) |
| C20 | 0.0370 (17) | 0.0226 (15) | 0.0212 (13) | −0.0017 (12) | 0.0022 (11) | 0.0005 (11) |
| C21 | 0.0390 (18) | 0.0312 (16) | 0.0207 (13) | 0.0076 (13) | 0.0009 (12) | 0.0016 (12) |
| C22 | 0.0355 (18) | 0.0304 (16) | 0.0295 (14) | 0.0064 (13) | −0.0091 (12) | −0.0080 (12) |
| C23 | 0.0290 (17) | 0.0281 (17) | 0.0401 (16) | −0.0035 (12) | −0.0034 (13) | −0.0031 (13) |
| C24 | 0.0324 (17) | 0.0234 (15) | 0.0275 (14) | 0.0017 (12) | 0.0053 (12) | −0.0008 (11) |
| C25 | 0.0360 (17) | 0.0225 (14) | 0.0201 (13) | 0.0025 (12) | 0.0045 (11) | −0.0036 (11) |
| C26 | 0.0376 (17) | 0.0241 (15) | 0.0159 (12) | 0.0001 (12) | 0.0048 (11) | −0.0054 (10) |
| C27 | 0.0417 (18) | 0.0212 (14) | 0.0152 (12) | −0.0024 (12) | −0.0006 (11) | −0.0024 (10) |
| C28 | 0.0417 (19) | 0.0287 (16) | 0.0203 (13) | 0.0059 (13) | −0.0035 (12) | −0.0023 (11) |
| C29 | 0.0324 (17) | 0.0429 (19) | 0.0236 (14) | −0.0015 (14) | −0.0002 (12) | −0.0016 (13) |
| C30 | 0.046 (2) | 0.0344 (18) | 0.0225 (13) | −0.0070 (14) | 0.0031 (13) | 0.0022 (12) |
| C31 | 0.0433 (19) | 0.0231 (15) | 0.0208 (13) | 0.0022 (13) | 0.0006 (12) | −0.0008 (11) |
| C32 | 0.053 (2) | 0.0387 (19) | 0.0301 (15) | 0.0231 (15) | 0.0078 (14) | 0.0043 (13) |

*Geometric parameters (Å, °)*

| S1—O1 | 1.423 (2) | C14—H14 | 0.93 |
|---|---|---|---|
| S1—O2 | 1.433 (2) | C15—C16 | 1.387 (4) |
| S1—N1 | 1.638 (2) | C15—C18 | 1.506 (4) |
| S1—C12 | 1.773 (3) | C16—C17 | 1.397 (4) |
| N1—C11 | 1.491 (3) | C16—H16 | 0.93 |

| | | | |
|---|---|---|---|
| N1—C1 | 1.497 (3) | C17—H17 | 0.93 |
| N2—C9 | 1.410 (4) | C18—H18A | 0.96 |
| N2—C10 | 1.448 (3) | C18—H18B | 0.96 |
| N2—H1N2 | 0.87 (3) | C18—H18C | 0.96 |
| C1—C2 | 1.512 (4) | C19—C24 | 1.379 (4) |
| C1—H1A | 0.97 | C19—C20 | 1.401 (4) |
| C1—H1B | 0.97 | C20—C21 | 1.388 (4) |
| C2—C10 | 1.510 (4) | C20—H20 | 0.93 |
| C2—C3 | 1.532 (4) | C21—C22 | 1.386 (4) |
| C2—H2 | 0.98 | C21—H21 | 0.93 |
| C3—C19 | 1.522 (4) | C22—C23 | 1.382 (4) |
| C3—C4 | 1.530 (4) | C22—H22 | 0.93 |
| C3—H3 | 0.98 | C23—C24 | 1.392 (4) |
| C4—C5 | 1.400 (4) | C23—H23 | 0.93 |
| C4—C9 | 1.408 (4) | C24—H24 | 0.93 |
| C5—C6 | 1.382 (4) | C25—C26 | 1.502 (4) |
| C5—H5 | 0.93 | C25—H25A | 0.97 |
| C6—C7 | 1.391 (5) | C25—H25B | 0.97 |
| C6—C32 | 1.512 (4) | C26—C31 | 1.400 (4) |
| C7—C8 | 1.385 (4) | C26—C27 | 1.401 (4) |
| C7—H7 | 0.93 | C27—C28 | 1.381 (4) |
| C8—C9 | 1.388 (4) | C27—H27 | 0.93 |
| C8—H8 | 0.93 | C28—C29 | 1.394 (4) |
| C10—C11 | 1.527 (4) | C28—H28 | 0.93 |
| C10—H10 | 0.98 | C29—C30 | 1.390 (4) |
| C11—C25 | 1.541 (3) | C29—H29 | 0.93 |
| C11—H11 | 0.98 | C30—C31 | 1.383 (4) |
| C12—C13 | 1.389 (4) | C30—H30 | 0.93 |
| C12—C17 | 1.390 (4) | C31—H31 | 0.93 |
| C13—C14 | 1.388 (4) | C32—H32A | 0.96 |
| C13—H13 | 0.93 | C32—H32B | 0.96 |
| C14—C15 | 1.393 (4) | C32—H32C | 0.96 |
| | | | |
| O1—S1—O2 | 119.99 (12) | C13—C14—C15 | 121.1 (3) |
| O1—S1—N1 | 107.33 (12) | C13—C14—H14 | 119.4 |
| O2—S1—N1 | 106.16 (12) | C15—C14—H14 | 119.4 |
| O1—S1—C12 | 108.10 (13) | C16—C15—C14 | 118.2 (3) |
| O2—S1—C12 | 106.62 (13) | C16—C15—C18 | 121.1 (3) |
| N1—S1—C12 | 108.18 (12) | C14—C15—C18 | 120.6 (3) |
| C11—N1—C1 | 110.2 (2) | C15—C16—C17 | 121.7 (3) |
| C11—N1—S1 | 116.96 (17) | C15—C16—H16 | 119.2 |
| C1—N1—S1 | 117.64 (17) | C17—C16—H16 | 119.2 |
| C9—N2—C10 | 113.3 (2) | C12—C17—C16 | 118.8 (3) |
| C9—N2—H1N2 | 108.1 (19) | C12—C17—H17 | 120.6 |
| C10—N2—H1N2 | 118.8 (19) | C16—C17—H17 | 120.6 |
| N1—C1—C2 | 103.4 (2) | C15—C18—H18A | 109.5 |
| N1—C1—H1A | 111.1 | C15—C18—H18B | 109.5 |
| C2—C1—H1A | 111.1 | H18A—C18—H18B | 109.5 |

| | | | |
|---|---|---|---|
| N1—C1—H1B | 111.1 | C15—C18—H18C | 109.5 |
| C2—C1—H1B | 111.1 | H18A—C18—H18C | 109.5 |
| H1A—C1—H1B | 109.0 | H18B—C18—H18C | 109.5 |
| C10—C2—C1 | 101.9 (2) | C24—C19—C20 | 118.3 (2) |
| C10—C2—C3 | 110.8 (2) | C24—C19—C3 | 121.1 (2) |
| C1—C2—C3 | 117.9 (2) | C20—C19—C3 | 120.6 (2) |
| C10—C2—H2 | 108.6 | C21—C20—C19 | 120.6 (3) |
| C1—C2—H2 | 108.6 | C21—C20—H20 | 119.7 |
| C3—C2—H2 | 108.6 | C19—C20—H20 | 119.7 |
| C19—C3—C4 | 112.7 (2) | C22—C21—C20 | 120.1 (3) |
| C19—C3—C2 | 113.0 (2) | C22—C21—H21 | 119.9 |
| C4—C3—C2 | 109.1 (2) | C20—C21—H21 | 119.9 |
| C19—C3—H3 | 107.3 | C23—C22—C21 | 119.8 (3) |
| C4—C3—H3 | 107.3 | C23—C22—H22 | 120.1 |
| C2—C3—H3 | 107.3 | C21—C22—H22 | 120.1 |
| C5—C4—C9 | 117.5 (3) | C22—C23—C24 | 119.8 (3) |
| C5—C4—C3 | 119.9 (2) | C22—C23—H23 | 120.1 |
| C9—C4—C3 | 122.6 (2) | C24—C23—H23 | 120.1 |
| C6—C5—C4 | 123.5 (3) | C19—C24—C23 | 121.4 (3) |
| C6—C5—H5 | 118.3 | C19—C24—H24 | 119.3 |
| C4—C5—H5 | 118.3 | C23—C24—H24 | 119.3 |
| C5—C6—C7 | 117.6 (3) | C26—C25—C11 | 109.4 (2) |
| C5—C6—C32 | 120.8 (3) | C26—C25—H25A | 109.8 |
| C7—C6—C32 | 121.4 (3) | C11—C25—H25A | 109.8 |
| C8—C7—C6 | 120.7 (3) | C26—C25—H25B | 109.8 |
| C8—C7—H7 | 119.6 | C11—C25—H25B | 109.8 |
| C6—C7—H7 | 119.6 | H25A—C25—H25B | 108.2 |
| C7—C8—C9 | 121.2 (3) | C31—C26—C27 | 117.3 (3) |
| C7—C8—H8 | 119.4 | C31—C26—C25 | 120.4 (2) |
| C9—C8—H8 | 119.4 | C27—C26—C25 | 122.1 (3) |
| C8—C9—C4 | 119.5 (3) | C28—C27—C26 | 121.5 (3) |
| C8—C9—N2 | 119.5 (3) | C28—C27—H27 | 119.2 |
| C4—C9—N2 | 121.0 (3) | C26—C27—H27 | 119.2 |
| N2—C10—C2 | 108.9 (2) | C27—C28—C29 | 120.3 (3) |
| N2—C10—C11 | 115.6 (2) | C27—C28—H28 | 119.9 |
| C2—C10—C11 | 104.4 (2) | C29—C28—H28 | 119.9 |
| N2—C10—H10 | 109.2 | C30—C29—C28 | 119.1 (3) |
| C2—C10—H10 | 109.2 | C30—C29—H29 | 120.5 |
| C11—C10—H10 | 109.2 | C28—C29—H29 | 120.5 |
| N1—C11—C10 | 102.4 (2) | C31—C30—C29 | 120.3 (3) |
| N1—C11—C25 | 113.2 (2) | C31—C30—H30 | 119.8 |
| C10—C11—C25 | 114.3 (2) | C29—C30—H30 | 119.8 |
| N1—C11—H11 | 108.9 | C30—C31—C26 | 121.5 (3) |
| C10—C11—H11 | 108.9 | C30—C31—H31 | 119.2 |
| C25—C11—H11 | 108.9 | C26—C31—H31 | 119.2 |
| C13—C12—C17 | 120.4 (2) | C6—C32—H32A | 109.5 |
| C13—C12—S1 | 119.9 (2) | C6—C32—H32B | 109.5 |
| C17—C12—S1 | 119.7 (2) | H32A—C32—H32B | 109.5 |

| | | | |
|---|---|---|---|
| C14—C13—C12 | 119.7 (3) | C6—C32—H32C | 109.5 |
| C14—C13—H13 | 120.2 | H32A—C32—H32C | 109.5 |
| C12—C13—H13 | 120.2 | H32B—C32—H32C | 109.5 |
| | | | |
| O1—S1—N1—C11 | 175.82 (17) | C2—C10—C11—N1 | 31.8 (2) |
| O2—S1—N1—C11 | −54.7 (2) | N2—C10—C11—C25 | −85.8 (3) |
| C12—S1—N1—C11 | 59.4 (2) | C2—C10—C11—C25 | 154.5 (2) |
| O1—S1—N1—C1 | 41.1 (2) | O1—S1—C12—C13 | 149.6 (2) |
| O2—S1—N1—C1 | 170.60 (19) | O2—S1—C12—C13 | 19.4 (3) |
| C12—S1—N1—C1 | −75.3 (2) | N1—S1—C12—C13 | −94.4 (2) |
| C11—N1—C1—C2 | −16.8 (3) | O1—S1—C12—C17 | −28.3 (3) |
| S1—N1—C1—C2 | 120.77 (19) | O2—S1—C12—C17 | −158.5 (2) |
| N1—C1—C2—C10 | 35.8 (2) | N1—S1—C12—C17 | 87.6 (2) |
| N1—C1—C2—C3 | 157.3 (2) | C17—C12—C13—C14 | 1.5 (4) |
| C10—C2—C3—C19 | −167.9 (2) | S1—C12—C13—C14 | −176.5 (2) |
| C1—C2—C3—C19 | 75.3 (3) | C12—C13—C14—C15 | 0.4 (4) |
| C10—C2—C3—C4 | −41.8 (3) | C13—C14—C15—C16 | −2.0 (4) |
| C1—C2—C3—C4 | −158.6 (2) | C13—C14—C15—C18 | 175.7 (3) |
| C19—C3—C4—C5 | −44.2 (3) | C14—C15—C16—C17 | 1.7 (4) |
| C2—C3—C4—C5 | −170.5 (2) | C18—C15—C16—C17 | −175.9 (3) |
| C19—C3—C4—C9 | 136.4 (2) | C13—C12—C17—C16 | −1.7 (4) |
| C2—C3—C4—C9 | 10.1 (3) | S1—C12—C17—C16 | 176.2 (2) |
| C9—C4—C5—C6 | −1.1 (4) | C15—C16—C17—C12 | 0.1 (4) |
| C3—C4—C5—C6 | 179.5 (2) | C4—C3—C19—C24 | 121.5 (3) |
| C4—C5—C6—C7 | 0.9 (4) | C2—C3—C19—C24 | −114.3 (3) |
| C4—C5—C6—C32 | −174.8 (2) | C4—C3—C19—C20 | −58.1 (3) |
| C5—C6—C7—C8 | 0.0 (4) | C2—C3—C19—C20 | 66.1 (3) |
| C32—C6—C7—C8 | 175.6 (3) | C24—C19—C20—C21 | 0.0 (4) |
| C6—C7—C8—C9 | −0.5 (4) | C3—C19—C20—C21 | 179.6 (2) |
| C7—C8—C9—C4 | 0.2 (4) | C19—C20—C21—C22 | 0.5 (4) |
| C7—C8—C9—N2 | −179.3 (3) | C20—C21—C22—C23 | −0.6 (4) |
| C5—C4—C9—C8 | 0.5 (3) | C21—C22—C23—C24 | 0.2 (5) |
| C3—C4—C9—C8 | 179.9 (2) | C20—C19—C24—C23 | −0.4 (4) |
| C5—C4—C9—N2 | −179.9 (2) | C3—C19—C24—C23 | 179.9 (3) |
| C3—C4—C9—N2 | −0.6 (4) | C22—C23—C24—C19 | 0.3 (4) |
| C10—N2—C9—C8 | −156.3 (2) | N1—C11—C25—C26 | 179.6 (2) |
| C10—N2—C9—C4 | 24.2 (3) | C10—C11—C25—C26 | 62.9 (3) |
| C9—N2—C10—C2 | −56.6 (3) | C11—C25—C26—C31 | 76.8 (3) |
| C9—N2—C10—C11 | −173.7 (2) | C11—C25—C26—C27 | −97.3 (3) |
| C1—C2—C10—N2 | −166.6 (2) | C31—C26—C27—C28 | −2.2 (4) |
| C3—C2—C10—N2 | 67.1 (3) | C25—C26—C27—C28 | 172.1 (2) |
| C1—C2—C10—C11 | −42.5 (2) | C26—C27—C28—C29 | 1.5 (4) |
| C3—C2—C10—C11 | −168.8 (2) | C27—C28—C29—C30 | 0.1 (4) |
| C1—N1—C11—C10 | −9.1 (2) | C28—C29—C30—C31 | −0.8 (4) |
| S1—N1—C11—C10 | −146.95 (17) | C29—C30—C31—C26 | 0.0 (4) |
| C1—N1—C11—C25 | −132.6 (2) | C27—C26—C31—C30 | 1.5 (4) |
| S1—N1—C11—C25 | 89.6 (2) | C25—C26—C31—C30 | −173.0 (2) |
| N2—C10—C11—N1 | 151.4 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1$A$···O1 | 0.97 | 2.53 | 2.914 (4) | 104 |
| C13—H13···O2 | 0.93 | 2.57 | 2.912 (3) | 103 |
| C25—H25$A$···O2 | 0.97 | 2.56 | 3.182 (3) | 122 |
| C28—H28···O2[i] | 0.93 | 2.49 | 3.282 (4) | 143 |
| N2—H1$N$2···$Cg$3 | 0.87 (3) | 2.69 (3) | 3.461 (3) | 148 (2) |
| C3—H3···$Cg$3[i] | 0.98 | 2.93 | 3.852 (3) | 158 |
| C18—H18$B$···$Cg$2[ii] | 0.96 | 2.90 | 3.723 (4) | 145 |
| C21—H21···$Cg$1[iii] | 0.93 | 2.74 | 3.637 (3) | 162 |

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