

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

K. Chinnakali,<sup>a\*</sup> D. Sudha,<sup>a‡</sup> M. Jayagobi,<sup>b</sup>  
R. Raghunathan<sup>b</sup> and Hoong-Kun Fun<sup>c§</sup>

<sup>a</sup>Department of Physics, Anna University Chennai, Chennai 600 025, India,  
<sup>b</sup>Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India, and <sup>c</sup>X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia  
Correspondence e-mail: kali@annauniv.edu

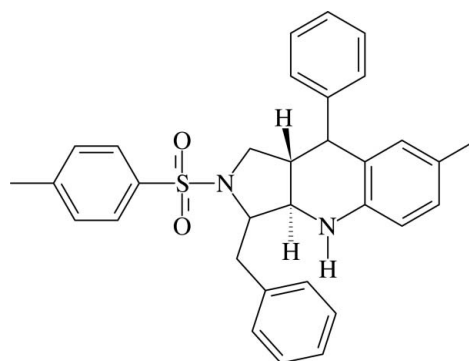
Received 24 October 2009; accepted 26 October 2009

Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  
R factor = 0.061; wR factor = 0.178; data-to-parameter ratio = 15.1.

In the title compound,  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2\text{S}$ , 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  $72.54(14)^\circ$ . The molecular structure is stabilized by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, and  $\text{N}-\text{H}\cdots\pi$  interactions involving the benzyl phenyl ring. The screw-related molecules are linked into chains along the *b* axis by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds and  $\text{C}-\text{H}\cdots\pi$  interactions. Adjacent inversion-related chains interact *via*  $\text{C}-\text{H}\cdots\pi$  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

$\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2\text{S}$   $V = 2624.07(18) \text{ \AA}^3$   
 $M_r = 508.66$   $Z = 4$   
Monoclinic,  $P2_1/c$  Mo  $K\alpha$  radiation  
 $a = 9.0445(4) \text{ \AA}$   $\mu = 0.16 \text{ mm}^{-1}$   
 $b = 10.6014(4) \text{ \AA}$   $T = 100 \text{ K}$   
 $c = 27.533(1) \text{ \AA}$   $0.38 \times 0.20 \times 0.17 \text{ mm}$   
 $\beta = 96.294(3)^\circ$

#### Data collection

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

#### Refinement

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

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}25-\text{H}25\text{A}\cdots\text{O}2$	0.97	2.56	3.182 (3)	122
$\text{C}28-\text{H}28\cdots\text{O}2^i$	0.93	2.49	3.282 (4)	143
$\text{N}2-\text{H}1\text{N}2\cdots\text{C}g3$	0.87 (3)	2.69 (3)	3.461 (3)	148 (2)
$\text{C}3-\text{H}3\cdots\text{C}g3^i$	0.98	2.93	3.852 (3)	158
$\text{C}18-\text{H}18\text{B}\cdots\text{C}g2^{ii}$	0.96	2.90	3.723 (4)	145
$\text{C}21-\text{H}21\cdots\text{C}g1^{iii}$	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)  $-x + 2, -y, -z$ .  $\text{C}g1$ ,  $\text{C}g2$  and  $\text{C}g3$  are the centroids of the  $\text{C}4-\text{C}9$ ,  $\text{C}12-\text{C}17$  and  $\text{C}26-\text{C}31$  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.

<sup>‡</sup> Working at: Department of Physics, R.M.K Engineering College, R.S.M. Nagar, Kavaraipettai 601 206, Tamil Nadu, India.  
<sup>§</sup> Additional correspondence author, e-mail: hkfun@usm.my.

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

## References

- Barraja, P., Diana, P., Lauria, A., Montalbano, A., Almerico, A. M., Dattolo, G., Cirrincione, G., Viola, G. & Dall'Acqua, F. (2003). *Bioorg. Med. Chem. Lett.* **13**, 2809–2811.
- Bruker (2005). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Duax, W. L., Weeks, C. M. & Rohrer, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel & N. L. Allinger, pp. 271–383. New York: John Wiley.
- Ferlin, M. G., Marzano, C., Dalla Via, L., Chilin, A., Zagotto, G., Guiotto, A. & Moro, S. (2005). *Bioorg. Med. Chem.* **13**, 4733–4739.
- Gasparotto, V., Castagliuolo, I. & Ferlin, M. G. (2007). *J. Med. Chem.* **50**, 5509–5513.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Sudha, D., Chinnakali, K., Jayagobi, M., Raghunathan, R. & Fun, H.-K. (2009). *Acta Cryst.* **E65**, o2923.

**supplementary materials**

*Acta Cryst.* (2009). E65, o2924-o2925 [ doi:10.1107/S1600536809044481 ]

### 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 H.-K. Fun

#### 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  $\phi$  (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  $Q$ ,  $\theta$ ,  $\phi$  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 $\cdots$ O hydrogen bonds and N—H $\cdots$  $\pi$  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 $\cdots$ O hydrogen bonds and C—H $\cdots$  $\pi$  interactions involving the C26—C31 ring (Table 1). Adjacent inversion-related chains interact *via* C—H $\cdots$  $\pi$  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 $\cdots$  $\pi$  interactions. But the presence of the methyl group resulted in a two-dimensional network parallel to the *bc* plane, as discussed above.

#### Experimental

InCl<sub>3</sub> (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 Na<sub>2</sub>SO<sub>4</sub>. 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.

## 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  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ . A rotating group model was used for methyl groups. Reflection 002 was partially obscured by the beam stop and was omitted.

## Figures

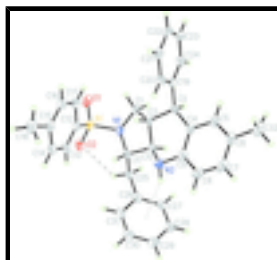


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a C—H...O hydrogen bond and the dotted line indicates an N—H... $\pi$  interaction.

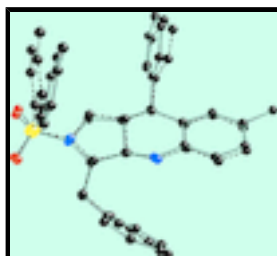


Fig. 2. Fit of the title molecule (solid lines) with (II) (dashed lines). H atoms have been omitted for clarity.

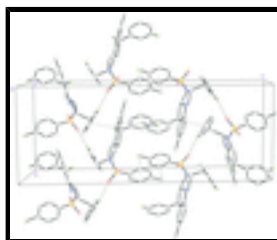


Fig. 3. Crystal packing of the title compound. C—H...O hydrogen bonds are shown as dashed lines and C—H... $\pi$  interactions are shown as dotted lines. For the sake of clarity, H atoms not involved in the interactions have been omitted.

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

### Crystal data

$\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_2\text{S}$

$M_r = 508.66$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.0445$  (4) Å

$b = 10.6014$  (4) Å

$c = 27.533$  (1) Å

$\beta = 96.294$  (3)°

$V = 2624.07$  (18) Å<sup>3</sup>

$F_{000} = 1080$

$D_x = 1.288$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 5605 reflections

$\theta = 2.3$ – $30.1$ °

$\mu = 0.16$  mm<sup>-1</sup>

$T = 100$  K

Block, colourless

$0.38 \times 0.20 \times 0.17$  mm

$Z = 4$

*Data collection*

Bruker SMART APEXII CCD area-detector diffractometer	5138 independent reflections
Radiation source: fine-focus sealed tube	3615 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.078$
$T = 100$ K	$\theta_{\text{max}} = 26.0^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 2.6^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -10 \rightarrow 11$
$T_{\text{min}} = 0.360$ , $T_{\text{max}} = 0.974$	$k = -13 \rightarrow 12$
22823 measured reflections	$l = -33 \rightarrow 33$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.178$	$w = 1/[\sigma^2(F_o^2) + (0.1011P)^2 + 1.1335P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
5138 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
340 parameters	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.50 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
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)

## supplementary materials

---

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 ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)



## supplementary materials

---

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

## supplementary materials

---

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, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C1—H1A $\cdots$ O1	0.97	2.53	2.914 (4)	104
C13—H13 $\cdots$ O2	0.93	2.57	2.912 (3)	103
C25—H25A $\cdots$ O2	0.97	2.56	3.182 (3)	122
C28—H28 $\cdots$ O2 <sup>i</sup>	0.93	2.49	3.282 (4)	143
N2—H1N2 $\cdots$ Cg3	0.87 (3)	2.69 (3)	3.461 (3)	148 (2)
C3—H3 $\cdots$ Cg3 <sup>i</sup>	0.98	2.93	3.852 (3)	158
C18—H18B $\cdots$ Cg2 <sup>ii</sup>	0.96	2.90	3.723 (4)	145
C21—H21 $\cdots$ Cg1 <sup>iii</sup>	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)  $-x+2, -y, -z$ .

Fig. 1

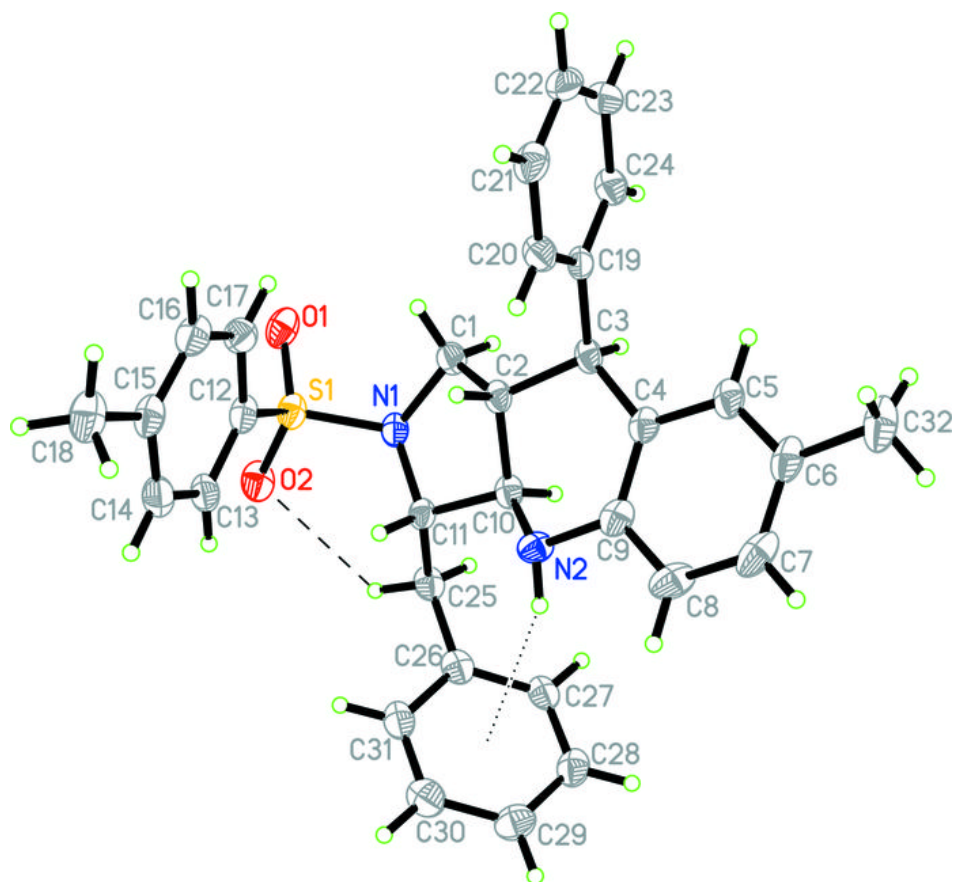


Fig. 2

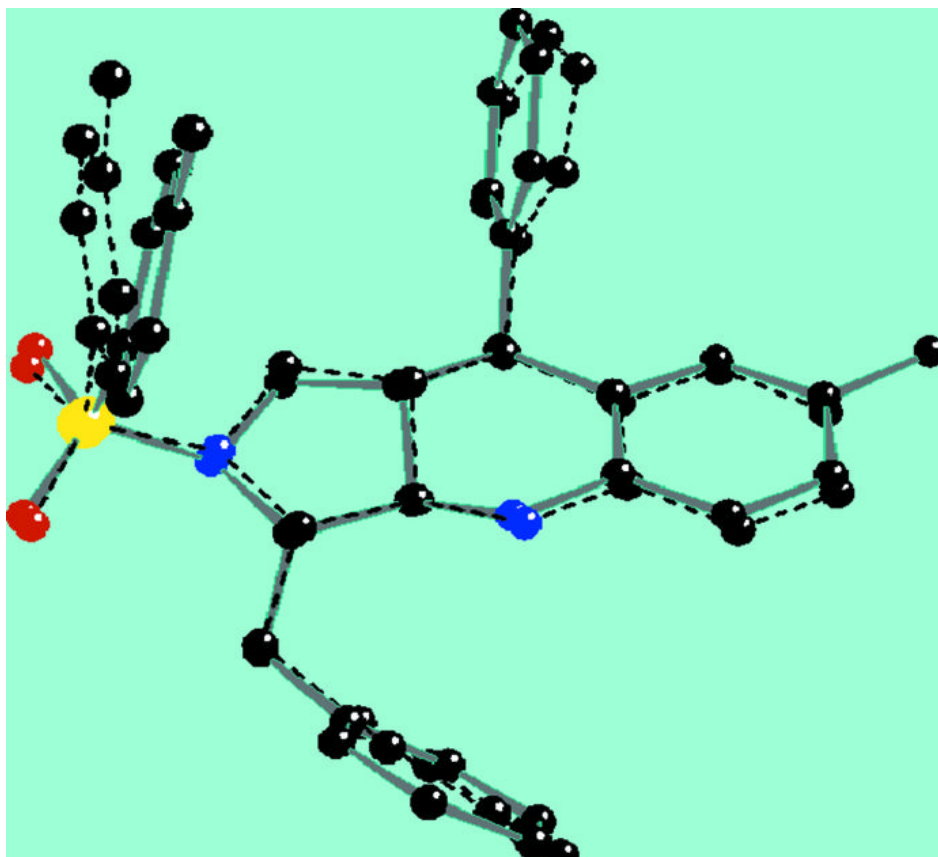


Fig. 3

