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3-(2,2′:6′,2″-Terpyridin-4′-yloxy)propyl toluene-4-sulfonate

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Key indicators

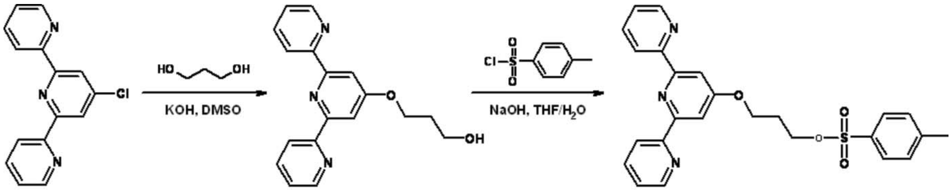
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.125
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{25}H_{23}N_3O_4S$, was synthesized by tosylation of 3-(2,2′;6′,2″-terpyridin-4′-yloxy)propan-1-ol. The dihedral angles formed by the substituent pyridine rings with the central ring are 4.27 (4) and 17.27 (5)°. The crystal packing is stabilized by intermolecular C—H···O hydrogen-bond interactions, with no stacking interaction between the aromatic rings.

Comment

The 2,2′;6′,2″-terpyridine ligand is a popular chelating ligand for the construction of supramolecular architectures (Hofmeier & Schubert, 2004) including metallodendrimers (Constable, 1997), metallosupramolecular polymers (Schubert & Eschbaumer, 2002) and macrocycles (Newkome *et al.*, 2006). The synthesis of functionalized 2,2′;6′,2″-terpyridines was recently reviewed by Fallahpour (2003) as well as Heller & Schubert (2003). 4′-Substituted 2,2′;6′,2″-terpyridines have received major attention due to their symmetry, which prevents the formation of enantiomers upon complexation. In addition, the outer rings flip upon complexation, which is easier without substituents on these rings.



(1) (2) (3)

The first reported 2,2′;6′,2″-terpyridine crystal structure was the unsubstituted compound (Bessel *et al.*, 1992). Recently, the structure of the 4′-chloro-2,2′;6′,2″-terpyridine precursor (1) that was used to synthesize the title compound (3) was reported (Beves *et al.*, 2006). In addition, several other crystal structures of 4′-*R*-alkoxy-2,2′;6′,2″-terpyridines were reported, including the aliphatic substituted compounds 4′-butoxy-, 4′-dodecyloxy- (both Andres *et al.*, 2003) and 4′-octadecyloxy-2,2′;6′,2″-terpyridine (Constable *et al.*, 2006). Crystal structures of terpyridines with functional substituents were also reported, such as 4′-(5-isocyanato-pentyloxy)-2,2′;6′,2″-terpyridine (Hoogenboom *et al.*, 2004) and 4′-(hex-5-ynyloxy)-2,2′;6′,2″-terpyridine (Constable *et al.*, 2005). The crystal packing of these compounds revealed interactions between the functional group and the π-electron system of the terpyridines. Moreover, crystal structures for 4′-[2-(2-hydroxyethoxy)ethoxy]-2,2′;6′,2″-terpyridine (Chow *et al.*, 2006*a*), 4′-(norborn-2-ene-5-ylmethyleneoxy)-2,2′;6′,2″-ter-

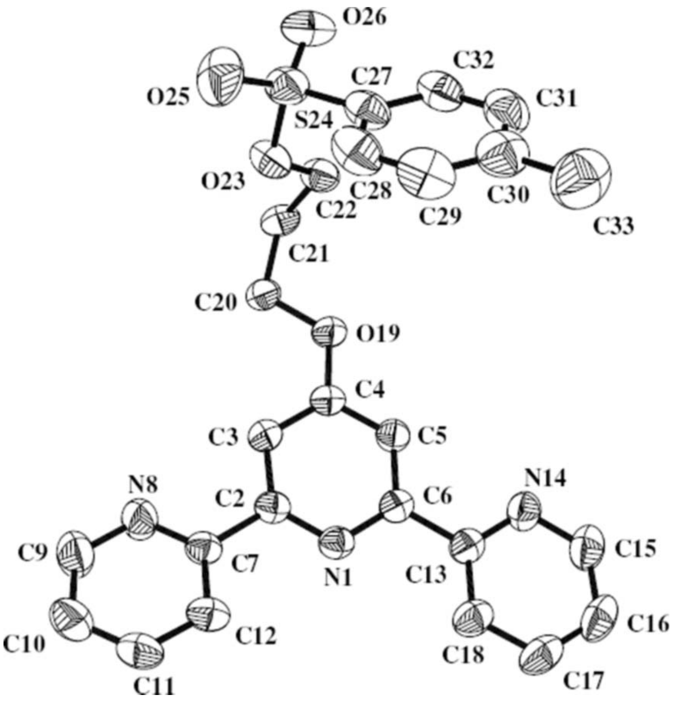


Figure 1
The structure structure of title compound, with displacement ellipsoids shown at the 50% probability level. For clarity, H atoms have been omitted.

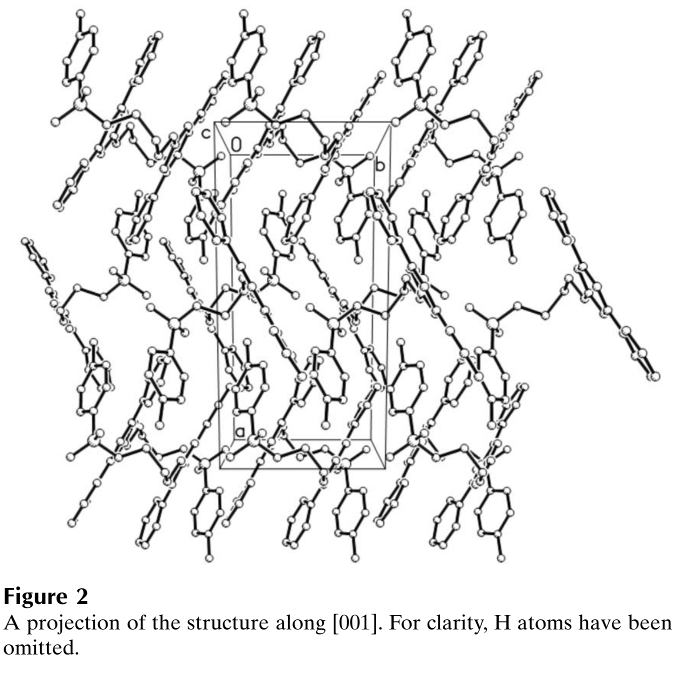


Figure 2
A projection of the structure along [001]. For clarity, H atoms have been omitted.

pyridine (Kröll *et al.*, 2001), 4′-(3,5-bisbenzyloxybenzyloxy)-2,2′;6′,2″-terpyridine (Constable *et al.*, 2004), 4′-(3-*o*-carboranylpropyloxy)-2,2′;6′,2″-terpyridine (Armsprach, *et al.*, 1998) and a series of chiral 4′-*R*-alkoxy-2,2′;6′,2″-terpyridine ligands [*R* is (1*S*) or (1*R*)-*endo*-bornyloxyquininylepiquininyl and camphorsulphonate; Constable *et al.*, 1997] were reported. Furthermore, one crystal structure of a bisterpyridine connected *via* an alkoxy spacer was reported, namely 2,7-[bis(2,2′;6′,2″-terpyridin-4′-yl)-1,4,7-trioxaheptyl]naphthalene (Chow *et al.*, 2006*b*). Here we report the crystal structure of the title compound (3).

The three pyridine rings in the molecule are nearly coplanar with each other. The planes through the central ring (N1/C2–C6) and one of the two substituent rings (C13/N14/C15–C18) are nearly coplanar and deviate only by an angle of 4.27 (4)°, while the angle between the plane through the central ring and the second substituent ring (C7/N8/C9–C12) is much larger [17.27 (5)°]. The reason for this distortion is most likely packing effects. The alkyl chain attached to the terpyridine structure is not extended in an all *trans* manner, but the terminal toluene-4-sulfonic acid group shows a *cis* conformation, possibly as a result of the presence of intramolecular C—H···O hydrogen interactions (Table 1). The crystal packing is stabilized by intermolecular C—H···O hydrogen bonds (Table 1), without any π-stacking interaction between the aromatic rings.

Experimental

The title compound (3) was synthesized by reaction of 4′-chloro-2,2′:6′,2″-terpyridine (1) with propanediol resulting in 3-(2,2′;6′,2″-terpyridin-4′-yloxy)propan-1-ol (2) as reported previously (Sampath *et al.*, 1999). Subsequent tosylation was performed by reacting (2) (0.959 g; 3.1 mmol) with *p*-toluenesulfonic acid chloride (tosyl chloride; 0.606 g; 3.2 mmol) in the presence of NaOH (0.187 g; 4.7 mmol). To a solution of the tosyl chloride in tetrahydrofuran (7 ml) was added dropwise a solution of (2) and NaOH in a mixture of tetrahydrofuran (12 ml) and water (7 ml). After complete addition of the tosyl chloride, the reaction was heated overnight to 333 K. Subsequently, one drop of ethanolamine was added to react with the small excess of tosyl chloride followed by the addition of water (50 ml) and chloroform (50 ml). The organic layer was separated, washed with water (3 × 50 ml) and dried with sodium sulfate. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography [aluminium oxide with ethyl acetate: hexane (1:1) as eluant]. Slow evaporation of an ethyl acetate solution of the purified compound (3) yielded single crystals suitable for X-ray analysis (0.149 g, 10.3%).

Crystal data

$C_{25}H_{23}N_3O_4S$
$M_r = 461.52$
Monoclinic, $P2_1/n$
$a = 16.7370\ (16)$ Å
$b = 7.8191\ (8)$ Å
$c = 18.3486\ (18)$ Å
$\beta = 109.217\ (2)^\circ$
$V = 2267.4\ (4)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 295\ (2)$ K
0.78 × 0.66 × 0.33 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.872$, $T_{\max} = 0.943$
28480 measured reflections
5692 independent reflections
4697 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.125$
$S = 1.04$
5692 reflections
299 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22*B*···O26	0.97	2.43	2.866 (2)	107
C32—H32···O26	0.93	2.59	2.937 (2)	103
C10—H10···O26^{i}	0.93	2.57	3.272 (3)	133
C21—H21*A*···O25^{ii}	0.97	2.41	3.375 (2)	172

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

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) values of 1.2 or 1.5 times $U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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