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# Redetermination of 8-tosyloxyquinoline at 100 K: supramolecular aggregation through weak C–H···O and C–H···N interactions

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**Key indicators**

Single-crystal X-ray study
*T* = 100 K
Mean σ(C–C) = 0.003 Å
*R* factor = 0.049
*wR* factor = 0.128
Data-to-parameter ratio = 12.6

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



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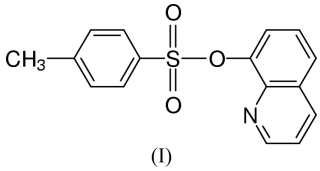
The crystal structure of the title compound, $C_{16}H_{13}NO_3S$, is stabilized by weak C—H···O and C—H···N interactions. The crystal structure has three pairs of bifurcated donor hydrogen bonds and two pairs of bifurcated acceptor hydrogen bonds. Both the O atoms of the sulfonyl group form a fork-like intermolecular hydrogen-bonding motif with the CH groups of the quinoline ring. The sulfonyl O atoms also form a three-center symmetrical hydrogen-bonded chelate motif with the H atom of the neighboring quinoline ring. One of the sulfonyl O atoms and the O atom of the quinoline moiety form weak C—H···O bonds with the H atoms of the neighboring 4-tolyl ring to generate another ring motif. The quinoline N atom forms an almost linear C—H···N bond with the H atom of the neighboring 4-tolyl ring. The supramolecular aggregation is completed by several other C—H···O and C—H···N interactions. The dihedral angle between the mean planes of the 4-tolyl and the quinoline rings is 47.53 (6)°.

## Comment

*p*-Toluenesulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989), studying membrane fusion during acrosome reaction (Spungin *et al.*, 1992), development of immunoaffinity chromatography for the purification of human coagulation factor (Tharakan *et al.*, 1992), chemical studies on viruses (Alford *et al.*, 1991), development of technology for linking photosensitizers to model monoclonal antibodies (Jiang *et al.*, 1990) and chemical modification of σ sub-units of the *E. coli* RNA polymerase (Narayanan & Krakow, 1983). Derivatives of 8-hydroxyquinoline are known for their *anti*-amoebic, antibacterial and antifungal activities (Balasubramanian & Muthiah, 1996). The present crystal structure determination may serve as a forerunner for assessing the biological activity of the title compound, (I). The crystal structure of (I) has already been reported at 298 K (Lee *et al.*, 2001), and no significant intermolecular interactions were found. In order to check this result, the present investigation was undertaken at 100 K. A search of the July 2002 release of the Cambridge Structural Database (Allen, 2002) revealed 16 structures (with the following refcodes: KAWDAN, FIXCAQ, NEDXUP, NEDYAW, NEDYIE, NUNCII, RASSOT, RELVUZ, SIMVUF, TCPTOS, TEBFOV, TMPDTS, TSMIPH, WOHCUR, ZZZBDA10 and MIWHIJ) that are closely related to the title compound. The S—C, S—O and S═O bond lengths (Table 1) are comparable to those found in these structures. The bond lengths and angles within the quinoline moiety are comparable to those values observed in 8-hydroxyquinoline (Banerjee & Saha, 1986). The dihedral angle between the mean planes of the quinoline and the 4-tolyl rings is 47.53 (6)°, confirming their non-coplanar orien-

tation. This is similar to the non-coplanar orientation of the 2-chlorophenyl and 4-tolyl rings in 2-chlorophenyl 4-toluenesulfonate (Vembu *et al.*, 2003*b*) and in contrast to the near-coplanar orientation of the 4-tolyl and 2,4-dinitrophenyl rings in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu *et al.*, 2003*a*).




(I)

The crystal structure of (I) is stabilized by weak C—H···O and C—H···N interactions. The range of H···O distances (Table 2) found in (I) agrees with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). The existence of bifurcated hydrogen bonds in the crystal structures of molecular complexes and derivatives of 8-hydroxyquinoline has been pointed out (Prout & Wheeler, 1967; Castellano & Prout, 1971; Polyakova *et al.*, 1980). The present crystal structure has five pairs of bifurcated hydrogen bonds, consisting of three pairs of donor and two pairs of acceptor bonds. The C16—H16···O2/C15—H15···O2 and C10—H10···O1/C11—H11···O1 interactions constitute two pairs of bifurcated acceptor bonds. There are two types of bifurcated donor

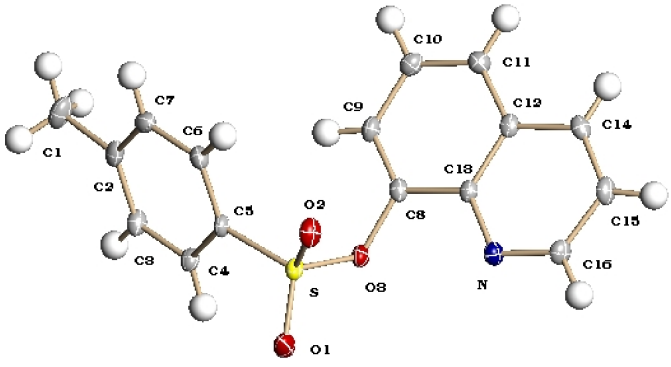



**Figure 1**
The molecular structure of the title compound, showing ellipsoids at the 50% probablity level.

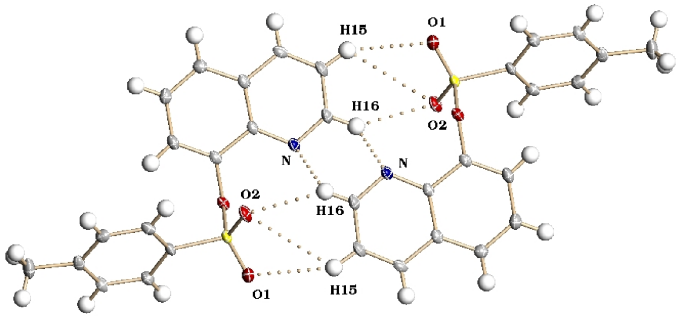



**Figure 2**
Diagram showing hydrogen bonds 1–4 in the title compound (the numbering relates to the sequence of entries in Table 2).

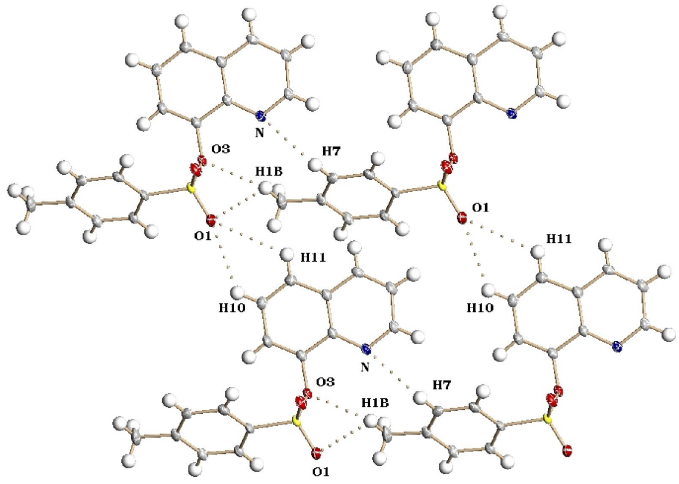



**Figure 3**
Diagram showing hydrogen bonds 5–7, 9 and 10 in the title compound (the numbering relates to the sequence of entries in Table 2).

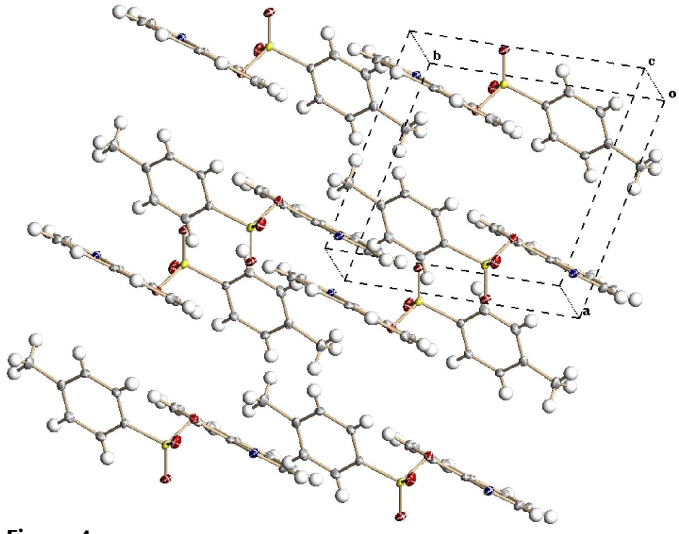



**Figure 4**
The packing, viewed along the *c* axis.

bonds. The C1—H1*B*···O3/C1—H1*B*···O1 and C15—H15···O1/C15—H15···O2 interactions constitute two pairs of bifurcated homo bonds with oxygen acceptor atoms. The C16—H16···O2/C16—H16···N interactions form a pair of bifurcated hetero bonds. Atoms O1 and O2 of the sulfonyl group act as acceptors to form a fork-like (Vembu *et al.*, 2003*a*) intermolecular weak hydrogen bond (Fig. 2), with atoms H15 and H16, with the graph-set motif $R_2^2(7)$ (Etter, 1990; Bernstein *et al.*, 1995). Atoms O1 and O2 of the sulfonyl group act as acceptors, forming weak hydrogen bonds with H15 of a neighboring quinoline moiety (Fig. 2). The H15···O1 and H15···O2 distances differ by only 0.10 Å. The resulting configuration is best regarded as a three-center symmetrical hydrogen-bonded chelate (Desiraju, 1989) with the graph-set motif $R_1^2(4)$, and is also observed in 2-chlorophenyl 4-toluenesulfonate (Vembu *et al.*, 2003*b*). The C15—H15···O2 and C16—H16···O2 interactions (Fig. 2) together form a ring with the graph-set motif $R_2^1(5)$. The $R_1^2(4)$ chelate motif and

the $R_2^1(5)$ motif are present within the $R_2^2(7)$ fork motif (Fig. 2). The quinoline N atom forms a weak C—H···N interaction with H16. The C16—H16···O2 and C16—H16···N interactions together form a ring (Fig. 2) with the graph-set motif $R_1^2(7)$. A pair of fork-like C16—H16···N interactions generate a six-membered ring with the graph-set motif $R_2^2(6)$, which links two $R_2^2(7)$ fork motifs and two $R_1^2(7)$ ring motifs together (Fig. 2), to generate a supramolecular network. Atoms O1, H15, O2, H16 and N form a hydrogen-bonded chain with the graph-set motif $C_2^3(5)$. Two such symmetry-related chains are linked through an $R_2^2(6)$ ring motif. Sulfonyl atom O1 acts as an acceptor to form weak C—H···O bonds with H10 and H11 of a neighboring quinoline moiety, generating a ring of the graph-set motif $R_2^1(5)$ (Fig. 3). Atoms O3 and O1 act as acceptors to form weak hydrogen bonds with H1*B* of a neighboring 4-tolyl ring, generating a ring motif with the graph-set notation $R_1^2(4)$ (Fig. 3). The quinoline N atom forms an almost linear C—H···N bond with H7 of a neighboring 4-tolyl ring (Fig. 3). The C7—H7···N and C1—H1*B*···O3 interactions together generate a ring (Fig. 3) of graph-set motif $R_2^2(9)$. Sulfonyl atom O2 acts as an acceptor to form a weak hydrogen bond with C6 of a neighboring 4-tolyl ring (Table 2). The view of the packing along the *c* axis shows that the molecules are arranged in parallel layers (Fig. 4).

## Experimental

4-Toluenesulfonyl chloride (4.7 mmol), dissolved in acetone (4 ml), was added dropwise to 8-hydroxyquinoline (4 mmol) in aqueous NaOH (2.5 ml, 10%) with vigorous shaking. The precipitated 8-tosyloxyquinoline (1.8 mmol, yield: 45%) was filtered off and recrystallized from ethyl acetate.

*Crystal data*

$C_{16}H_{13}NO_3S$
$M_r$ = 299.33
Triclinic, $P\overline{1}$
$a$ = 8.984 (3) Å
$b$ = 9.248 (3) Å
$c$ = 9.330 (3) Å
$\alpha$ = 66.957 (4)°
$\beta$ = 79.762 (5)°
$\gamma$ = 73.983 (5)°
$V$ = 683.5 (4) Å$^3$
$Z$ = 2
$D_x$ = 1.454 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4490 reflections
$\theta$ = 2.4–28.3°
$\mu$ = 0.25 mm$^{-1}$
$T$ = 100 (2) K
Block, colorless
0.45 × 0.30 × 0.20 mm

*Data collection*

Bruker Apex CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.897, $T_{max}$ = 0.952
5712 measured reflections
3053 independent reflections
2776 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033
$\theta_{max}$ = 28.0°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -11 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.128
$S$ = 1.10
3053 reflections
242 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.4098P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.65 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.40 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S—O1 | 1.4224 (15) | O3—C8 | 1.410 (2) |
| S—O2 | 1.4255 (15) | N—C16 | 1.324 (2) |
| S—O3 | 1.6062 (14) | N—C13 | 1.367 (2) |
| S—C5 | 1.7564 (19) | C1—C2 | 1.502 (3) |
| | | | |
| O1—S—O2 | 120.79 (9) | O2—S—C5 | 109.50 (9) |
| O1—S—O3 | 103.43 (8) | O3—S—C5 | 102.67 (8) |
| O2—S—O3 | 108.94 (8) | C8—O3—S | 118.81 (11) |
| O1—S—C5 | 109.85 (8) | C16—N—C13 | 116.74 (16) |
| | | | |
| C5—S—O3—C8 | 83.57 (13) | | |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C16—H16···N$^{i}$ | 0.95 (2) | 3.00 (2) | 3.376 (3) | 105.4 (16) |
| C16—H16···O2$^{i}$ | 0.95 (2) | 2.46 (2) | 3.266 (3) | 142.2 (19) |
| C15—H15···O2$^{i}$ | 0.95 (2) | 3.09 (2) | 3.569 (3) | 112.6 (17) |
| C15—H15···O1$^{i}$ | 0.95 (2) | 2.99 (3) | 3.665 (2) | 129.4 (18) |
| C11—H11···O1$^{ii}$ | 0.95 (2) | 3.03 (2) | 3.634 (2) | 123.1 (16) |
| C10—H10···O1$^{ii}$ | 0.98 (2) | 2.85 (2) | 3.558 (3) | 130.1 (17) |
| C7—H7···N$^{iii}$ | 0.93 (2) | 2.66 (2) | 3.510 (3) | 151.6 (18) |
| C6—H6···O2$^{iv}$ | 0.98 (2) | 2.63 (2) | 3.435 (2) | 139.8 (18) |
| C1—H1*B*···O3$^{iii}$ | 0.95 (4) | 2.68 (4) | 3.586 (3) | 160 (3) |
| C1—H1*B*···O1$^{iii}$ | 0.95 (4) | 2.96 (4) | 3.591 (3) | 125 (3) |

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

All the H atoms were located in a difference Fourier map, and their positional coordinates and isotropic displacement parameters were refined. The C—H bond lengths are in the range 0.91 (3)–0.98 (2) Å and the H—C—H angles for the methyl group are in the range 104 (3)–110 (3)°.

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

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