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## Hydrogen-Bonding Patterns in Substituted Oxines. Redetermination of 8-Hydroxy-7-iodoquinoline-5-sulfonic Acid

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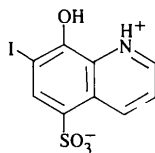
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### Abstract

For the title compound, C<sub>9</sub>H<sub>6</sub>INO<sub>4</sub>S, only a structure derived from photographic data is available in the literature, with  $R = 0.14$  [Merritt & Duffin (1970). *Acta Cryst.* **B26**, 734–744]. The structure has now been redetermined using diffractometer data. H atoms were located from Fourier maps. The sulfonic group is deprotonated, the proton having migrated to the quinoline N atom which forms intramolecular and intermolecular hydrogen bonds. The protonation of N1 causes an enhancement of the internal angle at N1 and asymmetry in the external angles at C8. The H atom of the hydroxy group is distal to the ring N atom.

### Comment

Derivatives of 8-hydroxyquinoline (oxine) are known for their anti-amoebic, antibacterial and antifungal activities, which are correlated to their metal-chelating ability (Banerjee & Saha, 1986). The structure of the title compound (I) was determined as part of our studies on substituted 8-hydroxyquinolines and their complexes (Balasubramanian & Thomas Muthiah, 1994*a,b*).



(I)

Fig. 1 shows an *ORTEP* (Johnson, 1965) diagram of the molecule with the atomic numbering scheme. Bond lengths and angles (Table 2) are in good agreement with those reported earlier for similar compounds. The sulfonic group is deprotonated, the proton having migrated to the quinoline N atom. The protonation of the ring N atom leads to an enhancement in the internal angle at N1. It also increases the difference between the external angles at C8; a comparison of these angles

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with those of other quinoline compounds is given in Table 3. This can be attributed to the N1—H···O8 intramolecular interaction. Similar short intramolecular contacts are reported for the structure of 8-hydroxyquinoline-5-sulfonic acid dihydrate (Banerjee, Basak & Mazumdar, 1984). In addition, N1—H forms an intermolecular hydrogen bond with one of the sulfonic O atoms. There is a weak C—H···O intramolecular interaction between C6—H and one of the O atoms of the sulfonic group. The hydroxy group also forms an intermolecular hydrogen bond with one of the O atoms of the sulfonic group. These interactions are summarized in Table 4.

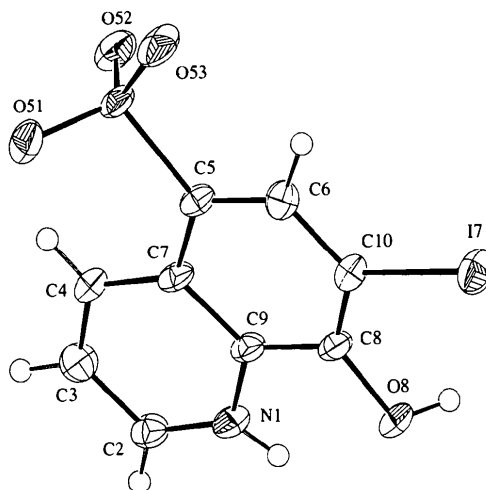


Fig. 1. An *ORTEP* (Johnson, 1965) view of the molecule with displacement ellipsoids at the 50% probability level.

A strong I···O [3.039 (4) Å] interaction exists between the I atom and one of the O atoms of the sulfonic group related by an *a* translation, which was also identified from the earlier photographic data (3.07 Å).

### Experimental

The title compound was recrystallized from water.

#### Crystal data

C<sub>9</sub>H<sub>6</sub>INO<sub>4</sub>S  
 $M_r = 351.11$   
 Monoclinic  
 $P2_1/c$   
 $a = 9.5704$  (9) Å  
 $b = 13.364$  (2) Å  
 $c = 8.748$  (2) Å  
 $\beta = 108.834$  (10)°  
 $V = 1059.0$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.202$  Mg m<sup>-3</sup>

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 15 reflections  
 $\theta = 8\text{--}13^\circ$   
 $\mu = 3.218$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Thin needle  
 0.35 × 0.15 × 0.125 mm  
 Yellow

**Data collection**

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.0262$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 22.98^\circ$
Absorption correction: none	$h = -10 \rightarrow 9$
1497 measured reflections	$k = 0 \rightarrow 14$
1401 independent reflections	$l = 0 \rightarrow 9$
1190 observed reflections [ $I > 2\sigma(I)$ ]	2 standard reflections
	frequency: 60 min
	intensity decay: negligible

**Refinement**

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = -0.096$
$R[F^2 > 2\sigma(F^2)] = 0.0298$	$\Delta\rho_{\text{max}} = 1.033 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.0689$	$\Delta\rho_{\text{min}} = -0.702 \text{ e } \text{\AA}^{-3}$
$S = 1.097$	Extinction correction: none
1401 reflections	Atomic scattering factors
163 parameters	from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
H-atom coordinates refined with $U = 0.05 \text{ \AA}^2$	
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.1978P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
N1	-0.2167 (5)	0.1204 (3)	-0.3415 (5)	0.0277 (11)
C2	-0.3625 (6)	0.1110 (4)	-0.4043 (7)	0.0275 (13)
C3	-0.4464 (6)	0.1012 (4)	-0.3039 (7)	0.0305 (13)
C4	-0.3805 (6)	0.1034 (4)	-0.1390 (7)	0.0261 (12)
C5	-0.1445 (6)	0.1196 (4)	0.0966 (6)	0.0224 (11)
S5	-0.23373 (15)	0.09869 (10)	0.2430 (2)	0.0260 (3)
O51	-0.3552 (4)	0.1675 (3)	0.2107 (5)	0.0357 (9)
O52	-0.2834 (4)	-0.0049 (3)	0.2205 (5)	0.0370 (9)
O53	-0.1204 (5)	0.1160 (3)	0.3964 (4)	0.0433 (11)
C6	0.0052 (6)	0.1334 (4)	0.1469 (7)	0.0270 (12)
I7	0.31040 (4)	0.16897 (3)	0.12018 (4)	0.0340 (2)
C7	-0.2260 (6)	0.1167 (4)	-0.0717 (6)	0.0230 (11)
O8	0.0737 (4)	0.1433 (3)	-0.2450 (5)	0.0324 (9)
C9	-0.1430 (6)	0.1245 (4)	-0.1795 (6)	0.0222 (11)
C8	0.0105 (6)	0.1359 (4)	-0.1279 (6)	0.0229 (12)
C10	0.0839 (6)	0.1432 (4)	0.0370 (6)	0.0234 (11)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S5—C5	1.776 (5)	S5—O52	1.456 (4)
S5—O51	1.437 (4)	I7—C10	2.080 (5)
S5—O53	1.446 (4)	O8—C8	1.351 (6)
C2—N1—C9	123.6 (5)	O51—S5—C5	107.7 (2)
C6—C5—C7	120.1 (5)	O53—S5—C5	104.6 (2)
C6—C5—S5	119.1 (4)	O52—S5—C5	105.3 (2)
C7—C5—S5	120.7 (4)	O8—C8—C10	125.6 (5)
O51—S5—O53	113.4 (3)	O8—C8—C9	116.3 (5)
O51—S5—O52	111.9 (2)	C8—C10—I7	119.7 (4)
O53—S5—O52	113.1 (3)		

Table 3. Comparison of the angle at N1 and the difference in external angle at C8 of  $\text{C}_9\text{H}_6\text{INO}_4\text{S}$  with derivatives of 8-hydroxyquinoline

	Angle at N1	Difference in external angles at C8
N1 protonated		
Bis-8HQ chloride	122.4	10.1
Bis-8HQ tetrachloride ferrate(III)*	123.6	8.9

8-HQ-5-sulfonic acid dihydrate†	122.7	11.0
This work	123.6	9.3
N1 unprotonated		
8-HQ‡	117.9	2.0
5-Chloro-8-HQ‡	117.5	1.9

\* Gerald *et al.* (1984). † Banerjee, Basak & Mazumdar (1984). ‡ Banerjee & Saha (1986).

Table 4. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O8	0.83 (8)	2.22 (6)	2.649 (6)	112 (6)
C6—H6 $\cdots$ O53	1.03 (7)	2.44 (8)	2.821 (8)	102 (5)
N1—H1 $\cdots$ O53 <sup>i</sup>	0.83 (8)	2.00 (8)	2.737 (7)	153 (7)
O8—H8 $\cdots$ O52 <sup>ii</sup>	0.83 (7)	1.86 (7)	2.681 (6)	170 (7)

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

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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