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8-Hydroxyquinoline-*O*-sulfuric Acid and its Monohydrate

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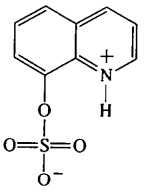
Abstract

8-Hydroxyquinoline-*O*-sulfuric acid exists as a zwitterion in both its anhydrous, $C_9H_7NO_4S$, and monohydrated, $C_9H_7NO_4S.H_2O$, forms. In each case, one of the terminal O atoms of the sulfate group is *trans* to the C8 atom. The structures are stabilized by intermolecular hydrogen bonds.

Comment

It has long been known that many sulfate esters are present in plants and animals (Soda & Hattori, 1931; Soda & Egami, 1943; Mumma & Verlangieri, 1972), and that these esters play an important role in biological processes (Jeffrey & Martin, 1966; Moser, Moser & Orr, 1966; Mumma, 1968; Benesch, Edalji & Benesch, 1976). 8-Hydroxyquinoline-*O*-sulfuric acid is reported to be a good sulfating agent in the synthesis of biologically important compounds, such as D-galactose-*O*-sulfate, adenosine-5′-*O*-sulfate, *etc.* (Nagasawa & Yoshidome, 1974). Kinetic studies of the hydrolysis of 8-hydroxyquinoline-*O*-sulfates catalysed by some divalent and trivalent metal ions have been reported (Hay & Edmonds, 1967; Nagasawa & Yoshidome, 1974).



(I)
(II) = (I).H_2O

8-Hydroxyquinoline-*O*-sulfuric acid, (I), crystallizes as a zwitterion with a protonated N atom and a deprotonated sulfate group (Fig. 1). The deviations of the O1 and S atoms from the quinoline mean plane are 0.012 (3) and 1.167 (4) Å, respectively. The dihedral angle between the quinoline plane and the S, O1, C8 plane is 52.5 (2)°. The S—O1 ester bond length is 1.653 (2) Å, while the non-ester S—O bond lengths range from 1.422 (3) to 1.437 (2) Å (Table 1). The ester O—S—O angles are much narrower than the other O—S—O angles (*cf.* Allen *et al.*, 1991). The O1—C8—C7 angle is significantly wider than the O1—C8—C9 angle [125.0 (3) *versus* 115.8 (3)°]. This may be a result of the intramolecular hydrogen-bond-type interaction between the O1 and N atoms.

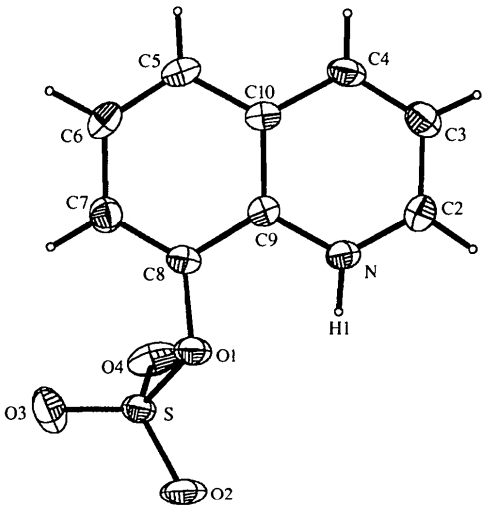


Fig. 1. The molecular structure and numbering scheme of 8-hydroxyquinoline-*O*-sulfuric acid, (I). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

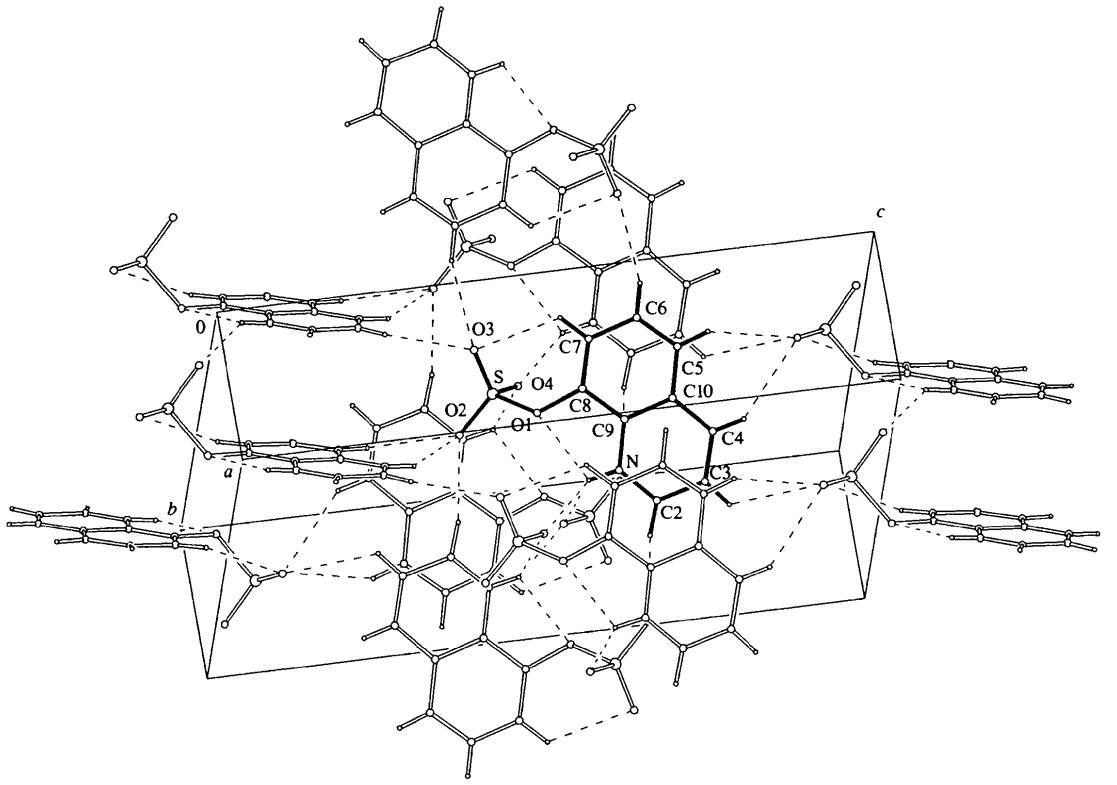


Fig. 2. The packing in (I).

In (I), the symmetry-related quinoline rings overlap slightly and participate in π–π interactions with short distances; N···C7^{i} and C7···N^{ii} 3.352 (4), and C3···C5^{i} and C5···C3^{ii} 3.368 (5) Å [symmetry codes: (i) $1+x$, y, z; (ii) $x-1$, y, z]. In addition, there are N—H···O inter- and intramolecular hydrogen bonds in (I) and weak C—H···O interactions (Table 2 and Fig. 2). The distances between the planes of the quinoline rings are slightly less than the van der Waals separation (3.4 Å) for aromatic rings, but it is difficult to say whether the N—H···O and C—H···O interactions between two overlapping molecules are important or a consequence of the π–π interactions. However, the interactions in which the sulfate O atoms are acceptors of hydrogen bonds from neighbouring molecules are clearly the cause of the bending of the sulfate group from the quinoline plane. The proposed hydrogen bonds are summarized in Table 2.

Crystals of 8-hydroxyquinoline-*O*-sulfuric acid monohydrate, (II), consist of zwitterionic 8-hydroxyquinoline-*O*-sulfuric acid (Fig. 3) and water molecules in a 1:1 ratio. In (II), the S, O1, C8 plane is almost perpendicular to the plane of quinoline rings [84.1 (2)°]. The S and O1 atoms are located on opposite sides of the quinoline plane, deviating from it by 1.300 (2) and 0.101 (2) Å, respectively. The S—O1 ester bond length is 1.647 (2) Å and the non-ester S—O bond lengths [1.424 (2), 1.424 (2) and 1.428 (2) Å] are equal within 3σ. As in (I), the values of the ester O—S—O angles are narrower than the other O—S—O angles.

The molecules of 8-hydroxyquinoline-*O*-sulfuric acid in (II) form columns along the *a* axis. The quino-

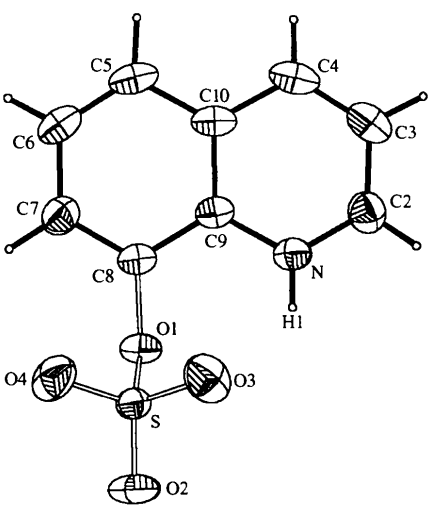


Fig. 3. The molecular structure and numbering scheme of 8-hydroxyquinoline-*O*-sulfuric acid in the crystal of (II). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

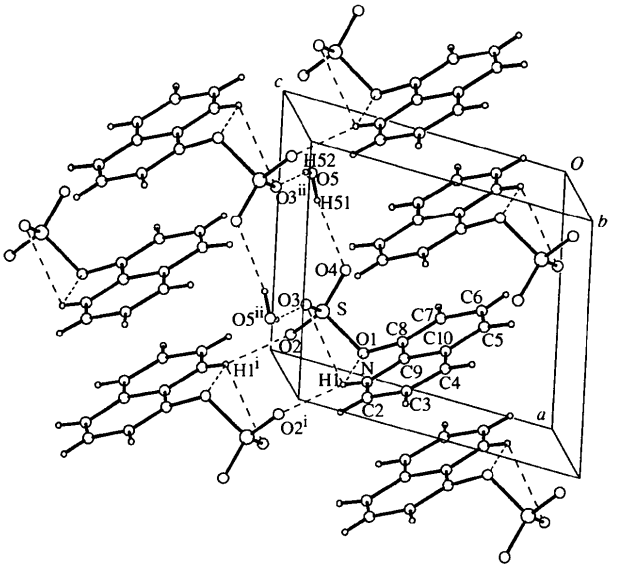


Fig. 4. The packing in (II). For clarity, the C—H···O contacts have been omitted. Symmetry codes are as in Table 4.

line rings within the columns partially overlap, forming pairs where the shortest C—C distances are for C2···C7^{viii} and C7···C2^{viii} [3.465 (3) Å; symmetry code: (viii) $2-x$, $1-y$, $1-z$] and for C9···C9^{viii} [3.449 (3) Å]. The shortest distances between quinoline rings from different pairs occur for C4···C7^{v} and C7···C4^{v} [3.522 (3) Å; symmetry code: (v) $1-x$, $1-y$, $1-z$], C5···C9^{v} [3.516 (3) Å], and C4···C6^{v} and C6···C4^{v} [3.541 (3) Å]. The interplanar separations are about 3.45 Å. The structure of (II) is stabilized by hydrogen bonds. Although most of the C—H···O bonds are very weak [the exception is C2—H2···O5^{iii}; symmetry code: (iii) $1+x$, $1+y$, z] (Table 4) and seem to be the result of stronger interactions, they may have an important role in stabilizing the packing in the crystal.

Although the plane through C8, O1 and S is twisted with respect to the quinoline plane in both (I) and (II), the differences in the interplanar angles suggests conformational flexibility of the sulfate group around the ester C—O bond. A search of the Cambridge Structural Database (Allen *et al.*, 1991) showed that the deformation of the sulfate groups from ideal tetrahedral geometry is similar to that seen in other sulfate mono-esters. The ester bonds in (I) and (II) are among the longest ester linkages known in ester sulfates. This is especially interesting in view of the ability of 8-hydroxyquinoline-*O*-sulfuric acid to donate its sulfate group effectively to other compounds; the longer ester S—O bond may be relatively easy to break. The ester C—O bonds are shorter than in most other sulfate mono-esters. This is not unexpected because the ester C—O bond involves an sp^2-hybridized C atom. The differences in the bond distances and angles in the quinoline rings of the present compounds may be compared with those found for 8-hydroxyquinoline (Banerjee & Saha, 1986).

Experimental

8-Hydroxyquinoline-*O*-sulfuric acid monohydrate, (II), was synthesized according to the literature method of Nagasawa & Yoshidome (1974) and recrystallization from water gave crystals of (II). Crystals of (I) were obtained by dissolving (II) in methanol, followed by slow evaporation of the solvent.

Compound (I)

Crystal data

$C_9H_7NO_4S$
$M_r = 225.22$
Monoclinic
$P2_1/c$
$a = 4.965\ (4)$ Å
$b = 9.728\ (5)$ Å
$c = 18.168\ (12)$ Å
$\beta = 94.38\ (8)°$
$V = 874.9\ (10)$ Å^3
$Z = 4$
$D_x = 1.710\ (3)$ Mg m^{-3}
$D_m = 1.68$ Mg m^{-3}
D_m measured by flotation in CCl_4/C_2H_5I

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–$14°$
$\mu = 0.361$ mm^{-1}
$T = 298\ (2)$ K
Acicular
0.40 × 0.15 × 0.10 mm
Pale yellow

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
2587 measured reflections
2279 independent reflections
1364 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 30°$
$h = -6 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = -25 \rightarrow 25$
3 standard reflections
every 100 reflections
intensity decay: 4.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.134$
$S = 1.021$
2279 reflections
164 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 0.43P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.10$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—O1	1.653 (2)	S—O4	1.437 (2)
S—O2	1.433 (2)	O1—C8	1.374 (3)
S—O3	1.422 (3)		
O1—S—O2	101.1 (2)	O3—S—O4	114.4 (2)
O1—S—O3	105.1 (2)	C8—O1—S	117.9 (2)
O1—S—O4	104.1 (2)	O1—C8—C7	125.0 (3)
O2—S—O3	115.1 (2)	O1—C8—C9	115.8 (3)
O2—S—O4	114.8 (2)		

O2—S—O1—C8	163.2 (2)	S—O1—C8—C7	53.7 (4)
O3—S—O1—C8	−76.8 (2)	S—O1—C8—C9	−128.4 (2)
O4—S—O1—C8	43.8 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1···O1	0.85 (4)	2.30 (4)	2.688 (4)	108 (3)
N—H1···O4^{i}	0.85 (4)	2.08 (4)	2.797 (4)	142 (4)
N—H1···O4^{ii}	0.85 (4)	2.45 (4)	2.896 (3)	114 (3)
C2—H2···O2^{iii}	0.94 (4)	2.34 (4)	3.263 (4)	168 (3)
C5—H5···O2^{iv}	0.93 (4)	2.49 (4)	3.311 (4)	148 (3)
C7—H7···O3	0.96 (4)	2.56 (4)	3.131 (4)	118 (3)
C3—H3···O3^{v}	0.91 (4)	2.60 (4)	3.212 (4)	125 (3)
C6—H6···O3^{vi}	0.94 (4)	2.49 (4)	3.390 (4)	160 (3)

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

Compound (II)

Crystal data

$C_9H_7NO_4S.H_2O$
$M_r = 243.23$
Triclinic
$P\bar{1}$
$a = 7.572$ (4) Å
$b = 8.475$ (4) Å
$c = 8.567$ (4) Å
$\alpha = 111.60$ (5)°
$\beta = 97.05$ (4)°
$\gamma = 99.53$ (4)°
$V = 493.9$ (4) Å^3
$Z = 2$
$D_x = 1.636$ (3) Mg m^{-3}
$D_m = 1.63$ Mg m^{-3}
D_m measured by flotation in CCl_4/C_2H_5I

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.333$ mm^{-1}
$T = 293$ (2) K
Acicular
0.6 × 0.4 × 0.2 mm
Pale yellow

Data collection

Kuma KM-4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
2873 measured reflections
2873 independent reflections
2206 reflections with $I > 2\sigma(I)$

$\theta_{max} = 31°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 11$
3 standard reflections
every 100 reflections
intensity variation: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.105$
$S = 1.032$
2873 reflections
181 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.15P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.086$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

S—O1	1.647 (2)	S—O4	1.428 (2)
S—O2	1.424 (2)	O1—C8	1.384 (2)
S—O3	1.424 (2)		
O1—S—O2	100.4 (1)	O3—S—O4	113.5 (2)
O1—S—O3	104.7 (1)	C8—O1—S	117.3 (1)
O1—S—O4	105.2 (1)	C7—C8—C9	119.8 (2)
O2—S—O3	116.2 (2)	O1—C8—C7	121.8 (2)
O2—S—O4	114.6 (1)	O1—C8—C9	118.3 (2)
O2—S—O1—C8	176.4 (2)	S—O1—C8—C7	−86.0 (2)
O3—S—O1—C8	−62.8 (2)	S—O1—C8—C9	97.8 (2)
O4—S—O1—C8	57.2 (2)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H1···O1	0.82 (3)	2.44 (3)	2.766 (2)	105 (2)
N—H1···O2^{i}	0.82 (3)	2.01 (3)	2.714 (2)	144 (3)
N—H1···O3	0.82 (3)	2.66 (3)	3.115 (2)	117 (3)
O5—H51···O4	0.77 (4)	2.14 (4)	2.897 (3)	169 (4)
O5—H52···O3^{ii}	0.73 (4)	2.20 (4)	2.908 (3)	163 (4)
C2—H2···O5^{iii}	0.92 (3)	2.37 (3)	3.078 (3)	133 (3)
C7—H7···O4^{iv}	0.95 (2)	2.52 (3)	3.217 (3)	131 (2)

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

Approximate unit-cell dimensions were determined by preliminary oscillation and Weissenberg photographs. H atoms were located from difference Fourier maps.

For both compounds, data collection: *Kuma KM-4 Software* (Kuma Diffraction, 1987); cell refinement: *Kuma KM-4 Software*; data reduction: *Kuma KM-4 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1154). Services for accessing these data are described at the back of the journal.

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