Structure of 8-Hydroxy-5-quinolinesulphonic Acid Dihydrate, C₉H₇NO₄S.2H₂O

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Abstract. $M_r = 261 \cdot 26$, monoclinic, $P2_1/n$, $a = 6 \cdot 699$ (2), $b = 16 \cdot 711$ (3), $c = 10 \cdot 203$ (1) Å, $\beta = 109 \cdot 22$ (1)°, $V = 1078 \cdot 6$ (7) Å³, $Z = 4$, $D_m = 1 \cdot 59$, $D_x = 1 \cdot 61$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å, $\mu = 0 \cdot 318$ mm⁻¹, $F(000) = 544$, $T = 297$ K, final $R = 0 \cdot 030$ using 1585 observed reflections. The structure is compared with other quinoline structures. Centrosymmetrically related molecules dimerize through water-bridged hydrogen bonds. These dimers themselves form water-bridged hydrogen-bonded chains extended along the a and c axes. These chains are held together through van der Waals forces.

Introduction. 8-Hydroxyquinoline is a well-known antifungal and antibacterial agent; its activity depends on its ability to chelate biochemically important metal ions (Bambury, 1979). 8-Hydroxy-5-quinolinesulphonic acid exists as a zwitterion in acidic solution (Nasanen & Ekman, 1952), the proton being transferred from the sulphonic acid group to the quinoline nitrogen. The X-ray structural study of this compound was undertaken as part of a programme to study the effects of protonation and the hydrogen-bonding patterns of derivatives of 8-hydroxyquinoline. It has been observed that in the crystal structures of 5-chloro-8-hydroxyquinoline hydrochloride and 8-hydroxyquinoline hydrochloride monohydrate (Banerjee, 1983) the Cl⁻ ions and the water molecules of crystallization play important roles through hydrogen bonding in the packing arrangements of these protonated molecules.

Experimental. Light-yellow plate-shaped crystals (from ethanol), density by flotation (benzene–bromoform), crystal size: $0 \cdot 20 \times 0 \cdot 20 \times 0 \cdot 35$ mm, symmetry from oscillation and Weissenberg photographs, $P2_1/n$ (absences: $0k0$, k odd and $h0l$, $h+l$ odd), Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, cell parameters from 25 reflections $14 \leq \theta \leq 20$°, 1970 unique reflections ($-7 \leq h \leq 7$, $0 \leq k \leq 19$, $0 \leq l \leq 19$, $2 \leq \theta \leq 25$°), 1585 with $I \geq 3\sigma(I)$, corrected for Lp, absorption ignored, intensity variation < 2%; direct methods (*MULTAN*; Main,

Hull, Lessinger, Germain, Declercq & Woolfson, 1978), anisotropic full-matrix refinement based on F (*ORFLS*; Busing, Martin & Levy, 1962), H (from ΔF synthesis) refined isotropically; $R = 0 \cdot 030$, $R_w = 0 \cdot 044$, $S = 1 \cdot 749$, $w = 1/\sigma^2(|F_o|)$; max. $\Delta/\sigma \leq 0 \cdot 04$, residual $\Delta\rho$ excursions $-0 \cdot 16$ to $0 \cdot 19$ e Å⁻³ in final ΔF synthesis; scattering factors for non-H from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections for non-H atoms from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the atomic labelling scheme. The final atomic coordinates together with their thermal parameters are listed in Table 1.* The molecular dimensions are listed in Table 2.

The bond-length distribution in the quinoline ring agrees with the theoretically calculated values (Dewar & Gleicher, 1966) and also with the values reported in the literature for similar compounds (Polyakova, Starikova, Trunov, Parusnikov &

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* Lists of structure factors, anisotropic thermal parameters and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39007 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
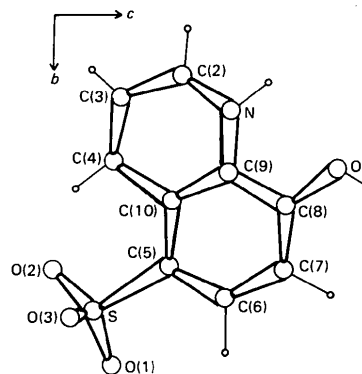

Fig. 1. Perspective view of the molecule down the a axis.

Krasavin, 1980; Hughes & Truter, 1979; Kashino & Haisa, 1973).

The molecule exists in the zwitterionic state with the sulphonic acid proton transferred to the quinoline nitrogen. This protonation has resulted in the enlargement of the C(2)—N—C(9) angle, an effect similar to that observed in protonated pyrimidines (Taylor & Kennard, 1982).

The atoms around sulphur are arranged in a somewhat distorted tetrahedral fashion. The O—S—O angles, in the range 112–113° (Table 2), are larger than the ideal tetrahedral value, while the C—S—O angles are smaller. Similar effects have been observed in other quinolinesulphonic acid structures (Boeyens, 1976; Merrit & Duffin, 1970). This type of distortion from ideal configuration has been attributed by Cotton & Stokley (1970) to non-bonded interactions involving the neighbouring oxygen atoms and has been observed in a number of sulphonamide structures (Kálmán, Czugler & Argay, 1981; Kruger & Gafner, 1971; Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976; Basak, Mazumdar & Chaudhuri, 1982, 1983). The slight increase in the S—O(3) bond length compared with the other two S—O bonds may be attributed to the additional hydrogen bonding in which it participates (Boeyens, 1976; Kruger & Gafner, 1971).

The benzene and pyridine rings of the quinoline moiety are nearly co-planar, the dihedral angle between them being 1·3 (3)°. The hydroxyl oxygen and the sulphur deviate slightly [by −0·024 (1) and 0·073 (1) Å, respectively] from the plane of the quinoline moiety, while all three oxygen atoms of the sulphonic acid group are completely out of the plane.

The molecular packing projected onto the ab plane is shown in Fig. 2. All the available hydrogen atoms participate in hydrogen bonding (Table 3), forming an extensive network. The proton attached to the quinoline nitrogen atom takes part in an intermolecular N–H···O hydrogen bond with a water oxygen. There is an additional intramolecular N—H···O contact with the hydroxyl oxygen leading to the formation of a five-membered ring as found in other protonated derivatives of 8-hydroxyquinoline (Banerjee, 1983).

The oxygen atom, $O_w(5)$, of a water molecule links two centrosymmetrically related quinoline molecules through $O_w(5)$—H···O(1) and N—H···$O_w(5)$ hydrogen bonds, forming a dimer. This water molecule is again hydrogen bonded to one of the oxygen atoms, O(3), of the sulphonic acid group of a third molecule. The second water molecule, which appears to be trapped in a relatively hydrophobic region, is also involved in the formation of three hydrogen bonds linking up three translation-related molecules through $O_w(4)$—H···O(3), $O_w(4)$—H···O(2) and O—H···$O_w(4)$ bonds, resulting in chains extended along the a and c directions. The molecules are held together in the b direction by van der Waals forces.

Table 1. *Fractional atomic coordinates and thermal parameters* (Å²) *with e.s.d.'s in parentheses*

Equivalent isotropic temperature factors B_{eq} (Hamilton, 1959) are given for non-hydrogen atoms and isotropic temperature factors B for hydrogen atoms.

	x	y	z	B_{eq}/B
S	0·5248 (1)	0·1353 (1)	0·1564 (1)	2·25
O	0·8637 (2)	−0·0058 (1)	0·7215 (1)	2·79
O(1)	0·4499 (2)	0·2139 (1)	0·1778 (1)	3·41
O(2)	0·3581 (2)	0·0827 (1)	0·0758 (1)	3·14
O(3)	0·7002 (2)	0·1390 (1)	0·1020 (1)	3·34
$O_w(4)$	0·4316 (2)	0·4021 (1)	0·4213 (1)	4·26
$O_w(5)$	0·0937 (2)	0·1985 (1)	0·2745 (1)	3·48
N	0·7836 (2)	−0·1013 (1)	0·5023 (1)	2·17
C(2)	0·7529 (3)	−0·1530 (1)	0·3999 (2)	2·72
C(3)	0·6807 (3)	−0·1272 (1)	0·2626 (2)	2·99
C(4)	0·6398 (3)	−0·0477 (1)	0·2347 (2)	2·45
C(5)	0·6295 (2)	0·0920 (1)	0·3251 (1)	1·97
C(6)	0·6708 (3)	0·1406 (1)	0·4392 (2)	2·29
C(7)	0·7513 (3)	0·1104 (1)	0·5754 (2)	2·36
C(8)	0·7882 (2)	0·0306 (1)	0·5975 (2)	2·06
C(9)	0·7475 (2)	−0·0208 (1)	0·4804 (2)	1·88
C(10)	0·6699 (2)	0·0084 (1)	0·3429 (2)	1·85
H(O)	0·878 (4)	0·033 (2)	0·788 (2)	5·3 (6)
H(N)	0·823 (3)	−0·124 (1)	0·594 (2)	3·5 (5)
H(O$_w$)1	0·355 (4)	0·395 (2)	0·473 (3)	5·6 (6)
H(O$_w$)2	0·539 (4)	0·412 (2)	0·475 (3)	6·8 (8)
H(O$_w$)1	−0·003 (4)	0·181 (2)	0·221 (3)	6·0 (6)
H(O$_w$)2	0·168 (4)	0·199 (2)	0·236 (3)	5·8 (6)
H(2)	0·786 (3)	−0·210 (1)	0·423 (2)	3·5 (5)
H(3)	0·670 (3)	−0·166 (1)	0·187 (2)	3·1 (5)
H(4)	0·587 (3)	−0·033 (1)	0·137 (2)	3·3 (5)
H(6)	0·647 (3)	0·194 (1)	0·429 (2)	2·8 (5)
H(7)	0·779 (3)	0·148 (1)	0·654 (2)	3·1 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

S—O(1)	1·448 (2)	C(8)—C(9)	1·423 (3)
S—O(2)	1·446 (2)	C(9)—C(10)	1·413 (3)
S—O(3)	1·457 (1)	C(9)—N	1·372 (2)
S—C(5)	1·784 (2)	N—C(2)	1·319 (2)
		C(2)—C(3)	1·391 (3)
C(5)—C(6)	1·371 (2)	C(3)—C(4)	1·367 (2)
C(6)—C(7)	1·408 (3)	C(4)—C(10)	1·411 (3)
C(7)—C(8)	1·361 (2)	C(10)—C(5)	1·423 (2)
C(8)—O	1·344 (2)		
O(1)—S—O(2)	113·3 (1)	O—C(8)—C(9)	115·2 (1)
O(1)—S—O(3)	112·4 (1)	C(8)—C(9)—N	118·7 (1)
O(1)—S—C(5)	105·5 (1)	C(9)—N—C(2)	122·7 (1)
O(2)—S—O(3)	112·2 (1)	N—C(2)—C(3)	120·4 (2)
O(2)—S—C(5)	106·7 (1)	C(2)—C(3)—C(4)	119·3 (2)
O(3)—S—C(5)	105·9 (1)	C(3)—C(4)—C(10)	121·0 (2)
S—C(5)—C(10)	121·3 (1)	C(4)—C(10)—C(5)	125·4 (1)
S—C(5)—C(6)	119·0 (1)	C(4)—C(10)—C(9)	117·3 (2)
C(5)—C(6)—C(7)	122·0 (2)	C(5)—C(10)—C(9)	117·3 (1)
C(6)—C(7)—C(8)	120·3 (2)	C(6)—C(5)—C(10)	119·8 (1)
C(7)—C(8)—C(9)	118·5 (2)	C(10)—C(9)—N	119·2 (1)
C(7)—C(8)—O	126·2 (2)	C(10)—C(9)—C(8)	122·1 (1)

Table 3. *Geometry of the hydrogen bonds*

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

A—H···B	A—H (Å)	A—B (Å)	H···B (Å)	A—H···B (°)
N—H(N)···$O_w(5^i)$	0·96 (2)	2·696 (2)	1·78 (2)	158 (2)
N—H(N)···O*	0·96 (2)	2·654 (2)	2·33 (2)	98 (1)
O—H(O)···$O_w(4^{ii})$	0·92 (3)	2·599 (2)	1·68 (3)	173 (3)
$O_w(4)$—H(O$_w$)2···O(2^{ii})	0·76 (3)	2·783 (2)	2·05 (3)	162 (3)
$O_w(4)$—H(O$_w$)1···O(3^{iii})	0·86 (3)	2·856 (2)	2·01 (3)	171 (3)
$O_w(5)$—H(O$_w$)2···O(1)	0·73 (3)	2·878 (2)	2·17 (3)	163 (3)
$O_w(5)$—H(O$_w$)1···O(3^{iv})	0·75 (3)	2·825 (2)	2·08 (3)	168 (3)

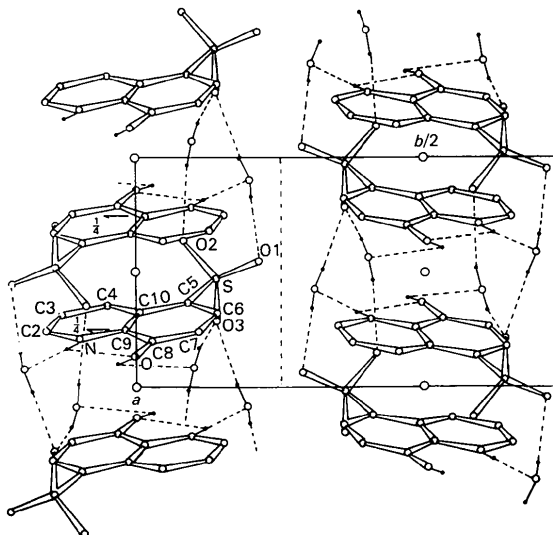* Short intramolecular contact.

Fig. 2. Projection of the crystal structure of 8-hydroxy-5-quinoline-sulphonic acid dihydrate on the *ab* plane.

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Structure of 1,4-Dicinnamoylbenzene, C24H18O2, a Photodimerizable Crystal

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Abstract. $M_r = 338\cdot4$, triclinic, $P\bar{1}$, $a = 5\cdot798$ (1), $b = 7\cdot923$ (1), $c = 19\cdot307$ (6) Å, $\alpha = 89\cdot12$ (2), $\beta = 82\cdot12$ (2), $\gamma = 88\cdot67$ (1)°, $V = 878\cdot2$ (4) Å^3, $Z = 2$, $D_m = 1\cdot28$, $D_x = 1\cdot280$ Mg m^{-3}, λ(Cu $K\alpha$) = $1\cdot5418$ Å, $\mu = 0\cdot55$ mm^{-1}, $F(000) = 356$, $T = 298$ K. Final $R = 0\cdot050$ for 2014 observed diffractometer-measured intensities. Two independent molecules, both of which have a center of symmetry, are stacked along the b axis with close contacts between double bonds. Pairs of reacting double bonds have no symmetry so that the distances between photo-adductive olefin C atoms are 3·973 (4), 4·086 (4), 3·903 (4) and 3·955 (4) Å.

Introduction. 1,4-Dicinnamoylbenzene (1,4-DCB) photodimerizes in the crystalline state to give a dimer containing two cyclobutane rings (Hasegawa, Nohara, Saigo, Mori & Nakanishi, 1983). The fact that the double photoaddition (named 'dupledimerization' by the authors) is such a rare solid-state photocyclization –