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Structure of 3-Amino-5-hydroxyquinoline-7-sulfonic Acid Monohydrate

BY PETER E. LAKS*

Faculty of Forestry, University of British Columbia, Vancouver, BC, Canada V6T 1W5

AND STEVEN J. RETTIG AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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Abstract. $C_9H_8N_2O_4S.H_2O$, $M_r = 258{\cdot}25$, monoclinic, $P2_1/c$, $a = 9{\cdot}912\ (1)$, $b = 14{\cdot}775\ (1)$, $c = 7{\cdot}093\ (1)$ Å, $\beta = 98{\cdot}585\ (5)°$, $V = 1027{\cdot}1\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}670\ (1)$ g cm^{-3}, Mo $K\alpha$, $\lambda\alpha_1 = 0{\cdot}70930$ Å, $\mu = 3{\cdot}1$ cm^{-1}, $F(000) = 536$, $T = 295$ K, $R = 0{\cdot}033$ for 1188 reflections. The molecule exists in the crystal as a zwitterion, with an approximately planar quinoline ring system and normal dimensions; molecules are linked by hydrogen bonds *via* the water molecule.

Introduction. Cleavage of western hemlock bark tannins by treatment with ammonium sulfite in concentrated ammonium hydroxide solution (Laks, 1984) yields products which may be useful as adhesives in the forest products industry. Chemical methods did not define the molecular structure of one of these products unambiguously, and the present X-ray study was designed to establish the structure.

Experimental. Golden plates elongated along **c**, dimensions 0·06 × 0·17 × 0·6 mm, faces {100}, {010}, {011}, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 17{\cdot}4$–$21{\cdot}4°$. Intensities for $\theta \le 27{\cdot}5°$, *hkl*: −12 to 12, 0 to 19, 0 to 9, ω–2θ scan, ω-scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$ at 0·9–10° min^{-1}, extended 25% on each side for background measurement, three standard reflections (no decay), Lp and absorption corrections, transmission factors 0·945–0·980. 2335 reflections measured, 1188 with $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04S)^2$, S = scan, B_1 and B_2 = background counts. Structure by Patterson and Fourier methods, refined by full-matrix least squares on F, H atoms from a difference map, refined with isotropic thermal parameters, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written programs, and locally modified versions of *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), and *FORDAP* (A. Zalkin, unpublished). Final $R = 0{\cdot}033$, $wR = 0{\cdot}041$ for 1188 reflections, $S = 1{\cdot}61$, 194 parameters, $R = 0{\cdot}110$ for all 2335 reflections, $\Delta/\sigma = 0{\cdot}009$ (mean), 0·095 (max.), max. final difference density −0·25 to +0·36 e Å^{-3}. Thermal parameters interpretable in terms of rigid-body motion, bond lengths corrected for libration.

Table 1. *Final positional (fractional* ×10^5, H ×10^4*) and isotropic thermal parameters* (U ×10^3 Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$ trace of diagonalized U tensor.

	x	y	z	U_{eq}/U_{iso}
S	19693 (7)	40753 (5)	37637 (12)	32
O(1)	13256 (21)	36781 (16)	52731 (33)	45
O(2)	11333 (22)	39777 (18)	19171 (32)	53
O(3)	24300 (22)	49930 (15)	41811 (35)	50
O(4)	44589 (24)	10249 (14)	36553 (34)	41
O(5)	19889 (26)	3150 (16)	36393 (45)	45
N(1)	69760 (25)	36553 (19)	27965 (39)	35
N(2)	91655 (30)	17460 (27)	23106 (47)	51
C(2)	80595 (31)	31757 (23)	25288 (45)	37
C(3)	80307 (28)	22357 (22)	25825 (40)	34
C(4)	68418 (29)	18231 (23)	29421 (44)	32
C(4a)	56980 (26)	23389 (19)	32100 (37)	27
C(5)	44487 (28)	19346 (19)	35530 (40)	30
C(6)	33596 (27)	24746 (20)	37606 (42)	30
C(7)	34605 (27)	34225 (20)	36331 (39)	28
C(8)	46397 (28)	38410 (22)	33472 (43)	31
C(8a)	57616 (27)	32890 (20)	31303 (39)	28
H(O4)	3733 (37)	836 (25)	3724 (51)	51 (12)
H(O5a)	1613 (49)	535 (38)	4785 (71)	115 (19)
H(O5b)	1577 (41)	620 (33)	2712 (57)	75 (16)
H(N1)	7053 (36)	4220 (28)	2894 (53)	60 (12)
H(N2a)	9865 (38)	2042 (27)	1770 (56)	70 (13)
H(N2b)	9042 (46)	1140 (37)	2401 (65)	97 (18)
H(2)	8889 (30)	3505 (21)	2309 (39)	37 (9)
H(4)	6748 (28)	1238 (24)	2834 (44)	37 (9)
H(6)	2574 (33)	2206 (23)	3882 (45)	43 (9)
H(8)	4671 (25)	4433 (21)	3248 (40)	23 (7)

Discussion. Atomic positional parameters are given in Table 1.† The molecule (Fig. 1) contains a quinoline ring system, with amino, hydroxy, and sulfonate substituents, and exists in the crystal in a zwitterionic form, with the acidic H atom bonded to the ring N

* Present address: Institute of Wood Research, Michigan Technological University, Houghton, Michigan 49931, USA.

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† Lists of anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43187 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

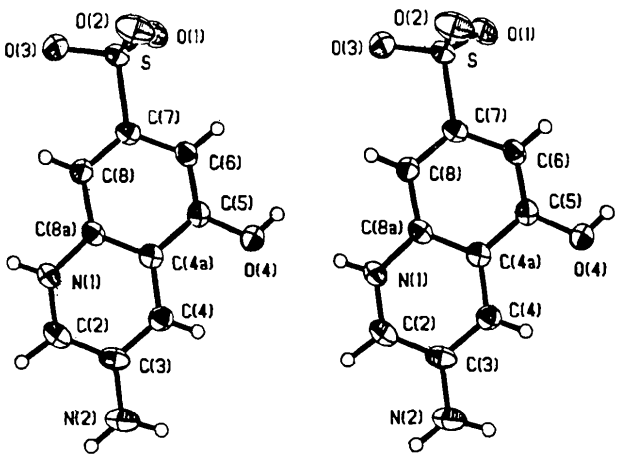

Fig. 1. Stereoview of the 3-amino-5-hydroxyquinoline-7-sulfonic acid molecule.

atom. The quinoline ring system is slightly folded, with an angle of 1·5° between the almost planar six-membered rings; the NH_2 group is slightly non-planar [N(2) is displaced by −0·083 (3) Å from the plane of the three bonded atoms, with this plane rotated 8·8° out of the attached ring plane], and S is 0·118 (1) Å from the plane of the six-membered ring to which it is bonded. Bond lengths and angles (Table 2) are generally close to those in related molecules, *e.g.* 8-hydroxy-2-methylquinoline-5-sulfonic acid monohydrate (Merritt & Duffin, 1970). The molecules are linked by a system of hydrogen bonds (Table 2) involving all the active H atoms.

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Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

	Uncorr.	Corr.		Uncorr.	Corr.
S–O(1)	1·450 (2)	1·461	C(3)–C(4)	1·384 (4)	1·387
S–O(2)	1·449 (2)	1·460	C(4)–C(4a)	1·402 (4)	1·405
S–O(3)	1·447 (2)	1·459	C(4a)–C(5)	1·428 (4)	1·431
S–C(7)	1·779 (3)	1·787	C(4a)–C(8a)	1·407 (4)	1·412
O(4)–C(5)	1·346 (4)	1·349	C(5)–C(6)	1·368 (4)	1·370
N(1)–C(2)	1·324 (4)	1·326	C(6)–C(7)	1·408 (4)	1·413
N(1)–C(8a)	1·372 (4)	1·375	C(7)–C(8)	1·364 (4)	1·367
N(2)–C(3)	1·375 (4)	1·377	C(8)–C(8a)	1·406 (4)	1·408
C(2)–C(3)	1·390 (5)	1·395			

O(1)–S–O(2)	111·84 (14)	C(4)–C(4a)–C(8a)	119·7 (3)
O(1)–S–O(3)	112·86 (14)	C(5)–C(4a)–C(8a)	118·0 (3)
O(1)–S–C(7)	106·24 (14)	O(4)–C(5)–C(4a)	115·3 (3)
O(2)–S–O(3)	113·49 (15)	O(4)–C(5)–C(6)	125·2 (3)
O(2)–S–C(7)	105·45 (14)	C(4a)–C(5)–C(6)	119·5 (3)
O(3)–S–C(7)	106·23 (13)	C(5)–C(6)–C(7)	120·6 (3)
C(2)–N(1)–C(8a)	124·4 (3)	S–C(7)–C(6)	117·9 (2)
N(1)–C(2)–C(3)	120·7 (3)	S–C(7)–C(8)	119·9 (2)
N(2)–C(3)–C(2)	120·1 (3)	C(6)–C(7)–C(8)	122·1 (3)
N(2)–C(3)–C(4)	122·1 (3)	C(7)–C(8)–C(8a)	117·6 (3)
C(2)–C(3)–C(4)	117·8 (3)	N(1)–C(8a)–C(4a)	116·5 (3)
C(3)–C(4)–C(4a)	120·9 (3)	N(1)–C(8a)–C(8)	121·2 (3)
C(4)–C(4a)–C(5)	122·3 (3)	C(4a)–C(8a)–C(8)	122·2 (3)

Hydrogen bonds

	X···O	*X*–H		
O(5)–H_a···O(2)	2·794 (3)	1·00 (5)	1·80 (5)	172 (5)
O(5)–H_b···O(1)	2·807 (4)	0·85 (4)	2·00 (4)	158 (4)
O(4)–H···O(5)	2·662 (3)	0·78 (4)	1·89 (4)	174 (4)
N(1)–H···O(5)	2·901 (4)	0·84 (4)	2·24 (4)	136 (3)
N(1)–H···O(3)	2·925 (4)	0·84 (4)	2·37 (4)	124 (3)
N(2)–H_a···O(1)	2·827 (4)	0·95 (4)	2·20 (4)	123 (3)
N(2)–H_b···O(3)	3·135 (5)	0·91 (5)	2·40 (5)	138 (4)

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Structure of 8-Bromo-6-*endo*-methylisofenchone*

BY STEVEN J. RETTIG AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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Abstract. $C_{11}H_{17}BrO$, $M_r = 245·16$, orthorhombic, $P2_12_12$, $a = 10·957$ (1), $b = 22·409$ (2), $c = 9·2455$ (6) Å, $V = 2270·1$ (3) Å^3, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1·434$ (1) g cm^{-3}, Mo $K\alpha$, $\lambda\alpha_1 = 0·70930$ Å, $\mu = 35$ cm^{-1}, $F(000) = 1008$, $T = 295$ K, $R = 0·054$ for 988 reflections. The geometry and dimensions of the molecule are similar to

* (1*S*,4*S*,5*S*,6*S*)-5-Bromomethyl-1,5,6-trimethylbicyclo[2.2.1]-heptan-2-one.

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