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4-Hydroxypyridinium-3-sulfonate

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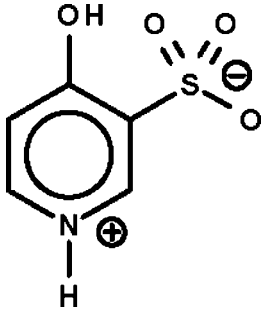
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.024; wR factor = 0.068; data-to-parameter ratio = 12.0.

The reaction of 4-hydroxypyridine and oleum produces 4-hydroxypyridinium-3-sulfonate, $C_5H_5NO_4S$, which shows delocalized bonds in the six-membered ring. In the crystal, adjacent zwitterions are linked by N—H···O and O—H···O hydrogen bonds into a layer motif. The crystal studied was a racemic twin.

Related literature

A previous synthesis yielded hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate; see: Zhu *et al.* (2009).



Experimental

Crystal data

$C_5H_5NO_4S$
M_r = 175.16
Orthorhombic, $P2_12_12_1$
a = 6.7980 (2) Å
b = 8.7618 (3) Å
c = 10.6797 (3) Å
V = 636.11 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 293 K
0.28 × 0.23 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.880, T_{max} = 0.925
6216 measured reflections
1449 independent reflections
1403 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.068
S = 1.09
1449 reflections
121 parameters
5 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 785 Friedel pairs
Flack parameter: 0.31 (8)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O2^{i}	0.83 (1)	1.76 (1)	2.581 (2)	166 (3)
N1—H1n···O3^{ii}	0.87 (1)	1.91 (1)	2.762 (2)	166 (2)

Symmetry codes: (i) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$; (ii) $x+1, y, z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2249).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zhu, Z.-B., Gao, S. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2687.

supplementary materials

Acta Cryst. (2011). E**67**, o11 [**doi:10.1107/S1600536810049603**]

4-Hydroxypyridinium-3-sulfonate

Z.-B. Zhu, S. Gao and S. W. Ng

Comment

A previous reaction of 4-hydroxpyridine and oleum gave the salt, hydronium 4-oxo-1,4-dihydropyridine-3-sulfonate dihydrate (Zhu *et al.*, 2009). Repeating this synthesis instead produced the zwitterionic title compound (Scheme I, Fig. 1). The bonds in the ring are delocalized bonds. Adjacent zwitterions are linked by N–H···O and O–H···O hydrogen bonds into a layer motif (Fig. 2).

Experimental

4-Hydroxypyridine (10 mmol) was dissolved in 20% oleum (10 ml). The solution was heated to 393 K for 4 days. After it was cooled to room temperature, the excess oleum was decanted. Recrystallization of the solid from ethanol gave colorless crystals.

Refinement

Carbon-bound H atoms were refind with a C–H 0.95±0.01 Å restraint. The amino and hydroxy H atoms were located in a difference Fourier map, and were refined with distance restraints of O–H 0.84±0.01 Å and N–H 0.88±0.01 Å. All temperature factors were refined.

Figures

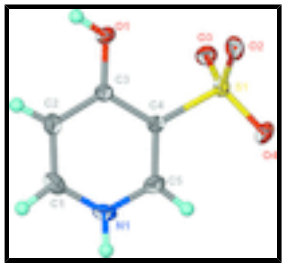

Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $C_5H_5NO_4S$ at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

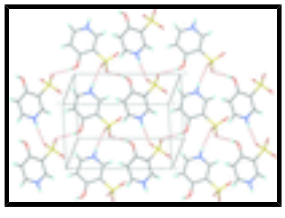

Fig. 2. Hydrogen-bonded layer structure.

4-Hydroxypyridinium-3-sulfonate

Crystal data

$C_5H_5NO_4S$	$F(000) = 360$
$M_r = 175.16$	$D_x = 1.829$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 6017 reflections
$a = 6.7980$ (2) Å	$\theta = 3.0$–$27.4°$
$b = 8.7618$ (3) Å	$\mu = 0.47$ mm^{-1}
$c = 10.6797$ (3) Å	$T = 293$ K
$V = 636.11$ (3) Å^3	Prism, colorless
$Z = 4$	0.28 × 0.23 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	1449 independent reflections
Radiation source: fine-focus sealed tube	1403 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.017$
Detector resolution: 10.000 pixels mm^{-1}	$\theta_{max} = 27.4°$, $\theta_{min} = 3.0°$
ω scans	$h = -8 \rightarrow 7$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$k = -11 \rightarrow 11$
$T_{min} = 0.880$, $T_{max} = 0.925$	$l = -13 \rightarrow 13$
6216 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.024$	All H-atom parameters refined
$wR(F^2) = 0.068$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.0899P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
1449 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
121 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
5 restraints	Absolute structure: Flack (1983), 785 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.31 (8)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.84628 (5)	0.31587 (4)	0.15713 (3)	0.02340 (12)

O1	0.81623 (18)	0.44053 (16)	0.41523 (12)	0.0304 (3)
O2	0.7512 (2)	0.46465 (15)	0.13994 (12)	0.0348 (3)
O3	0.71610 (16)	0.20834 (15)	0.21966 (11)	0.0307 (3)
O4	0.9407 (2)	0.25936 (17)	0.04580 (11)	0.0344 (3)
N1	1.37517 (19)	0.33180 (18)	0.31720 (15)	0.0310 (3)
C1	1.3417 (3)	0.3866 (2)	0.43239 (17)	0.0317 (4)
C2	1.1563 (3)	0.42245 (19)	0.47075 (15)	0.0282 (3)
C3	0.9993 (2)	0.40609 (18)	0.38677 (14)	0.0224 (3)
C4	1.0389 (2)	0.34817 (17)	0.26608 (14)	0.0216 (3)
C5	1.2292 (2)	0.3108 (2)	0.23489 (15)	0.0274 (3)
H1O	0.794 (5)	0.485 (3)	0.4827 (16)	0.064 (9)*
H1N	1.4924 (18)	0.306 (3)	0.2930 (19)	0.036 (6)*
H1	1.456 (2)	0.394 (3)	0.4826 (19)	0.038 (6)*
H2	1.138 (3)	0.463 (2)	0.5519 (11)	0.021 (4)*
H5	1.267 (3)	0.263 (3)	0.1575 (14)	0.042 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02372 (18)	0.02877 (19)	0.01770 (17)	0.00307 (16)	−0.00047 (14)	−0.00191 (14)
O1	0.0236 (6)	0.0426 (7)	0.0249 (6)	0.0052 (5)	0.0026 (5)	−0.0082 (5)
O2	0.0429 (7)	0.0352 (7)	0.0262 (6)	0.0118 (5)	−0.0080 (6)	0.0003 (5)
O3	0.0259 (5)	0.0354 (6)	0.0308 (6)	−0.0021 (5)	0.0030 (5)	−0.0030 (5)
O4	0.0361 (6)	0.0460 (7)	0.0212 (5)	0.0012 (6)	0.0036 (5)	−0.0086 (5)
N1	0.0174 (6)	0.0363 (8)	0.0393 (8)	0.0029 (6)	0.0028 (5)	0.0047 (6)
C1	0.0258 (8)	0.0326 (8)	0.0368 (9)	−0.0014 (7)	−0.0071 (8)	0.0052 (7)
C2	0.0298 (8)	0.0321 (7)	0.0227 (7)	−0.0004 (8)	−0.0030 (7)	0.0001 (6)
C3	0.0211 (7)	0.0237 (7)	0.0224 (7)	0.0004 (6)	0.0014 (6)	0.0017 (5)
C4	0.0210 (7)	0.0249 (7)	0.0189 (6)	0.0016 (5)	0.0009 (5)	0.0011 (6)
C5	0.0253 (7)	0.0296 (7)	0.0273 (7)	0.0022 (7)	0.0063 (6)	0.0018 (7)

Geometric parameters (Å, °)

S1—O4	1.4390 (12)	N1—H1N	0.868 (10)
S1—O3	1.4549 (12)	C1—C2	1.362 (3)
S1—O2	1.4666 (13)	C1—H1	0.947 (10)
S1—C4	1.7747 (15)	C2—C3	1.402 (2)
O1—C3	1.316 (2)	C2—H2	0.943 (9)
O1—H1O	0.834 (10)	C3—C4	1.411 (2)
N1—C5	1.338 (2)	C4—C5	1.375 (2)
N1—C1	1.340 (2)	C5—H5	0.961 (10)
O4—S1—O3	115.32 (8)	C1—C2—C3	119.25 (16)
O4—S1—O2	113.52 (8)	C1—C2—H2	119.0 (13)
O3—S1—O2	111.40 (8)	C3—C2—H2	121.6 (13)
O4—S1—C4	105.51 (7)	O1—C3—C2	123.29 (15)
O3—S1—C4	104.55 (7)	O1—C3—C4	118.31 (14)
O2—S1—C4	105.41 (7)	C2—C3—C4	118.40 (15)
C3—O1—H1O	118 (2)	C5—C4—C3	119.11 (14)

C5—N1—C1	121.76 (14)	C5—C4—S1	119.83 (12)
C5—N1—H1N	116.7 (15)	C3—C4—S1	121.01 (11)
C1—N1—H1N	121.5 (15)	N1—C5—C4	120.37 (15)
N1—C1—C2	121.07 (16)	N1—C5—H5	115.2 (14)
N1—C1—H1	113.9 (15)	C4—C5—H5	124.4 (14)
C2—C1—H1	125.0 (15)		
C5—N1—C1—C2	0.4 (3)	O3—S1—C4—C5	118.79 (15)
N1—C1—C2—C3	−2.0 (3)	O2—S1—C4—C5	−123.66 (15)
C1—C2—C3—O1	−178.80 (16)	O4—S1—C4—C3	179.33 (13)
C1—C2—C3—C4	1.9 (2)	O3—S1—C4—C3	−58.62 (15)
O1—C3—C4—C5	−179.69 (15)	O2—S1—C4—C3	58.93 (15)
C2—C3—C4—C5	−0.4 (2)	C1—N1—C5—C4	1.2 (3)
O1—C3—C4—S1	−2.3 (2)	C3—C4—C5—N1	−1.2 (3)
C2—C3—C4—S1	177.04 (12)	S1—C4—C5—N1	−178.64 (12)
O4—S1—C4—C5	−3.26 (17)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O2^{i}	0.83 (1)	1.76 (1)	2.581 (2)	166 (3)
N1—H1n···O3^{ii}	0.87 (1)	1.91 (1)	2.762 (2)	166 (2)

Symmetry codes: (i) −*x*+3/2, −*y*+1, *z*+1/2; (ii) *x*+1, *y*, *z*.

Fig. 1

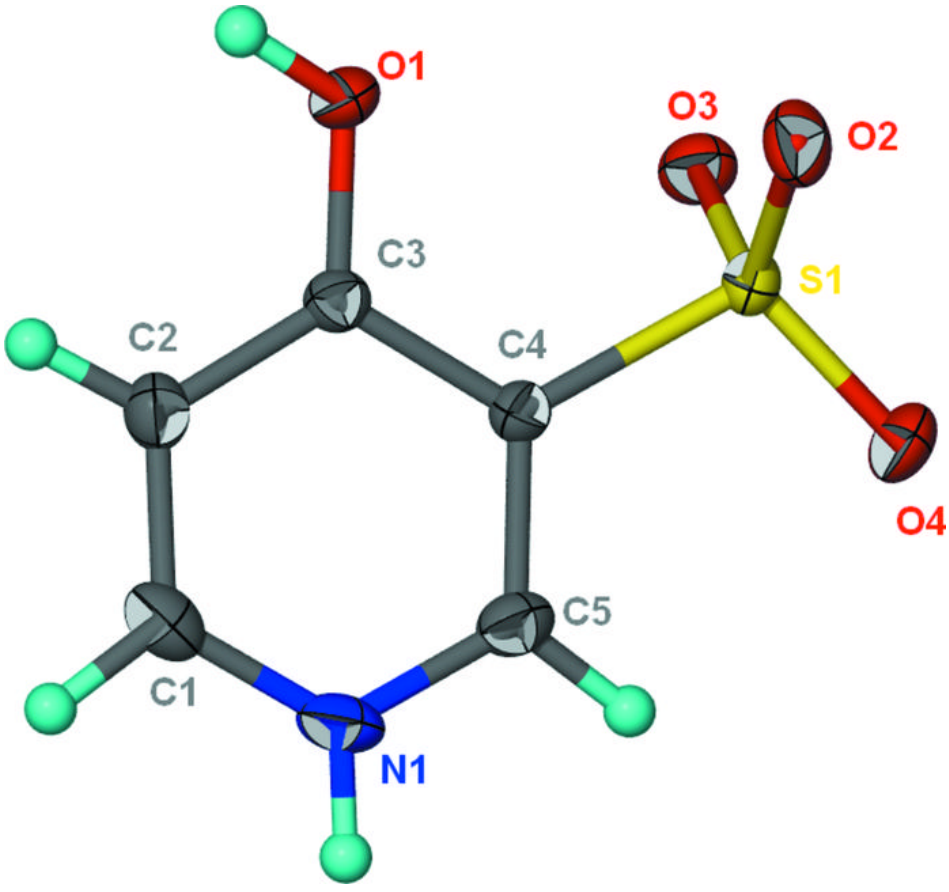

Fig. 2