organic compounds

Oxonium 5-aminouracil-6-sulfonate hydrate

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In the title compound, oxonium 5-amino-2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-sulfonate hydrate, $H_3O^+ \cdot C_4H_4N_3O_5S^- \cdot H_2O$, the sulfonate group is in the anionic form and charge balance is provided by an oxonium cation, H_3O^+. Screw-related molecules overlap significantly and are hydrogen bonded to form a zigzag chain of the uracil skeleton along the direction of the c screw axis. The partially stacked bases and their glide-related equivalents run parallel to the a axis to form hydrophobic zones separated by hydrophilic zones built up by a network of hydrogen bonds.

Comment

The structural analysis of the title compound, (I), is a continuation of our earlier work involving systematic conformational studies on nucleic acid constituents in the form of their derivatives and metal complexes to understand structure–function relationships. The purpose of the present study is to understand the effect of substituents on the ring structure of the uracil base.

(I)
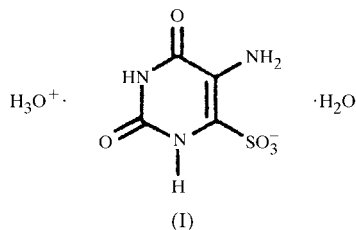
The bond lengths and angles of the uracil derivative (Fig. 1) are in close agreement with those of a neutral uracil base (Taylor *et al.*, 1982). As expected, the uracil base is planar, with a maximum deviation of 0.014 (3) Å for C2. The orientation of the sulfonyl group with respect to the uracil base is given by torsion angles about the bond C6—S1 (Table 1). The torsion angles C5—C6—S1—O5 [55.0 (3)°] and C5—C6—S1—O6 [−66.0 (3)°] indicate that the S1—O5 and S1—O6 bonds are staggered with respect to the base, while the torsion angle N1—C6—S1—O7 [−5.8 (3)°] indicates an eclipsed position

for the S1—O7 bond and brings the atom O7 closer to the N—H group [N1···O7 = 2.743 (3) Å] of the ring. This disposition is probably due to a weak electrostatic interaction between the N—H group and the O7 atom, which is further evidenced by the asymmetry of the exocyclic bond angles N1—C6—S1 and C5—C6—S1 of 116.5 (2) and 122.8 (2)°, respectively. The three S—O bond lengths, S1—O5 [1.443 (2) Å], S1—O6 [1.446 (2) Å] and S1—O7 [1.448 (2) Å], are equal within three standard deviations, indicating that the sulfonate group (SO₃) is in the anionic form. The three angles O5—S1—O6 [114.13 (5)°], O5—S1—O7 [114.58 (15)°] and O6—S1—O7 [112.89 (15)°], and the three angles O5—S1—C6 [105.48 (14)°], O6—S1—C6 [105.27 (14)°] and O7—S1—C6 [103.04 (14)°] have average values 113.9 (7) and 104.6 (11)°, respectively; these deviations from the normal tetrahedral angles in sulfonate groups have been established by many accurate structure analyses; *e.g.* 112.9 and 106.7° in the structure of taurine 2-aminoethyl sulfonic acid (Okaya, 1966), and 112.1 (2) and 106.6 (2)° in hexaaquacobalt(II) bis(2-aminotoluene-4-sulfonate) (Gunderman *et al.*, 1997). A search of the Cambridge Structural Database (Allen *et al.*, 1991) has shown that the deformation of the sulfonate groups from ideal tetrahedral geometry is common. The N5—C5 bond length [1.347 (4) Å] is close to the normal C—N bond distances found in other neutral nucleic acid bases (Taylor *et al.*, 1982).

The molecular packing and hydrogen-bonding scheme is shown in Fig. 2. The uracil bases are tilted at an angle of 24.9° to the screw axis and the centroid of the ring structure of the base is 0.38 Å away from this axis. Significant overlap is observed between the screw-related bases: the shortest intermolecular contacts between O4 of one molecule and C2 and O7 of the screw-related molecule at $(-x + 2, \frac{1}{2} + y, \frac{1}{2} - z)$ are of 3.455 (4) and 3.104 (3) Å, respectively, indicating that the screw-related bases are partially stacked. These bases are further linked by a hydrogen bond between N1 and O4, forming a chain of uracil bases along the direction of the screw axis (Table 2 and Fig. 2). The partially stacked bases, together with their glide-related equivalents, run parallel to the a axis and form hydrophobic zones separated by hydrophilic zones where the sulfonyl anions and H_3O^+ cations, a water molecule, the amino N5 atom and the ring N3 atom form a network of hydrogen bonds. O1W is part of an H_3O^+ cation which has three close neighbours; O7 (related by an inversion centre),
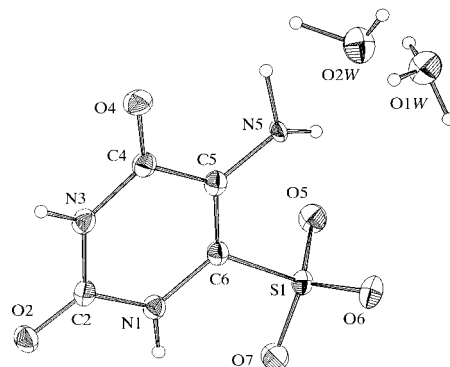

Figure 1
An *ORTEP*II (Johnson, 1976) plot of the title molecule showing the atom labelling. Ellipsoids are drawn at the 30% probability level.

O7 (screw-related) and O2W, with O$\cdots$O distances of 2.868 (4), 2.838 (4) and 2.871 (4) Å, respectively, and these are arranged in a fashion similar to that found in tris(1-phenacyl-2-pyridone) hydroxonium tetrafluoroborate (Zhukov *et al.*, 1997) and hydronium 2-carboxybenzenesulfonate (Ng, 1997). O2W forms a bifurcated hydrogen bond to O2 and O6 through H2WA and also links to O5 through H2WB. These interactions generate an infinite three-dimensional network of cations, anions and water molecules.
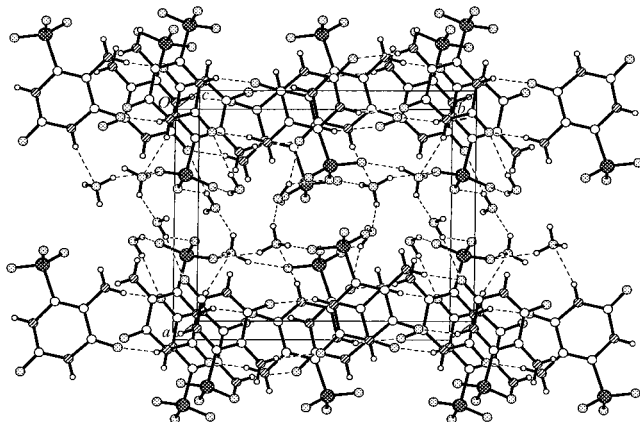

Figure 2
A view approximately along the c direction showing the extensive three-dimensional hydrogen-bonded network linking H$_3$O$^+$ cations, C$_4$H$_4$N$_3$O$_5$S$^-$ anions and water molecules. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound was synthesized by the reaction of a hot aqueous solution of sulfuric acid and 5-aminouracil. The mixture was kept on a hot water bath for about 6 h and crystals were obtained after a few days at room temperature.

Crystal data

H$_3$O$^+$·C$_4$H$_4$N$_3$O$_5$S$^-$·H$_2$O	D_x = 1.843 Mg m^{-3}
M_r = 243.20	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
a = 10.579 (2) Å	reflections
b = 12.104 (2) Å	θ = 20–30°
c = 7.003 (2) Å	μ = 3.644 mm^{-1}
β = 102.26 (3)$^\circ$	T = 293 (2) K
V = 876.3 (3) Å^3	Block, colourless
Z = 4	0.35 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffract-ometer	1474 reflections with $I > 2\sigma(I)$
ω–2θ scans	θ_{max} = 69.72°
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 12$
	$k = -14 \rightarrow 0$
	$l = -8 \rightarrow 8$
T_{min} = 0.419, T_{max} = 0.482	3 standard reflections
1551 measured reflections	every 100 reflections
1551 independent reflections	intensity decay: negligible

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0935P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$+ 1.9742P]$
$wR(F^2)$ = 0.139	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.922	$(\Delta/\sigma)_{max} < 0.001$
1551 reflections	$\Delta\rho_{max}$ = 0.55 e Å^{-3}
138 parameters	$\Delta\rho_{min}$ = −0.50 e Å^{-3}
H atoms: see below	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0169 (16)

Table 1
Selected geometric parameters (Å, $^\circ$).

S1—O5	1.443 (2)	S1—O7	1.448 (2)
S1—O6	1.446 (2)	N5—C5	1.347 (4)
O5—S1—O6	114.13 (15)	O6—S1—C6	105.27 (14)
O5—S1—O7	114.58 (15)	O7—S1—C6	103.04 (14)
O6—S1—O7	112.89 (15)	N1—C6—S1	116.5 (2)
O5—S1—C6	105.48 (14)	C5—C6—S1	122.8 (2)
C5—C6—S1—O5	55.0 (3)	N1—C6—S1—O7	−5.8 (3)
C5—C6—S1—O6	−66.0 (3)		

Table 2
Hydrogen-bonding geometry (Å, $^\circ$).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O4^i	0.86	2.08	2.890 (4)	158
N3—H3$\cdots$O1W^{ii}	0.86	2.18	2.940 (4)	148
N5—H5$B\cdots$O2^{iii}	0.86	2.10	2.671 (3)	123
N5—H5$A\cdots$O2W	0.86	2.54	3.024 (4)	116
O1W—H1$WA\cdots$O7^{iv}	0.85	2.14	2.867 (4)	144
O1W—H1$WB\cdots$O2W	0.83	2.28	2.871 (4)	129
O1W—H1$WC\cdots$O7^v	0.85	1.99	2.838 (4)	177
O2W—H2$WA\cdots$O6^{vi}	0.86	2.25	2.909 (4)	134
O2W—H2$WA\cdots$O2^{iii}	0.86	2.38	2.962 (4)	125
O2W—H2$WB\cdots$O5^{vii}	0.86	2.15	2.976 (4)	159

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

H atoms attached to N atoms were fixed geometrically and refined isotropically using a riding model with U_{iso}(H) = 1.2U_{eq}(N) for ring nitrogens and U_{iso}(H) = 1.5U_{eq}(N) for the amino group. H atoms of the water molecules were located from a difference Fourier synthesis and refined isotropically with U_{iso}(H) = 1.5U_{eq}(O) using restraints for O—H bond distances and H—O—H angles. The numbering scheme shown in Fig. 1 is consistent with the rules of the IUPAC–IUB Commission on Biochemical Nomenclature (IUPAC–IUB, 1983).

Data collection, cell refinement and data reduction: *CAD-4 Software* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983).

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