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Hydrogen-bonding patterns in 2-amino-4,6-dimethylpyrimidinium hydrogen sulfate

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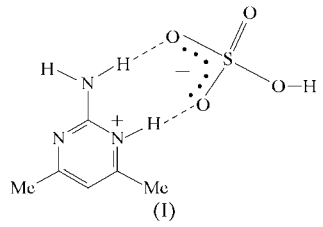
In the title compound, $C_6H_{10}N_3^+\cdot HSO_4^-$, the asymmetric unit consists of a hydrogen sulfate anion and a 2-amino-4,6-dimethylpyrimidinium cation. The hydrogen sulfate anions self-assemble through O—H···O hydrogen bonds, forming supramolecular chains along the *b* axis, while the organic cations form base pairs *via* N—H···N hydrogen bonds. The aminopyrimidinium cations join to the sulfate anions *via* a pair of hydrogen bonds donated from the pyrimidinium protonation site and from the *exo* amine group *cis* to the protonated site.

Comment

Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). 2-Aminopyrimidine and its derivatives are of particular interest as adduct formers because of their ability to form stable hydrogen-bonded chains *via* their stereochemically associative amine group and the ring N atoms (Lynch *et al.*, 2000). The crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982), aminopyrimidine carboxylates (Hu *et al.*, 2002) and co-crystals (Chinnakali *et al.*, 1999; Goswami *et al.*, 2000; Etter, 1990) have been reported. The crystal structure of 2,4-diaminopyrimidinium sulfate has also been reported (Muthiah *et al.*, 2001). Hydrogen-bonding patterns involving sulfate and sulfonate groups in biological systems and metal complexes are also of current interest (Onoda *et al.*, 2001). Benzoic acid and sulfuric acid form a stable hydrogen-bonded complex that favors aerosol formation in the atmosphere (Zhang *et al.*, 2004). In a sulfate-binding protein, the sulfate anion is bound mainly by seven hydrogen bonds, five of which are from the main-chain peptide NH groups (Pflugrath & Quiocho, 1985; Jacobson & Quiocho, 1988). The present study is aimed at understanding the hydrogen-bonding networks in the title compound, (I).



(I)

In (I), the asymmetric unit consists of a hydrogen sulfate anion and a 2-amino-4,6-dimethylpyrimidinium cation (ampyH) (Fig. 1). Protonation of the pyrimidine base on the N1 site is reflected in a change in bond angle. The C2—N3—C4 angle at unprotonated atom N3 is 117.6 (1)°, while for protonated atom N1 the C2—N1—C6 angle is 122.3 (1)°. The geometry of the ampyH cation agrees with that of other ampyH cations reported in the literature (Panneerselvam *et al.*, 2004). The S—O distances lie in the range 1.447 (1)–1.560 (1) Å, while the O—S—O angles range between 104.0 (1) and 113.3 (1)° (Table 1), indicating a distorted tetrahedral environment around the S atom. The S—O bond lengths and O—S—O bond angles of the sulfate group are consistent with the fact that the H atom is attached only to atom O1. Atoms O2 and O4 interact with the protonated pyrimidine moiety through a pair of nearly parallel N—H···O hydrogen bonds (Table 2), which are reminiscent of the carboxylate–amine interactions seen in ASP-27 of dihydrofolate reductase and the 2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidine cation (Kuyper, 1990). Thus, in compound (I), the pair of sulfate O atoms mimics the role of the carboxylate group in its hydrogen-bonding interaction with the aminopyrimidinium motif. This type of interaction has also been observed in the crystal structure of 2-amino-5-nitro-4,6-dipiperidinopyrimidinium hydrogen sulfate monohydrate (Quesada *et al.*, 2003). This pattern is also remarkably similar to that observed in the adeninium/sulfate systems (Langer & Huml, 1978) and in cytidinium salts with composite XY_n anions capable of accepting hydrogen bonds through their *Y* atoms, *e.g.* NO_3^-, HSO_4^-, SO_4^{2-}, $H_2PO_4^-$ and SiF_6^{2-} (Gilski & Jaskólski, 1998).

The ampyH cations are paired centrosymmetrically through N2—H2*A*···N3^{ii} and N3···H2*A*^{ii}—N2^{ii} hydrogen bonds (see Table 2 for symmetry code). This configuration can be

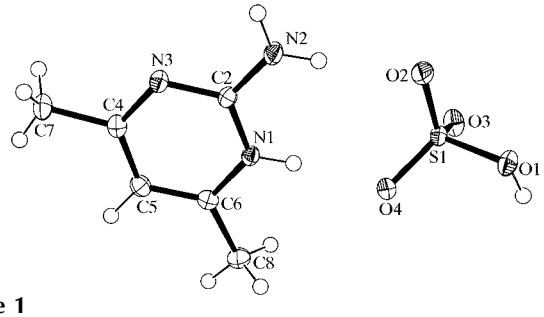


Figure 1
An *ORTEPII* (Johnson, 1976) diagram of the asymmetric unit of (I), showing 50% probability displacement ellipsoids.

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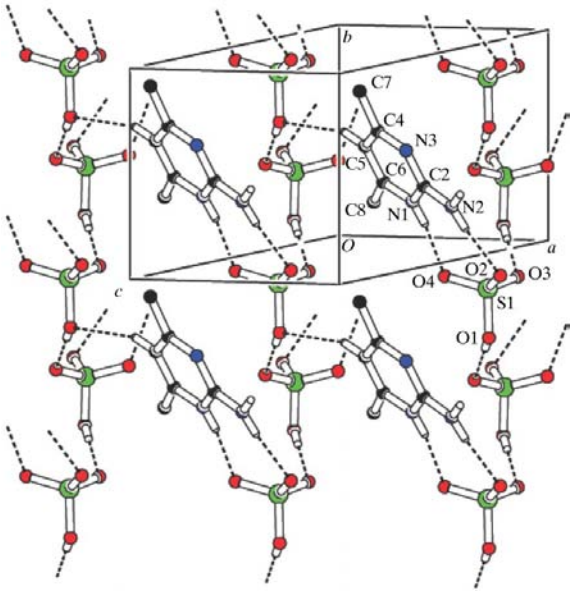

Figure 2
The crystal structure of (I). Broken lines denote hydrogen bonds.

described by the graph-set notation $R_2^2(8)$ (Etter, 1990; Bernstein *et al.*, 1995). This type of base pairing has also been reported in trimethoprim salicylate methanol solvate (Panneerselvam *et al.*, 2002), trimethoprim sulfate trihydrate (Muthiah *et al.*, 2001), trimethoprim maleate (Prabakaran *et al.*, 2001) and trimethoprim perchlorate (Muthiah *et al.*, 2002). The hydrogen sulfate ions in (I) self-assemble through O1—H1′···O3^{i} hydrogen bonds, leading to a supramolecular chain along the *b* axis (Fig. 2). There is also a C—H···O hydrogen bond involving atom C5 of the pyrimidine moiety and O1 of the hydrogen sulfate ion.

Experimental

To a hot methanol solution of 2-amino-4,6-dimethylpyrimidine (62 mg, Aldrich) were added a few drops of sulfuric acid. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Crystals of (I) appeared from the mother liquor after a few days.

Crystal data

$C_6H_{10}N_3^+\cdot HSO_4^-$
M_r = 221.24
Monoclinic, $P2_1/c$
a = 7.025 (1) Å
b = 6.724 (1) Å
c = 20.200 (4) Å
β = 90.27 (3)°
V = 954.2 (3) Å^3
Z = 4
D_x = 1.540 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4591 reflections
θ = 3.4–25.7°
μ = 0.33 mm^{-1}
T = 293 (2) K
Prism, colorless
0.50 × 0.35 × 0.10 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: multi-scan (*XEMP*; Siemens, 1990)
T_{min} = 0.877, T_{max} = 0.970
7253 measured reflections
1793 independent reflections
1622 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.7°
$h = -6 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -24 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.072
S = 1.07
1793 reflections
172 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.4073P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.015 (2)

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4470 (12)	N3—C4	1.3337 (19)
S1—O4	1.4594 (11)	N3—C2	1.3518 (19)
S1—O3	1.4599 (12)	C4—C5	1.402 (2)
S1—O1	1.5602 (11)	C4—C7	1.494 (2)
N1—C2	1.3587 (19)	C5—C6	1.369 (2)
N1—C6	1.3621 (19)	C6—C8	1.487 (2)
N2—C2	1.320 (2)		
O2—S1—O4	112.91 (7)	O4—S1—O1	107.89 (6)
O2—S1—O3	113.30 (7)	O3—S1—O1	106.35 (6)
O4—S1—O3	111.72 (7)	C2—N1—C6	122.27 (13)
O2—S1—O1	104.01 (7)	C4—N3—C2	117.57 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4	0.86 (2)	1.90 (2)	2.743 (2)	172 (2)
N2—H2B···O2	0.87 (2)	2.05 (2)	2.921 (2)	175 (2)
O1—H1′···O3^{i}	0.82 (2)	1.76 (2)	2.579 (2)	169 (2)
N2—H2A···N3^{ii}	0.85 (2)	2.17 (2)	3.017 (2)	179 (2)
C5—H5···O1^{iii}	0.96 (2)	2.51 (2)	3.422 (2)	159 (1)

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

The positions of the H atoms were determined from difference Fourier maps and were refined freely along with their isotropic displacement parameters. The C—H, N—H and O—H bond lengths are 0.86 (2)–0.96 (2), 0.85 (2)–0.87 (2) and 0.82 (2) Å, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1206). Services for accessing these data are described at the back of the journal.

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