

## 2-Aminopyrimidinium hydrogen sulfate

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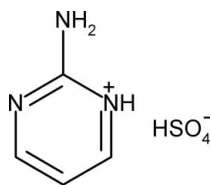
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.056;  $wR$  factor = 0.159; data-to-parameter ratio = 33.2.

In the crystal structure of the title compound,  $\text{C}_4\text{H}_6\text{N}_3^+\text{HSO}_4^-$ , hydrogen sulfate anions self-assemble through  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, forming chains along the  $b$  axis, while the cations form centrosymmetric pairs *via*  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds. The 2-aminopyrimidinium pairs are linked to the sulfate anions *via*  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, forming a two-dimensional network parallel to  $(10\bar{2})$ . In addition, weak intermolecular  $\text{C}-\text{H}\cdots\text{O}$  contacts generate a three-dimensional network.

## Related literature

For the biological properties of pyrimidines, see: Rabie *et al.* (2007); Rival *et al.* (1991). For applications of aminopyrimidines, see: Rospenk & Koll (2007). For aminopyrimidine salts, see: Hemamalini *et al.* (2005); Childs *et al.* (2007); Lee *et al.* (2003); Ye *et al.* (2002). For sulfate salts with organic cations, see: Xu *et al.* (2009a,b).



## Experimental

## Crystal data

$\text{C}_4\text{H}_6\text{N}_3^+\text{HSO}_4^-$   
 $M_r = 193.19$   
 Monoclinic,  $P2_1/c$   
 $a = 8.388$  (2) Å  
 $b = 5.208$  (3) Å  
 $c = 18.468$  (4) Å  
 $\beta = 112.84$  (2)°

$V = 743.6$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Ag  $K\alpha$  radiation  
 $\lambda = 0.56087$  Å  
 $\mu = 0.22$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.25 \times 0.21 \times 0.15$  mm

## Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 3738 measured reflections  
 3647 independent reflections

2520 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 2 standard reflections every 120 min  
 intensity decay: 1%

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.159$   
 $S = 1.07$   
 3647 reflections

110 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.82$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.71$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                               | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O1}-\text{H1}\cdots\text{O4}^{\text{i}}$    | 0.82         | 1.79               | 2.6100 (19) | 174                  |
| $\text{N1}-\text{H1B}\cdots\text{O1}^{\text{ii}}$  | 0.86         | 2.38               | 3.140 (2)   | 148                  |
| $\text{N1}-\text{H1B}\cdots\text{O4}$              | 0.86         | 2.58               | 3.155 (2)   | 125                  |
| $\text{N1}-\text{H1A}\cdots\text{N3}^{\text{iii}}$ | 0.86         | 2.16               | 3.017 (2)   | 172                  |
| $\text{N2}-\text{H2}\cdots\text{O3}$               | 0.86         | 1.91               | 2.756 (2)   | 168                  |
| $\text{C2}-\text{H2A}\cdots\text{O3}^{\text{iv}}$  | 0.93         | 2.40               | 3.294 (2)   | 160                  |
| $\text{C3}-\text{H3}\cdots\text{O2}^{\text{v}}$    | 0.93         | 2.51               | 3.262 (3)   | 138                  |
| $\text{C4}-\text{H4}\cdots\text{O4}^{\text{vi}}$   | 0.93         | 2.53               | 3.316 (2)   | 142                  |

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5222).

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**supplementary materials**

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## 2-Aminopyrimidinium hydrogen sulfate

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### Comment

Substantial attention has recently been focused on pyrimidine and its derivatives for their interesting properties as fungicides, vermicides, insecticides (Rabie *et al.*, 2007), antifungal agents and antiviral agents (Rival *et al.*, 1991). In particular, aminopyrimidines have been recognized as interesting nucleic bases, like cytosine, adenine and guanine which are responsible for molecular recognition and replication of DNA, through the formation and breakage of N—H···N hydrogen bonds (Rospenk & Koll, 2007). In continuation of our research on materials which could have interesting applications we report herein the synthesis and crystal structure of the title compound (I).

The asymmetric unit of the title compound (Fig. 1) consists of one hydrogen sulfate anion and one protonated 2-aminopyrimidine. The crystal packing of (I) is characterized by infinite chains built by HSO<sub>4</sub><sup>-</sup> anions extending along the *b*-direction. These chains are interconnected by cationic moieties *via* intermolecular N—H···O and C—H···O hydrogen bonds (Table 1) resulting in three-dimensional supra-molecular structure (Fig. 2).

As can be seen in table 1, the O1—H1···O4<sup>i</sup> hydrogen bond links two adjacent hydrogen sulfate anions generating corrugated chains stacked along *c* axis (Fig. 2). In the sulfate anion, the S—O bond [1.569 (2) Å] involving the O atom bearing the acid H atom is longer than the other three S—O bonds, which range from 1.429 (1) to 1.459 (1) Å because of the bond multiplicity and the electronic mesomerism as reported previously in the hydrogen sulfate ion (Xu *et al.*, 2009a,b).

With regard to the organic framework, the neighbouring cations of 2-aminopyrimidine linked by the hydrogen bonds N1—H1A···N3 (2 - *x*, 1 - *y*, 1 - *z*) and N3···H1A—N1 (2 - *x*, 1 - *y*, 1 - *z*) form the cyclic dimer of [C<sub>4</sub>N<sub>2</sub>H<sub>4</sub>NH<sub>2</sub>]<sup>2+</sup>. The cationic arrangement in crystal structure of 2-amino-4,6-dimethylpyrimidinium hydrogen sulfate (Hemamalini *et al.*, 2005) is closely related to that seen in the title compound. The dimers of the 2-aminopyrimidinium cations with planar rings (r.m.s. deviation = 0.008 Å) are connected to HSO<sub>4</sub><sup>-</sup> chains by hydrogen bonds N1—H1B···O4, N1—H1B···O1 (*x*, *y* + 1, *z*) and N2—H2···O3 to form a two-dimensional network (Fig. 2) which is linked into a three-dimensional network through weak intermolecular hydrogen bonds. These observations are similar to that of other 2-aminopyrimidinium salts (Childs *et al.*, 2007; Lee *et al.*, 2003; Ye *et al.*, 2002).

### Experimental

To a solution of 2-aminopyrimidine (0.19 g, 2 mmol) dissolved in a mixture of water/ethanol (10/5 ml) was added dropwise 2 mmol (0.15 ml) of commercial H<sub>2</sub>SO<sub>4</sub> (98%, Aldrich). The reaction mixture was stirred and left under slowly evaporation at room temperature until formation of large colorless single crystals of the title compound.

## Refinement

All H atoms attached to C, N and O atoms were fixed geometrically and treated as riding with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C, N})$  or  $1.5 U_{\text{eq}}(\text{O})$

## Figures



Fig. 1. The asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as spheres of arbitrary radii. Hydrogen bonds are represented as dashed lines.

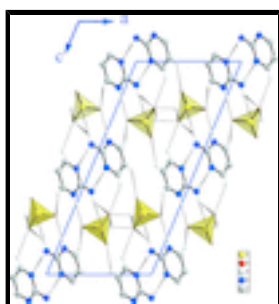
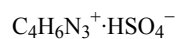


Fig. 2. Projection of (I) along the *b* axis. The H-atoms not involved in H-bonding are omitted. H bonds are shown as dashed lines.

## 2-Aminopyrimidinium hydrogen sulfate

### Crystal data



$M_r = 193.19$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.388$  (2) Å

$b = 5.208$  (3) Å

$c = 18.468$  (4) Å

$\beta = 112.84$  (2)°

$V = 743.6$  (5) Å<sup>3</sup>

$Z = 4$

$F(000) = 400$

$D_x = 1.726$  Mg m<sup>-3</sup>

Ag  $K\alpha$  radiation,  $\lambda = 0.56087$  Å

Cell parameters from 25 reflections

$\theta = 9\text{--}11^\circ$

$\mu = 0.22$  mm<sup>-1</sup>

$T = 293$  K

Prism, colorless

$0.25 \times 0.21 \times 0.15$  mm

### Data collection

Enraf-Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

non-profiled  $\omega$  scans

3738 measured reflections

$R_{\text{int}} = 0.015$

$\theta_{\text{max}} = 28.0^\circ$ ,  $\theta_{\text{min}} = 2.1^\circ$

$h = -14 \rightarrow 13$

$k = -8 \rightarrow 0$

$l = -30 \rightarrow 13$

3647 independent reflections  
2520 reflections with  $I > 2\sigma(I)$

2 standard reflections every 120 min  
intensity decay: 1%

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.159$

$S = 1.07$

3647 reflections

110 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0919P)^2 + 0.0037P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.82 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.71 \text{ e } \text{\AA}^{-3}$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

|     | $x$          | $y$          | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| S   | 0.67465 (5)  | -0.13645 (8) | 0.21545 (2)  | 0.02768 (11)                     |
| O1  | 0.66596 (17) | -0.4361 (3)  | 0.22175 (9)  | 0.0400 (3)                       |
| H1  | 0.5717       | -0.4774      | 0.2218       | 0.060*                           |
| O2  | 0.5491 (2)   | -0.0595 (3)  | 0.14085 (8)  | 0.0515 (4)                       |
| O3  | 0.85241 (16) | -0.0898 (3)  | 0.22478 (7)  | 0.0365 (3)                       |
| O4  | 0.64241 (17) | -0.0315 (3)  | 0.28174 (8)  | 0.0408 (3)                       |
| N1  | 0.9071 (2)   | 0.3742 (3)   | 0.39016 (9)  | 0.0430 (4)                       |
| H1A | 0.8905       | 0.4952       | 0.4181       | 0.052*                           |
| H1B | 0.8390       | 0.3583       | 0.3416       | 0.052*                           |
| N2  | 1.06403 (19) | 0.0245 (3)   | 0.37781 (8)  | 0.0319 (3)                       |
| H2  | 0.9966       | 0.0117       | 0.3291       | 0.038*                           |
| N3  | 1.1419 (2)   | 0.2419 (3)   | 0.49787 (8)  | 0.0358 (3)                       |
| C1  | 1.0366 (2)   | 0.2136 (3)   | 0.42160 (9)  | 0.0295 (3)                       |
| C2  | 1.1941 (2)   | -0.1444 (3)  | 0.40855 (11) | 0.0376 (3)                       |
| H2A | 1.2105       | -0.2737      | 0.3774       | 0.045*                           |
| C3  | 1.3011 (3)   | -0.1248 (4)  | 0.48528 (12) | 0.0429 (4)                       |

## supplementary materials

|    |            |            |              |            |
|----|------------|------------|--------------|------------|
| H3 | 1.3912     | -0.2404    | 0.5085       | 0.051*     |
| C4 | 1.2703 (3) | 0.0753 (4) | 0.52752 (10) | 0.0418 (4) |
| H4 | 1.3442     | 0.0939     | 0.5799       | 0.050*     |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|----|--------------|--------------|--------------|---------------|--------------|---------------|
| S  | 0.03166 (18) | 0.02383 (17) | 0.02574 (16) | -0.00177 (13) | 0.00914 (13) | -0.00139 (13) |
| O1 | 0.0418 (7)   | 0.0245 (5)   | 0.0581 (8)   | -0.0021 (5)   | 0.0240 (6)   | -0.0020 (5)   |
| O2 | 0.0539 (9)   | 0.0493 (9)   | 0.0337 (6)   | -0.0035 (7)   | -0.0023 (6)  | 0.0068 (6)    |
| O3 | 0.0380 (6)   | 0.0388 (7)   | 0.0365 (6)   | -0.0084 (5)   | 0.0186 (5)   | -0.0057 (5)   |
| O4 | 0.0423 (7)   | 0.0420 (7)   | 0.0409 (6)   | 0.0016 (5)    | 0.0192 (5)   | -0.0115 (5)   |
| N1 | 0.0456 (8)   | 0.0428 (9)   | 0.0325 (7)   | 0.0091 (7)    | 0.0062 (6)   | -0.0061 (6)   |
| N2 | 0.0408 (7)   | 0.0292 (6)   | 0.0263 (5)   | -0.0040 (5)   | 0.0135 (5)   | -0.0039 (5)   |
| N3 | 0.0420 (7)   | 0.0361 (8)   | 0.0250 (6)   | -0.0001 (6)   | 0.0084 (5)   | -0.0043 (5)   |
| C1 | 0.0361 (7)   | 0.0266 (6)   | 0.0255 (6)   | -0.0042 (6)   | 0.0116 (5)   | -0.0025 (5)   |
| C2 | 0.0461 (9)   | 0.0287 (7)   | 0.0438 (9)   | -0.0005 (7)   | 0.0238 (8)   | -0.0030 (7)   |
| C3 | 0.0450 (9)   | 0.0396 (10)  | 0.0436 (9)   | 0.0093 (8)    | 0.0168 (8)   | 0.0075 (8)    |
| C4 | 0.0439 (9)   | 0.0468 (10)  | 0.0289 (7)   | 0.0016 (8)    | 0.0078 (7)   | 0.0022 (7)    |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|            |             |           |             |
|------------|-------------|-----------|-------------|
| S—O2       | 1.4288 (14) | N2—C1     | 1.350 (2)   |
| S—O3       | 1.4535 (13) | N2—H2     | 0.8600      |
| S—O4       | 1.4588 (13) | N3—C4     | 1.324 (3)   |
| S—O1       | 1.5690 (17) | N3—C1     | 1.349 (2)   |
| O1—H1      | 0.8200      | C2—C3     | 1.355 (3)   |
| N1—C1      | 1.314 (2)   | C2—H2A    | 0.9300      |
| N1—H1A     | 0.8600      | C3—C4     | 1.385 (3)   |
| N1—H1B     | 0.8600      | C3—H3     | 0.9300      |
| N2—C2      | 1.343 (2)   | C4—H4     | 0.9300      |
| O2—S—O3    | 113.94 (9)  | C4—N3—C1  | 117.25 (16) |
| O2—S—O4    | 113.37 (10) | N1—C1—N3  | 119.05 (16) |
| O3—S—O4    | 110.72 (8)  | N1—C1—N2  | 120.26 (15) |
| O2—S—O1    | 108.21 (9)  | N3—C1—N2  | 120.69 (16) |
| O3—S—O1    | 103.46 (8)  | N2—C2—C3  | 119.50 (17) |
| O4—S—O1    | 106.34 (9)  | N2—C2—H2A | 120.3       |
| S—O1—H1    | 109.5       | C3—C2—H2A | 120.3       |
| C1—N1—H1A  | 120.0       | C2—C3—C4  | 116.90 (18) |
| C1—N1—H1B  | 120.0       | C2—C3—H3  | 121.5       |
| H1A—N1—H1B | 120.0       | C4—C3—H3  | 121.5       |
| C2—N2—C1   | 121.60 (15) | N3—C4—C3  | 124.04 (17) |
| C2—N2—H2   | 119.2       | N3—C4—H4  | 118.0       |
| C1—N2—H2   | 119.2       | C3—C4—H4  | 118.0       |

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

|                |     |              |              |                |
|----------------|-----|--------------|--------------|----------------|
| D—H $\cdots$ A | D—H | H $\cdots$ A | D $\cdots$ A | D—H $\cdots$ A |
|----------------|-----|--------------|--------------|----------------|

|                          |      |      |             |     |
|--------------------------|------|------|-------------|-----|
| O1—H1…O4 <sup>i</sup>    | 0.82 | 1.79 | 2.6100 (19) | 174 |
| N1—H1B…O1 <sup>ii</sup>  | 0.86 | 2.38 | 3.140 (2)   | 148 |
| N1—H1B…O4                | 0.86 | 2.58 | 3.155 (2)   | 125 |
| N1—H1A…N3 <sup>iii</sup> | 0.86 | 2.16 | 3.017 (2)   | 172 |
| N2—H2…O3                 | 0.86 | 1.91 | 2.756 (2)   | 168 |
| C2—H2A…O3 <sup>iv</sup>  | 0.93 | 2.40 | 3.294 (2)   | 160 |
| C3—H3…O2 <sup>v</sup>    | 0.93 | 2.51 | 3.262 (3)   | 138 |
| C4—H4…O4 <sup>vi</sup>   | 0.93 | 2.53 | 3.316 (2)   | 142 |

Symmetry codes: (i)  $-x+1, y-1/2, -z+1/2$ ; (ii)  $x, y+1, z$ ; (iii)  $-x+2, -y+1, -z+1$ ; (iv)  $-x+2, y-1/2, -z+1/2$ ; (v)  $x+1, -y-1/2, z+1/2$ ; (vi)  $-x+2, -y, -z+1$ .

Fig. 1

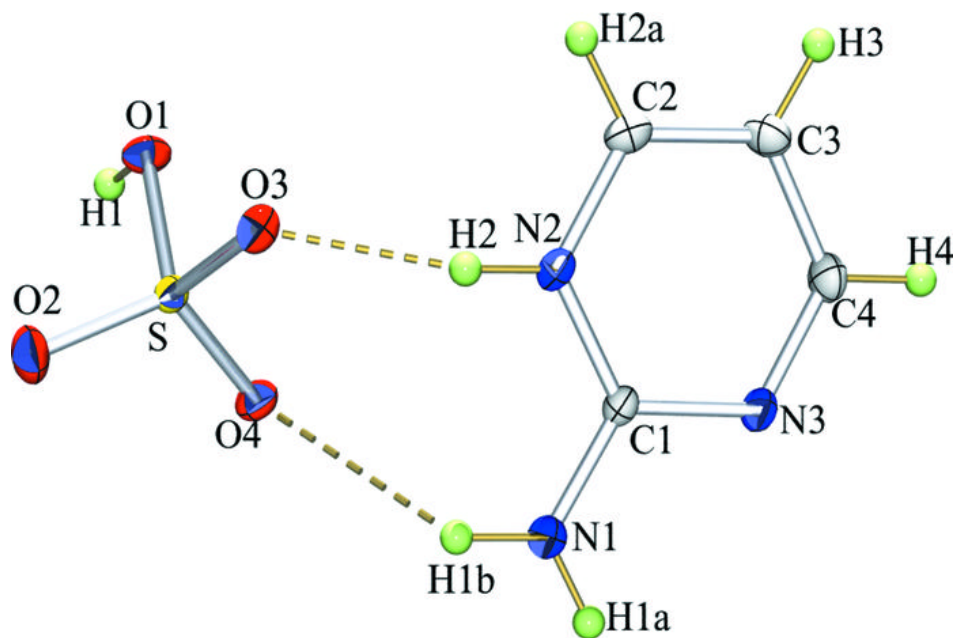




Fig. 2

