6-Amino-2-iminiumyl-4-oxo-1,2,3,4-tetrahydro-pyrimidin-5-aminium sulfate monohydrate

Lukas Tapmeyer* and Dragica Prill

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The title compound, $C_4H_9N_5O^{2+}\cdot SO_4^{2-}\cdot H_2O$, is the monohydrate of the commercially available compound '$C_4H_7N_5O\cdot H_2SO_4\cdot xH_2O$'. It is obtained by reprecipitation of $C_4H_7N_5O\cdot H_2SO_4\cdot xH_2O$ from dilute sodium hydroxide solution with dilute sulfuric acid. The crystal structure of anhydrous 2,4,5-triamino-1,6-dihydropyrimidin-6-one sulfate is known, although called by the authors 5-amminium-6-amino-isocytosinium sulfate [Bieri *et al.* (1993). Private communication (refcode HACDEU). CCDC, Cambridge, England]. In the structure, the sulfate group is deprotonated, whereas one of the amino groups is protonated ($R_2C-NH_3^+$) and one is rearranged to a protonated imine group ($R_2C=NH_2^+$). This arrangement is very similar to the known crystal structure of the anhydrate. Several tautomeric forms of the investigated molecule are possible, which leads to questionable proton attributions. The measured data allowed the location of all hydrogen atoms from the residual electron density. In the crystal, ions and water molecules are linked into a three-dimensional network by $N-H\cdots O$ and $O-H\cdots O$ hydrogen bonds.
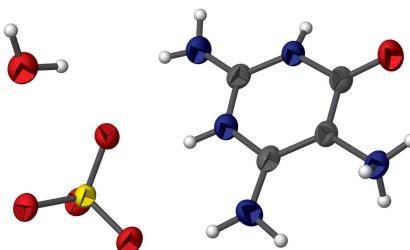
3D view	Chemical scheme
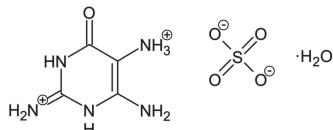
Structure description

2,4,5-Triamino-1,6-dihydropyrimidin-6-one (also called 2,4,5-triamino-6-hydroxy-pyrimidine sulfate) and/or its tautomer 2,4,5-triamino-6-hydroxypyrimidine are relevant starting materials for either very basic (Traube, 1900) or more advanced organic syntheses, including natural materials such as butterfly-wing pigments (Purrmann, 1940) and potential novel antiviral lead structures (Abbas *et al.*, 2017). The structure of the monohydrate form is herewith elucidated and confirms the protonation of the known structure (CSD refcode: HACDEU; Bieri *et al.*, 1993).

The title compound crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit is composed of one organic dication ($[C_4H_9N_5O]^{2+}$), one sulfate anion and one water

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N8—H8A···O4[i]	0.89	2.46	3.113 (4)	131
N8—H8A···O5[i]	0.89	1.99	2.827 (4)	157
N8—H8B···O3[ii]	0.89	1.94	2.788 (4)	159
N8—H8C···O5[iii]	0.89	2.13	2.942 (4)	152
N9—H9···O4[iv]	0.82 (4)	1.93 (4)	2.739 (5)	168 (4)
N10—H10···O2	0.88 (4)	1.87 (4)	2.677 (4)	152 (3)
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N11—H11A···O2	0.80 (5)	2.56 (7)	3.106 (6)	126 (5)
N11—H11A···OW1[v]	0.80 (5)	2.29 (5)	2.956 (4)	142 (5)
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N13—H13A···OW1[ii]	0.98 (6)	1.98 (7)	2.924 (5)	161 (5)
N13—H13B···O4	0.91 (5)	2.10 (5)	2.961 (4)	156 (5)
OW1—HW12···O2	0.96 (6)	2.10 (6)	2.798 (4)	128 (5)
OW1—HW11···OW1[vi]	0.96 (3)	2.59 (5)	3.390 (5)	141 (3)

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

molecule (Fig. 1). The present tautomer is the 2,4,5-triamino-1,6-dihydropyrimidin-6-one. The molecule is almost planar [r.m.s. deviation = 0.026 Å, maximum deviation 0.046 (4) Å for N13], except for the amino group H atoms.

The title compound shows a layered structure with the most polar compartments oriented in the (100) plane (Fig. 2). Within the layers, the dicationic molecules form hydrogen bonds to the water molecules and to the sulfate dianions. The layers are interlinked by hydrogen bonds between the sulfate dianion and the organic dication (Table 1).

Powder data confirmed the phase identity of the single crystals with experimentally obtained bulk material. Furthermore, a commercial sample of $C_4H_7N_5O\cdot H_2SO_4\cdot xH_2O$ could be quantitatively analyzed by Rietveld refinement with *TOPAS* (Coelho, 2018; Rietveld, 2010), resulting in a composition of 76.4 (3)% of the known anhydrate phase and 23.6 (3)% of the monohydrate described in this paper (Fig. 3). Since the monohydrate is a yellow solid and the anhydrous form rather colorless, the brown color of the commercial sample could be attributed to minor (and probably amorphous) impurities.


Figure 2
Partial packing diagram of the title compound viewed along the *a* axis.

Synthesis and crystallization

5 g (~20 mmol) of brown 2,4,5-triamino-6-hydroxypyrimidine sulfate ($C_4H_7N_5OH_2\cdot SO_4\cdot xH_2O$) as purchased from TCI (purity > 90.0%) were dissolved under stirring at 70°C in 100 ml of water with 2 g of sodium hydroxide (~50 mmol). The resulting reddish orange solution (with a pH of about 9–10) was filtered into a solution of 2.6 g of H_2SO_4 (96%, 25 mmol) in 900 ml water. The instantaneously formed red-to-brown aggregates were left to settle down for two h and the suspension was then filtered. The yellow filtrate was left at room temperature overnight. The formed pale-yellow crystals of the title compound were filtered off on a nutsch flask. The obtained yield for one purification cycle was about 15%. For efficiency, the filtrate can be boiled down and the brown solid precipitate can be reused in the next batch.

Figure 1
The asymmetric unit of the title compound with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
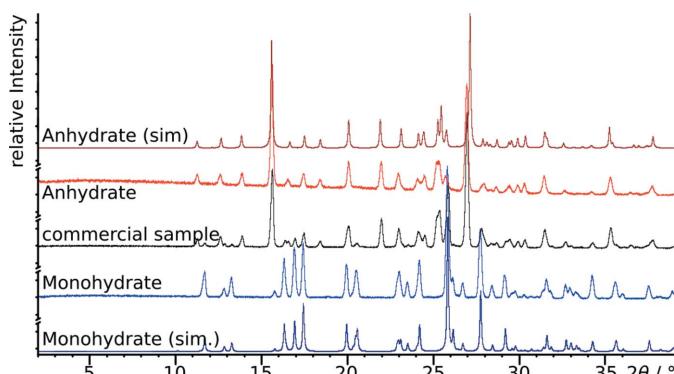

Figure 3
X-ray powder diagrams of (from top to bottom) the known anhydrous title compound (simulated, dark red), the vacuum-dried title compound (red), the commercial sample (black), the title compound (blue) and the pattern simulated from the title compound's single-crystal structure (dark blue).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_9N_5O^{2+}\cdot SO_4{}^{2-}\cdot H_2O$
M_r	257.24
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	7.0128 (7), 7.9882 (8), 9.0732 (9)
α, β, γ (°)	74.121 (4), 86.734 (4), 79.290 (4)
V (Å^3)	480.36 (8)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.34
Crystal size (mm)	$0.2 \times 0.15 \times 0.1$
Data collection	
Diffractometer	Siemens Bruker CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.526, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20827, 1720, 1599
R_{int}	0.051
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.080, 0.281, 1.40
No. of reflections	1720
No. of parameters	179
No. of restraints	20
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.63, −1.04

Computer programs: *APEX3* (Bruker, 2012), *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008), *ORTEPIII* (Burnett & Johnson, 1996) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2.

X-ray powder diffraction data were recorded at room temperature in transmission geometry on a Stoe Stadi-P diffractometer equipped with a curved Ge(111) primary monochromator and a linear position-sensitive detector, using Cu $K\alpha_1$ radiation (λ =1.5406 Å). Samples were rotated in 0.7 mm glass capillaries during measurement.

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full crystallographic data

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Crystal data
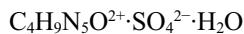
$C_4H_9N_5O^{2+} \cdot SO_4^{2-} \cdot H_2O$
$M_r = 257.24$
Triclinic, $P\bar{1}$
$a = 7.0128$ (7) Å
$b = 7.9882$ (8) Å
$c = 9.0732$ (9) Å
$\alpha = 74.121$ (4)°
$\beta = 86.734$ (4)°
$\gamma = 79.290$ (4)°
$V = 480.36$ (8) Å^3

$Z = 2$
$F(000) = 268$
$D_x = 1.778$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 9522 reflections
$\theta = 2.5–69.4°$
$\mu = 3.34$ mm^{-1}
$T = 296$ K
Block, pale yellow
$0.2 \times 0.15 \times 0.1$ mm

Data collection

Siemens Bruker CCD
    diffractometer
Radiation source: microfocus tube
ω and Phi scans
Absorption correction: multi-scan
    (SADABS; Bruker, 2015)
$T_{min} = 0.526$, $T_{max} = 0.753$
20827 measured reflections

1720 independent reflections
1599 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 71.1°$, $\theta_{min} = 5.1°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.281$
$S = 1.40$
1720 reflections
179 parameters
20 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent
    and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}
Extinction correction: SHELXL2018
    (Sheldrick, 2015b),
    Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.081 (15)

Special details

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

Refinement. All H atoms could be located by difference Fourier synthesis. Subsequently, H atoms bound to N atoms were refined using a riding model with the amino N–H distances constrained to 0.85 Å and the imino N–H distances constrained to 0.88 Å. For the H atoms of the amino groups, free rotation about their local threefold axis was allowed and their isotropic displacement parameters were set to $U_{iso}(H) = 1.5U_{eq}(N)$. The coordinates of the H atoms of the water molecules were refined with the O–H distances restrained to 0.84 (1) Å and the H–H distance restrained to 1.4 (1) Å. Their isotropic displacement parameters were coupled to the equivalent isotropic displacement parameters of the O atoms, with $U_{iso}(H) = 1.2U_{eq}(O)$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
S1	0.29190 (9)	0.72804 (10)	0.15928 (8)	0.0303 (6)
O2	0.3943 (4)	0.5471 (3)	0.1724 (3)	0.0397 (8)
O3	0.4276 (3)	0.8537 (4)	0.1119 (3)	0.0389 (8)
O4	0.2063 (4)	0.7360 (4)	0.3111 (3)	0.0430 (8)
O5	0.1362 (4)	0.7771 (4)	0.0452 (3)	0.0418 (8)
O6	0.2171 (5)	−0.1764 (4)	0.6728 (3)	0.0520 (9)
N8	0.2102 (4)	0.0973 (4)	0.8136 (3)	0.0338 (8)
H8A	0.098160	0.160461	0.833726	0.051*
H8B	0.307806	0.133069	0.847810	0.051*
H8C	0.211936	−0.016627	0.859976	0.051*
N9	0.2573 (4)	0.0009 (4)	0.4352 (3)	0.0354 (8)
H9	0.237 (4)	−0.085 (5)	0.410 (4)	0.028 (10)*
N10	0.2669 (4)	0.2969 (4)	0.3967 (3)	0.0369 (8)
H10	0.2779 (14)	0.401 (6)	0.335 (6)	0.076 (17)*
N11	0.2988 (6)	0.1773 (6)	0.1914 (4)	0.0481 (10)
H11A	0.325 (7)	0.261 (8)	0.128 (6)	0.055 (15)*
H11B	0.325 (7)	0.092 (7)	0.143 (6)	0.053 (14)*
C12	0.2422 (5)	0.2849 (5)	0.5513 (4)	0.0340 (9)
N13	0.2327 (5)	0.4357 (4)	0.5902 (4)	0.0412 (9)
H13A	0.200 (8)	0.434 (8)	0.697 (7)	0.073 (17)*
H13B	0.225 (7)	0.546 (7)	0.525 (6)	0.054 (13)*
C14	0.2309 (4)	0.1216 (5)	0.6496 (4)	0.0310 (9)
C15	0.2338 (5)	−0.0280 (5)	0.5956 (4)	0.0348 (9)
C16	0.2728 (5)	0.1591 (5)	0.3394 (4)	0.0353 (9)
OW1	0.7873 (5)	0.5365 (4)	0.0944 (3)	0.0496 (9)
HW12	0.687 (8)	0.467 (8)	0.119 (11)	0.16 (4)*
HW11	0.916 (4)	0.473 (7)	0.089 (8)	0.11 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0287 (8)	0.0328 (8)	0.0267 (8)	−0.0044 (5)	0.0017 (4)	−0.0048 (5)
O2	0.0407 (14)	0.0326 (15)	0.0406 (14)	−0.0032 (11)	0.0047 (10)	−0.0041 (11)

O3	0.0345 (13)	0.0414 (15)	0.0413 (15)	−0.0126 (11)	0.0060 (11)	−0.0094 (11)
O4	0.0493 (16)	0.0475 (17)	0.0340 (14)	−0.0118 (12)	0.0090 (12)	−0.0135 (13)
O5	0.0341 (13)	0.0532 (18)	0.0351 (14)	−0.0035 (11)	−0.0040 (10)	−0.0090 (12)
O6	0.075 (2)	0.0427 (18)	0.0351 (15)	−0.0137 (15)	0.0071 (13)	−0.0042 (13)
N8	0.0305 (14)	0.0418 (18)	0.0259 (15)	−0.0051 (12)	−0.0006 (11)	−0.0046 (13)
N9	0.0453 (16)	0.0334 (18)	0.0261 (16)	−0.0069 (13)	0.0025 (12)	−0.0063 (13)
N10	0.0466 (17)	0.0348 (18)	0.0274 (16)	−0.0073 (13)	0.0027 (12)	−0.0056 (13)
N11	0.070 (2)	0.043 (2)	0.0274 (16)	−0.0072 (17)	0.0056 (15)	−0.0061 (17)
C12	0.0307 (15)	0.040 (2)	0.0272 (17)	−0.0040 (14)	0.0026 (13)	−0.0050 (15)
N13	0.061 (2)	0.0304 (18)	0.0309 (16)	−0.0055 (14)	0.0007 (14)	−0.0073 (13)
C14	0.0297 (15)	0.0329 (19)	0.0258 (17)	−0.0026 (13)	−0.0013 (12)	−0.0018 (14)
C15	0.0351 (16)	0.035 (2)	0.0270 (17)	0.0000 (14)	−0.0019 (13)	0.0009 (14)
C16	0.0362 (17)	0.040 (2)	0.0274 (16)	−0.0037 (14)	0.0023 (13)	−0.0074 (15)
OW1	0.0542 (18)	0.0508 (19)	0.0437 (17)	−0.0107 (14)	0.0046 (14)	−0.0125 (14)

Geometric parameters (Å, º)

S1—O2	1.466 (3)	N10—C12	1.382 (4)
S1—O5	1.471 (2)	N10—H10	0.88 (4)
S1—O3	1.473 (2)	N11—C16	1.316 (5)
S1—O4	1.484 (3)	N11—H11A	0.80 (6)
O6—C15	1.223 (5)	N11—H11B	0.89 (5)
N8—C14	1.449 (4)	C12—N13	1.335 (5)
N8—H8A	0.8900	C12—C14	1.377 (5)
N8—H8B	0.8900	N13—H13A	0.98 (6)
N8—H8C	0.8900	N13—H13B	0.91 (5)
N9—C16	1.343 (5)	C14—C15	1.407 (5)
N9—C15	1.415 (4)	OW1—HW12	0.953 (10)
N9—H9	0.82 (3)	OW1—HW11	0.954 (10)
N10—C16	1.333 (5)		
O2—S1—O5	110.53 (16)	C16—N11—H11B	128 (3)
O2—S1—O3	110.29 (15)	H11A—N11—H11B	102 (5)
O5—S1—O3	108.68 (14)	N13—C12—C14	126.4 (3)
O2—S1—O4	108.20 (15)	N13—C12—N10	115.6 (3)
O5—S1—O4	109.32 (14)	C14—C12—N10	118.0 (3)
O3—S1—O4	109.81 (14)	C12—N13—H13A	117 (4)
C14—N8—H8A	109.5	C12—N13—H13B	126 (3)
C14—N8—H8B	109.5	H13A—N13—H13B	115 (4)
H8A—N8—H8B	109.5	C12—C14—C15	121.8 (3)
C14—N8—H8C	109.5	C12—C14—N8	121.3 (3)
H8A—N8—H8C	109.5	C15—C14—N8	116.9 (3)
H8B—N8—H8C	109.5	O6—C15—C14	126.6 (3)
C16—N9—C15	123.3 (3)	O6—C15—N9	118.4 (3)
C16—N9—H9	125 (3)	C14—C15—N9	115.0 (3)
C15—N9—H9	110 (3)	N11—C16—N10	120.3 (4)
C16—N10—C12	122.8 (3)	N11—C16—N9	120.6 (4)
C16—N10—H10	120 (4)	N10—C16—N9	119.0 (3)

C12—N10—H10	117 (4)	HW12—OW1—HW11	116 (5)	
C16—N11—H11A	128 (4)			

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
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OW1—HW12⋯O2	0.96 (6)	2.10 (6)	2.798 (4)	128 (5)
OW1—HW11⋯OW1[vi]	0.96 (3)	2.59 (5)	3.390 (5)	141 (3)

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