

2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate

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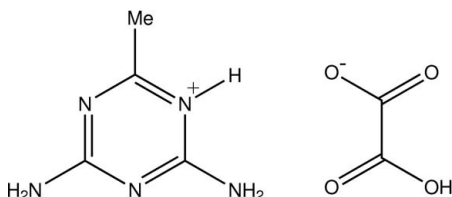
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 13.5.

The title compound, $\text{C}_4\text{H}_8\text{N}_5^+ \cdot \text{C}_2\text{HO}_4^-$, was obtained from the reaction of oxalic acid and 2,4-diamino-6-methyl-1,3,5-triazine. The protonated triazine ring is essentially planar with a maximum deviation of 0.035 (1) Å, but the hydrogen oxalate anion is less planar, with a maximum deviation of 0.131 (1) Å for both carbonyl O atoms. In the crystal, the ions are linked by intermolecular $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{N}$, $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional network. Weak $\pi-\pi$ [centroid-centroid distance = 3.763 Å] and $\text{C}-\text{O} \cdots \pi$ interactions [$\text{O} \cdots \text{centroid} = 3.5300$ (16) Å, $\text{C}-\text{O} \cdots \text{centroid} = 132.19$ (10)°] are also present.

Related literature

For bond-length data see: Allen *et al.* (1987) and for a description of the Cambridge Structural Database, see: Allen (2002). For background to triazine derivatives, see: Sebenik *et al.* (1989). For related structures, see: Kaczmarek *et al.* (2008); Xiao (2008); Fan *et al.* (2009); Qian & Huang (2010).



Experimental

Crystal data

$\text{C}_4\text{H}_8\text{N}_5^+ \cdot \text{C}_2\text{HO}_4^-$
 $M_r = 215.18$
 Triclinic, $P\bar{1}$
 $a = 5.6208$ (12) Å
 $b = 7.9828$ (17) Å
 $c = 10.857$ (2) Å
 $\alpha = 76.846$ (4)°
 $\beta = 75.882$ (4)°
 $\gamma = 75.954$ (4)°
 $V = 450.92$ (17) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 298$ K
 $0.50 \times 0.22 \times 0.19$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.935$, $T_{\max} = 0.974$
 5551 measured reflections
 1959 independent reflections
 1708 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.113$
 $S = 1.03$
 1959 reflections
 145 parameters
 1 restraint
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N3}-\text{H3} \cdots \text{O1}^{\text{i}}$	0.95 (2)	1.77 (2)	2.7134 (17)	174 (2)
$\text{N3}-\text{H3} \cdots \text{O4}^{\text{i}}$	0.95 (2)	2.50 (2)	2.9841 (17)	111.7 (16)
$\text{O4}-\text{H4} \cdots \text{O2}$	0.83 (2)	1.66 (2)	2.4921 (16)	175 (2)
$\text{N4}-\text{H4D} \cdots \text{O3}^{\text{ii}}$	0.86	2.17	2.9902 (19)	160
$\text{N4}-\text{H4E} \cdots \text{N1}^{\text{iii}}$	0.86	2.18	3.0399 (19)	174
$\text{N5}-\text{H5A} \cdots \text{N2}^{\text{iv}}$	0.86	2.14	3.0027 (19)	179
$\text{N5}-\text{H5B} \cdots \text{O2}^{\text{v}}$	0.86	2.28	2.8558 (17)	124
$\text{N5}-\text{H5B} \cdots \text{O3}^{\text{v}}$	0.86	2.59	3.2337 (19)	133
$\text{C4}-\text{H4C} \cdots \text{O1}^{\text{vi}}$	0.96	2.49	3.339 (2)	148

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2157).

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supporting information

Acta Cryst. (2012). E68, o1475 [https://doi.org/10.1107/S1600536812016637]

2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate

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S1. Comment

It is known that many triazine derivatives possess biological properties beside its usefulness as intermediates in the pharmaceutical industry (Sebenik *et al.*, 1989). 2,4-diamino-6-methyl-1,3,5-triazine has been reported to co-crystallize with methanol (Kaczmarek *et al.*, 2008) and ethanol (Xiao, 2008). On the other hand, the triazine nitrogen atom at position 1 can be easily protonated as in compound $(C_4H_8N_5)Cl$ (Qian & Huang, 2010) and $(C_4H_8N_5)NO_3$ (Fan *et al.*, 2009) which were obtained from the normal acid-base reaction. The title compound is a similar salt but having a hydrogen oxalate as counter anion (Fig. 1). The non hydrogen triazine ring, C1/N1/C2/N2/C3/N3, is planar with a maximum deviation of 0.035 (1) Å from the least square plane for N3 atom. The hydrogen oxalate anion O1/C1/O2/C2/O3/O4, is less planar with a maximum deviation of 0.131 (1) Å for O1 and O4 atoms. The bond lengths and angles are in normal ranges (Allen *et al.*, 1987; Allen, 2002). In the crystal structure the molecules are linked by N—H $\cdots$ O, N—H $\cdots$ N, O—H $\cdots$ O and C—H $\cdots$ O intermolecular hydrogen bonds (symmetry codes as in Table 2) to form a three-dimensional network (Fig. 2). In addition, there are weak π – π interactions between the triazine ring centroids Cg1 (symmetry code: 1-x, -y, 1-z) with a distance of 3.763 Å and a C6—O3 $\cdots\pi$ involving the triazine (C1/N1/C2/N2/C3/N3) centroid (symmetry code: 1-x, 1-y, 1-z) with a O3 $\cdots$ Cg1 distance of 3.5300 (16) Å and a C6—O3—Cg1 bond angle of 132.19 (10)°.

S2. Experimental

10 ml aqueous solution of ammonium thiocyanate (0.152 g, 2 mmol) was added into a beaker containing oxalate acid (0.126 g, 1 mmol) and 2,4-diamino-6-methyl-1,3,5-triazine (2 mmol) in 40 ml distilled water. After one week of evaporation at room temperature colourless crystals were obtained. Yield 92%; Melting point: 457.1–458.3 K.

S3. Refinement

After their location in the difference map, the H-atoms attached to the C and the amino N atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H = 0.93 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(N)$. However, the protonated amino and hydroxyl hydrogen atoms were located from the Fourier map and refined isotropically.

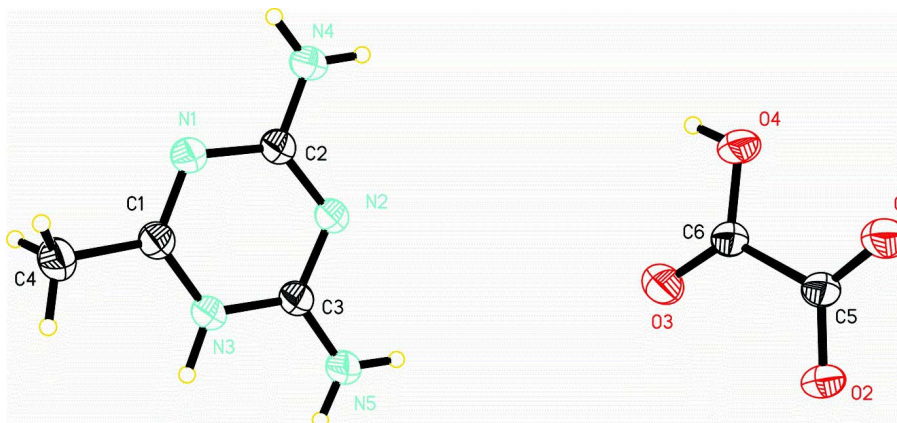


Figure 1

Molecular structure of the title compound with 50% probability displacement ellipsoids.

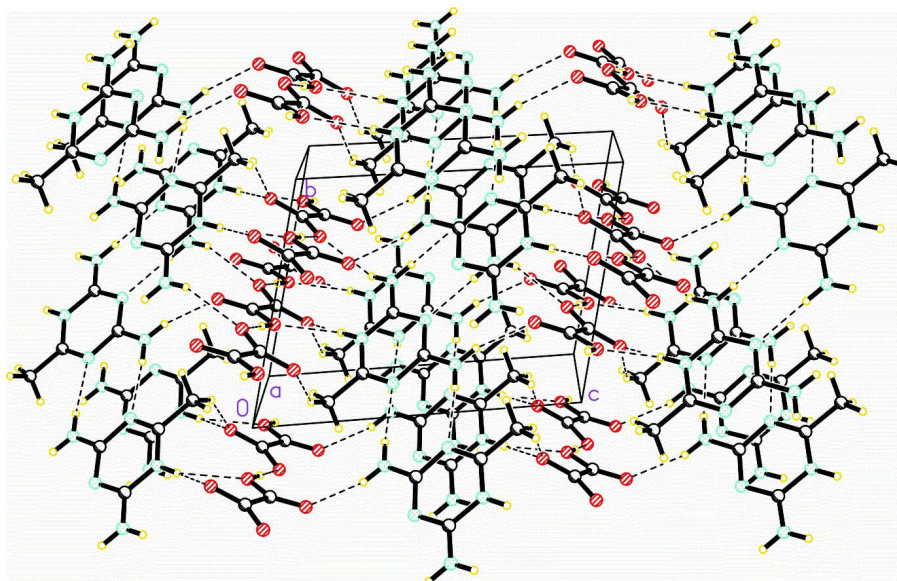


Figure 2

Packing diagram of the title compound viewed down *a* axis. The dashed lines denote hydrogen bonds.

2,4-Diamino-6-methyl-1,3,5-triazin-1-ium hydrogen oxalate

Crystal data

$\text{C}_4\text{H}_8\text{N}_5^+ \cdot \text{C}_2\text{HO}_4^-$

$M_r = 215.18$

Triclinic, $P\bar{1}$

Hall symbol: $-\text{P } 1$

$a = 5.6208$ (12) Å

$b = 7.9828$ (17) Å

$c = 10.857$ (2) Å

$\alpha = 76.846$ (4)°

$\beta = 75.882$ (4)°

$\gamma = 75.954$ (4)°

$V = 450.92$ (17) Å³

$Z = 2$

$F(000) = 224$

$D_x = 1.585$ Mg m⁻³

Melting point = 492.2–492.5 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1963 reflections

$\theta = 1.9$ – 27.0°

$\mu = 0.13$ mm⁻¹

$T = 298$ K

Block, colourless

$0.50 \times 0.22 \times 0.19$ mm

Data collection

Bruker SMART APEX CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 83.66 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.935$, $T_{\max} = 0.974$

5551 measured reflections

1959 independent reflections

1708 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -7 \rightarrow 7$

$k = -10 \rightarrow 10$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.113$

$S = 1.03$

1959 reflections

145 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.0976P]$

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

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

$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	1.01323 (19)	0.22067 (16)	1.09284 (10)	0.0435 (3)
O2	1.20977 (17)	0.36561 (14)	0.91142 (9)	0.0383 (3)
O3	0.8189 (2)	0.38620 (18)	0.80042 (10)	0.0490 (3)
O4	0.60164 (18)	0.30135 (15)	0.99698 (10)	0.0401 (3)
H4	0.476 (3)	0.322 (3)	0.964 (2)	0.076 (7)*
N1	0.2651 (2)	0.08398 (15)	0.40173 (11)	0.0342 (3)
N2	0.3693 (2)	0.31924 (15)	0.46944 (11)	0.0326 (3)
N3	0.5937 (2)	0.21615 (15)	0.28003 (11)	0.0324 (3)
H3	0.733 (4)	0.221 (2)	0.2103 (19)	0.049 (5)*
N4	0.0411 (2)	0.18887 (17)	0.58245 (12)	0.0421 (3)
H4D	0.0102	0.2572	0.6377	0.051*
H4E	-0.0506	0.1130	0.5922	0.051*
N5	0.7025 (2)	0.43757 (17)	0.34456 (12)	0.0393 (3)
H5A	0.6827	0.5064	0.3983	0.047*
H5B	0.8206	0.4415	0.2771	0.047*

C1	0.4493 (3)	0.09606 (17)	0.30219 (13)	0.0307 (3)
C2	0.2280 (3)	0.20042 (18)	0.48339 (13)	0.0316 (3)
C3	0.5530 (3)	0.32675 (18)	0.36537 (12)	0.0302 (3)
C4	0.5070 (3)	−0.0268 (2)	0.21033 (15)	0.0400 (4)
H4A	0.5078	−0.1442	0.2574	0.060*
H4B	0.6685	−0.0204	0.1560	0.060*
H4C	0.3822	0.0048	0.1580	0.060*
C5	1.0268 (2)	0.30348 (18)	0.98158 (13)	0.0296 (3)
C6	0.8009 (2)	0.33563 (18)	0.91548 (13)	0.0301 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0288 (5)	0.0646 (7)	0.0332 (6)	−0.0124 (5)	−0.0051 (4)	0.0009 (5)
O2	0.0237 (5)	0.0565 (7)	0.0344 (6)	−0.0147 (4)	−0.0014 (4)	−0.0052 (5)
O3	0.0351 (6)	0.0828 (9)	0.0297 (6)	−0.0157 (6)	−0.0046 (4)	−0.0093 (5)
O4	0.0234 (5)	0.0622 (7)	0.0351 (6)	−0.0161 (5)	−0.0038 (4)	−0.0035 (5)
N1	0.0374 (7)	0.0359 (6)	0.0315 (6)	−0.0161 (5)	0.0015 (5)	−0.0103 (5)
N2	0.0381 (6)	0.0360 (6)	0.0262 (6)	−0.0158 (5)	0.0009 (5)	−0.0091 (5)
N3	0.0344 (6)	0.0375 (6)	0.0265 (6)	−0.0140 (5)	0.0022 (5)	−0.0097 (5)
N4	0.0467 (7)	0.0500 (8)	0.0340 (7)	−0.0264 (6)	0.0091 (5)	−0.0165 (6)
N5	0.0447 (7)	0.0487 (7)	0.0297 (6)	−0.0263 (6)	0.0048 (5)	−0.0124 (5)
C1	0.0338 (7)	0.0308 (6)	0.0282 (7)	−0.0090 (5)	−0.0039 (5)	−0.0061 (5)
C2	0.0353 (7)	0.0343 (7)	0.0263 (7)	−0.0126 (6)	−0.0019 (5)	−0.0064 (5)
C3	0.0338 (7)	0.0337 (7)	0.0241 (6)	−0.0117 (5)	−0.0031 (5)	−0.0045 (5)
C4	0.0471 (9)	0.0389 (8)	0.0360 (8)	−0.0132 (6)	0.0003 (6)	−0.0147 (6)
C5	0.0222 (6)	0.0375 (7)	0.0291 (7)	−0.0064 (5)	−0.0002 (5)	−0.0110 (5)
C6	0.0247 (6)	0.0381 (7)	0.0289 (7)	−0.0084 (5)	−0.0013 (5)	−0.0103 (5)

Geometric parameters (Å, °)

O1—C5	1.2322 (17)	N4—C2	1.3112 (18)
O2—C5	1.2560 (16)	N4—H4D	0.8600
O3—C6	1.2093 (17)	N4—H4E	0.8600
O4—C6	1.2913 (16)	N5—C3	1.3104 (18)
O4—H4	0.831 (10)	N5—H5A	0.8600
N1—C1	1.3054 (18)	N5—H5B	0.8600
N1—C2	1.3727 (17)	C1—C4	1.4812 (19)
N2—C3	1.3329 (17)	C4—H4A	0.9600
N2—C2	1.3400 (17)	C4—H4B	0.9600
N3—C1	1.3465 (17)	C4—H4C	0.9600
N3—C3	1.3643 (18)	C5—C6	1.5476 (19)
N3—H3	0.950 (19)		
C6—O4—H4	113.8 (16)	N2—C2—N1	124.86 (12)
C1—N1—C2	116.03 (12)	N5—C3—N2	120.67 (12)
C3—N2—C2	116.42 (11)	N5—C3—N3	118.55 (12)
C1—N3—C3	119.67 (12)	N2—C3—N3	120.76 (12)

C1—N3—H3	122.3 (11)	C1—C4—H4A	109.5
C3—N3—H3	117.8 (11)	C1—C4—H4B	109.5
C2—N4—H4D	120.0	H4A—C4—H4B	109.5
C2—N4—H4E	120.0	C1—C4—H4C	109.5
H4D—N4—H4E	120.0	H4A—C4—H4C	109.5
C3—N5—H5A	120.0	H4B—C4—H4C	109.5
C3—N5—H5B	120.0	O1—C5—O2	127.05 (13)
H5A—N5—H5B	120.0	O1—C5—C6	118.95 (12)
N1—C1—N3	122.20 (12)	O2—C5—C6	113.99 (12)
N1—C1—C4	119.85 (12)	O3—C6—O4	126.24 (13)
N3—C1—C4	117.95 (12)	O3—C6—C5	121.73 (12)
N4—C2—N2	119.38 (12)	O4—C6—C5	112.03 (11)
N4—C2—N1	115.75 (12)		
C2—N1—C1—N3	−0.4 (2)	C2—N2—C3—N5	−179.22 (13)
C2—N1—C1—C4	178.65 (13)	C2—N2—C3—N3	−1.0 (2)
C3—N3—C1—N1	1.8 (2)	C1—N3—C3—N5	177.20 (13)
C3—N3—C1—C4	−177.27 (13)	C1—N3—C3—N2	−1.1 (2)
C3—N2—C2—N4	−178.67 (14)	O1—C5—C6—O3	−166.01 (14)
C3—N2—C2—N1	2.5 (2)	O2—C5—C6—O3	13.0 (2)
C1—N1—C2—N4	179.32 (13)	O1—C5—C6—O4	13.65 (18)
C1—N1—C2—N2	−1.8 (2)	O2—C5—C6—O4	−167.33 (12)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N3—H3 $\cdots$ O1 ⁱ	0.95 (2)	1.77 (2)	2.7134 (17)	174 (2)
N3—H3 $\cdots$ O4 ⁱ	0.95 (2)	2.50 (2)	2.9841 (17)	111.7 (16)
O4—H4 $\cdots$ O2	0.83 (2)	1.66 (2)	2.4921 (16)	175 (2)
N4—H4D $\cdots$ O3 ⁱⁱ	0.86	2.17	2.9902 (19)	160
N4—H4E $\cdots$ N1 ⁱⁱⁱ	0.86	2.18	3.0399 (19)	174
N5—H5A $\cdots$ N2 ^{iv}	0.86	2.14	3.0027 (19)	179
N5—H5B $\cdots$ O2 ^v	0.86	2.28	2.8558 (17)	124
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C4—H4C $\cdots$ O1 ^{vi}	0.96	2.49	3.339 (2)	148

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