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3,4-Diaminopyridinium hydrogen squarate

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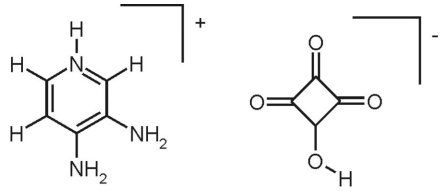
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.066; wR factor = 0.189; data-to-parameter ratio = 11.0.

Anions and cations of the title compound, $C_5H_8N_3^+\cdot C_4HO_4^-$, are connected by moderately strong intermolecular N—H···O hydrogen bonds into an infinite three-dimensional network. Hydrogen squarate anions form dimers through strong O—H···O interactions.

Related literature

For related literature, see: Kolev *et al.* (2004, 2007); Kolev, Fiser *et al.* (2005); Kolev, Wortmann *et al.* (2005).



Experimental

Crystal data

$C_5H_8N_3^+\cdot C_4HO_4^-$
M_r = 223.19
Monoclinic, $P2_1/c$
a = 10.069 (2) Å
b = 7.1925 (14) Å
c = 13.480 (3) Å
β = 96.56 (3)°
V = 969.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 294 (2) K
0.58 × 0.48 × 0.46 mm

Data collection

Siemens $P4$ four-circle diffractometer
Absorption correction: ψ scan (*XPREP*; Sheldrick, 1995)
T_{min} = 0.844, T_{max} = 0.938
2310 measured reflections
1698 independent reflections
1172 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.189
S = 1.09
1698 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3′—H3′···O2′^{i}	0.82	1.76	2.539 (3)	159
N2—H21···O1′^{ii}	0.86	2.13	2.972 (4)	166
N1—H1···O4′^{iii}	0.86	2.01	2.799 (4)	152
N2—H22···O2′^{iv}	0.86	2.14	2.973 (3)	164

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

Data collection: *R3m/V* (Siemens, 1989); cell refinement: *R3m/V*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2412).

References

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supplementary materials

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3,4-Diaminopyridinium hydrogen squarate

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Comment

In the course of our spectroscopic and structural studies of pyridine derivatives (Kolev *et al.*, 2004; Kolev, Wortmann *et al.*,2005; Kolev, Fiser *et al.*, 2005; Kolev *et al.*, 2007), the crystal structure of 3,4-diaminopyridinium hydrogensquarate is reported. Its molecular structure is depicted in Fig. 1. The crystal structure consists of chains of cations and anions connected by moderate hydrogen bonds (Fig. 2) with N···O lengths of 2.799 (4), 2.972 (4) and 2.973 (4) Å, respectively. Hydrogensquarate anions are linked into centrosymmetric dimers by strong O—H···O [O···O = 2.539 (3) Å] interactions.

Experimental

3,4-diaminopyridinium hydrogensquarate was obtained by mixing an equimolar ratio of 3,4-diaminopyridine (Merck) and squaric acid (Sigma-Aldrich) in 10 ml e thanol. Suitable crystals for X-ray analysis, were grown by allowing the solution to slowly evaporate for 10 days, and were subsequently filtered off, washed with methanol and dried under air.

Refinement

H atoms were constrained to idealized positions and refined using a riding model, with C—H distances of 0.93 Å [U_{iso}(H) = 1.2 U_{iso}(C)], NH distances of 0.86 Å [U_{iso}(H) = 1.5 U_{iso}(N) and O—H distances of 0.82 Å [U_{iso}(H) = 1.5 U_{iso}(O)].

Figures

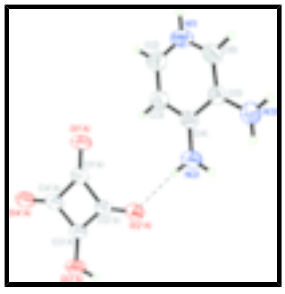

Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

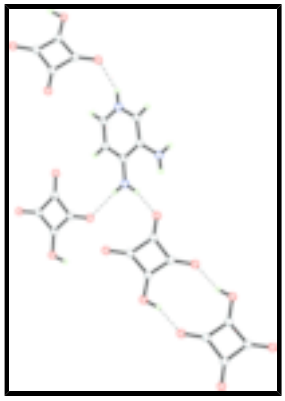

Fig. 2. Hydrogen bonding between the anions and cations of (I).

3,4-Diaminopyridinium hydrogen squarate

Crystal data

$C_5H_8N_3^+·C_4HO_4^-$	F_{000} = 464
M_r = 223.19	D_x = 1.529 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 27 reflections
a = 10.069 (2) Å	θ = 7.5–15º
b = 7.1925 (14) Å	μ = 0.12 mm^{-1}
c = 13.480 (3) Å	T = 294 (2) K
β = 96.56 (3)º	Prsim, colourless
V = 969.8 (3) Å^3	0.58 × 0.48 × 0.46 mm
Z = 4	

Data collection

Siemens P4 four-circle diffractometer	R_{int} = 0.044
Radiation source: fine-focus sealed tube	θ_{max} = 25.0º
Monochromator: graphite	θ_{min} = 2.0º
T = 294(2) K	h = −1→11
ω scans	k = −1→8
Absorption correction: ψ scan (XPREP; Sheldrick, 1995)	l = −16→16
T_{min} = 0.844, T_{max} = 0.938	3 standard reflections
2310 measured reflections	every 100 reflections
1698 independent reflections	intensity decay: 1%
1172 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.066$	H-atom parameters constrained
$wR(F^2) = 0.189$	$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.5492P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
1698 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.7328 (3)	0.3740 (5)	1.0145 (2)	0.0559 (9)
H1	0.6586	0.3990	1.0375	0.067*
C2	0.8249 (3)	0.2759 (5)	1.0705 (3)	0.0520 (9)
H2	0.8086	0.2368	1.1338	0.062*
C3	0.9425 (3)	0.2325 (5)	1.0359 (2)	0.0472 (9)
H3	1.0057	0.1624	1.0754	0.057*
N2	1.0874 (2)	0.2506 (4)	0.9064 (2)	0.0498 (8)
H21	1.1031	0.2865	0.8480	0.060*
H22	1.1465	0.1877	0.9434	0.060*
C4	0.9699 (3)	0.2929 (5)	0.9401 (2)	0.0400 (8)
N3	0.8886 (3)	0.4537 (5)	0.7857 (2)	0.0568 (9)
H31	0.8270	0.5150	0.7503	0.068*
H32	0.9620	0.4277	0.7619	0.068*
C5	0.8693 (3)	0.3965 (5)	0.8816 (2)	0.0403 (8)
C6	0.7522 (3)	0.4362 (5)	0.9219 (3)	0.0511 (9)
H6	0.6860	0.5061	0.8854	0.061*
C1'	0.2926 (3)	0.0429 (5)	0.2041 (2)	0.0429 (8)
O1'	0.1804 (2)	0.0879 (4)	0.22347 (18)	0.0579 (8)
C2'	0.3618 (3)	0.0417 (5)	0.1124 (2)	0.0417 (8)
O2'	0.3283 (2)	0.0894 (4)	0.02326 (16)	0.0519 (7)
C3'	0.4780 (3)	−0.0317 (5)	0.1697 (2)	0.0414 (8)
O3'	0.5998 (2)	−0.0799 (4)	0.15119 (17)	0.0576 (8)
H3'	0.6030	−0.0814	0.0907	0.086*
C4'	0.4173 (3)	−0.0327 (5)	0.2619 (3)	0.0465 (9)

O4'	0.4548 (2)	−0.0753 (4)	0.34977 (18)	0.0589 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0358 (14)	0.072 (2)	0.062 (2)	−0.0045 (15)	0.0139 (13)	−0.0134 (18)
C2	0.049 (2)	0.060 (2)	0.048 (2)	−0.0107 (18)	0.0109 (16)	−0.0025 (18)
C3	0.0440 (17)	0.052 (2)	0.0449 (19)	−0.0018 (16)	0.0021 (14)	−0.0001 (17)
N2	0.0357 (14)	0.063 (2)	0.0504 (17)	0.0070 (13)	0.0061 (12)	0.0012 (15)
C4	0.0335 (15)	0.0413 (18)	0.0444 (18)	−0.0026 (14)	0.0012 (13)	−0.0080 (15)
N3	0.0509 (17)	0.076 (2)	0.0430 (17)	0.0126 (16)	0.0020 (13)	0.0090 (16)
C5	0.0364 (16)	0.0447 (19)	0.0389 (17)	−0.0023 (14)	−0.0003 (13)	−0.0048 (15)
C6	0.0375 (17)	0.056 (2)	0.058 (2)	0.0015 (16)	−0.0040 (15)	−0.0087 (19)
C1'	0.0296 (15)	0.053 (2)	0.0465 (18)	−0.0003 (14)	0.0043 (13)	−0.0021 (16)
O1'	0.0304 (11)	0.090 (2)	0.0544 (14)	0.0110 (12)	0.0107 (10)	0.0002 (14)
C2'	0.0284 (15)	0.053 (2)	0.0438 (18)	0.0011 (14)	0.0040 (13)	−0.0060 (16)
O2'	0.0322 (11)	0.0770 (18)	0.0462 (14)	0.0142 (11)	0.0023 (9)	−0.0022 (13)
C3'	0.0277 (14)	0.056 (2)	0.0415 (18)	0.0034 (14)	0.0076 (12)	−0.0001 (16)
O3'	0.0303 (11)	0.094 (2)	0.0500 (14)	0.0170 (12)	0.0092 (10)	0.0092 (14)
C4'	0.0272 (15)	0.059 (2)	0.053 (2)	0.0003 (15)	0.0026 (14)	−0.0006 (18)
O4'	0.0330 (12)	0.095 (2)	0.0495 (14)	0.0065 (12)	0.0070 (10)	0.0134 (14)

Geometric parameters (Å, °)

N1—C2	1.330 (5)	N3—H32	0.8600
N1—C6	1.360 (5)	C5—C6	1.383 (4)
N1—H1	0.8600	C6—H6	0.9300
C2—C3	1.358 (5)	C1'—O1'	1.232 (4)
C2—H2	0.9300	C1'—C2'	1.486 (4)
C3—C4	1.420 (5)	C1'—C4'	1.501 (4)
C3—H3	0.9300	C2'—O2'	1.259 (4)
N2—C4	1.349 (4)	C2'—C3'	1.427 (4)
N2—H21	0.8600	C3'—O3'	1.325 (3)
N2—H22	0.8600	C3'—C4'	1.446 (4)
C4—C5	1.421 (4)	O3'—H3'	0.8200
N3—C5	1.391 (4)	C4'—O4'	1.241 (4)
N3—H31	0.8600		
C2—N1—C6	122.1 (3)	C6—C5—C4	118.4 (3)
C2—N1—H1	118.9	N3—C5—C4	120.3 (3)
C6—N1—H1	118.9	N1—C6—C5	120.7 (3)
N1—C2—C3	120.4 (3)	N1—C6—H6	119.7
N1—C2—H2	119.8	C5—C6—H6	119.7
C3—C2—H2	119.8	O1'—C1'—C2'	134.9 (3)
C2—C3—C4	120.7 (3)	O1'—C1'—C4'	135.9 (3)
C2—C3—H3	119.7	C2'—C1'—C4'	89.2 (2)
C4—C3—H3	119.7	O2'—C2'—C3'	137.0 (3)
C4—N2—H21	120.0	O2'—C2'—C1'	133.8 (3)
C4—N2—H22	120.0	C3'—C2'—C1'	89.2 (3)

H21—N2—H22	120.0	O3'—C3'—C2'	135.6 (3)
N2—C4—C5	121.9 (3)	O3'—C3'—C4'	130.7 (3)
N2—C4—C3	120.4 (3)	C2'—C3'—C4'	93.8 (2)
C5—C4—C3	117.7 (3)	C3'—O3'—H3'	109.5
C5—N3—H31	120.0	O4'—C4'—C3'	135.2 (3)
C5—N3—H32	120.0	O4'—C4'—C1'	136.9 (3)
H31—N3—H32	120.0	C3'—C4'—C1'	87.9 (3)
C6—C5—N3	121.3 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3'—H3'···O2'^{i}	0.82	1.76	2.539 (3)	159
N2—H21···O1'^{ii}	0.86	2.13	2.972 (4)	166
N1—H1···O4'^{iii}	0.86	2.01	2.799 (4)	152
N2—H22···O2'^{iv}	0.86	2.14	2.973 (3)	164

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) *x*+1, −*y*+1/2, *z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) *x*+1, *y*, *z*+1.

Fig. 1

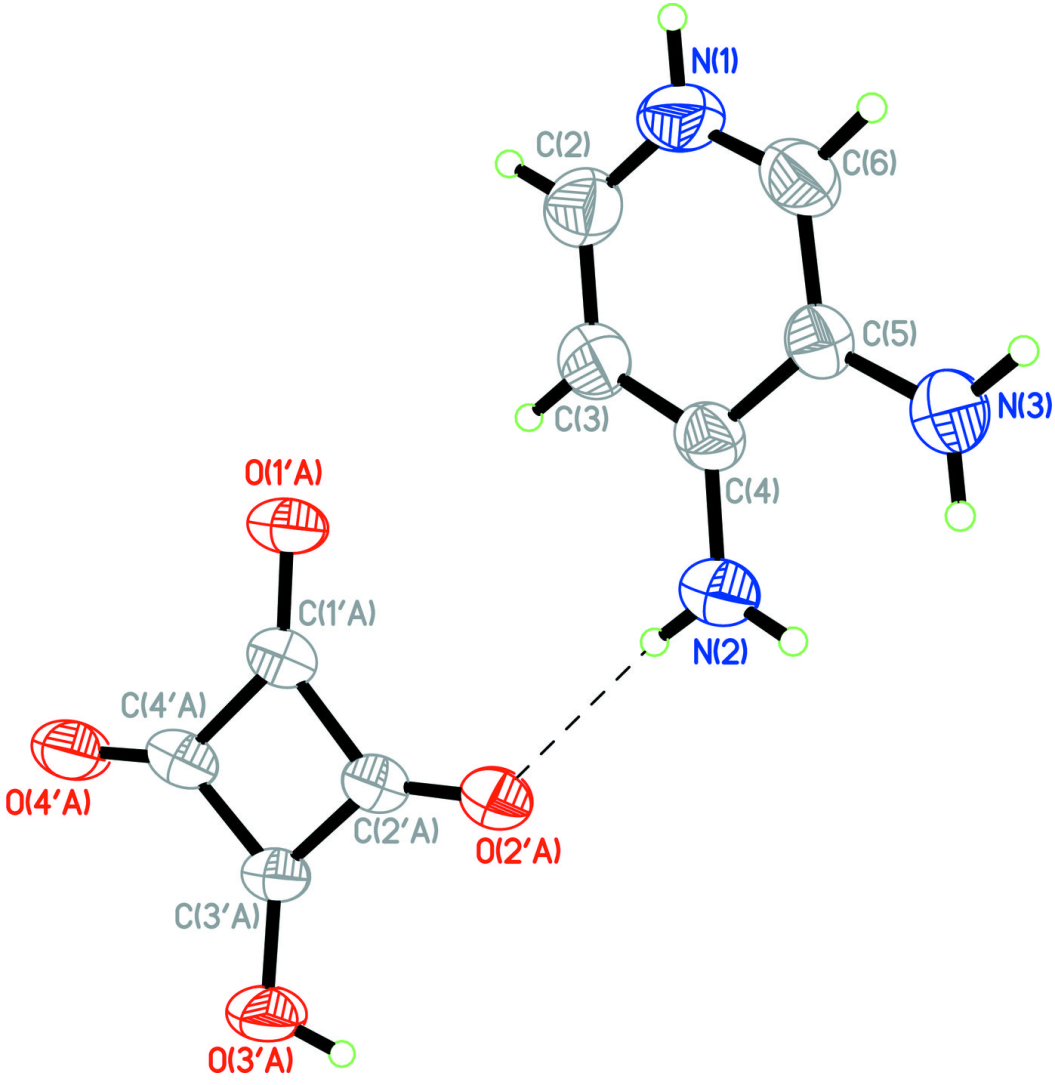

Fig. 2