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4-Aminopyridinium isonicotinate monohydrate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.090
Data-to-parameter ratio = 11.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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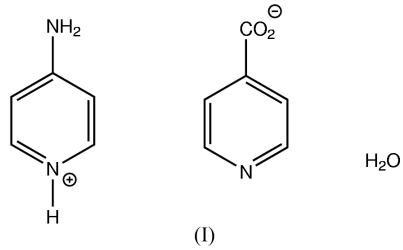
The 4-aminopyridinium isonicotinate salt was isolated as a monohydrate, $C_5H_7N_2^+\cdot C_6H_4NO_2^-\cdot H_2O$, with a layered cation–water–anion structure. Hydrogen-bonding between layers utilizes all hydrogen-bonding donors and acceptors, whilst π stacking dominates interactions within the organic layers.

Comment

The isonicotinate anion is well known as a ligand capable of forming supramolecular metal–organic structures. Here, the serendipitous isolation of the title compound, (I), highlights that it is also capable of supporting organic supramolecular architectures. Isolated with the 4-aminopyridinium cation [itself well known in studies of organic supramolecular structures; see for example Cowan *et al.* (2001) and Teulon *et al.* (1985)], (I) is found as a monohydrate (Fig. 1) with, in the *c* direction, alternating layers of cations and anions separated by water molecules (Fig. 2). These layers are held together by the participation of all the molecular fragments in a three-dimensional hydrogen-bonding network. Each cation acts as a threefold donor using all its N—H bonds, each anion acts as a fourfold acceptor with atom O1 accepting two hydrogen bonds and atoms O2 and N1 accepting one each, and the water molecule both accepts a single hydrogen-bond and acts as a twofold donor. Within each organic layer, π stacking interactions are observed. The shortest such contacts appear between antiparallel 4-aminopyridinium cations, with a centroid-to-centroid distance of 3.473 Å, whilst the isonicotinate anions are separated by 3.520 Å.



(I)

Experimental

Compound (I) was formed during an attempt to prepare *N*-(pyridine-4-methylene)pyridin-4-amine. 4-Aminopyridine (1.24 g, 13.2 mmol) was dissolved in anhydrous xylene (80 ml), and pyridine-4-carbaldehyde (1.3 ml, 13.6 mmol) and acetic acid (0.38 ml, 6.6 mmol) were added dropwise with stirring. The mixture was heated to reflux in a Dean–Stark apparatus for 20 h. After removing the solvent *in vacuo*, a yellow oil was obtained. Crystalline (I) was obtained from a

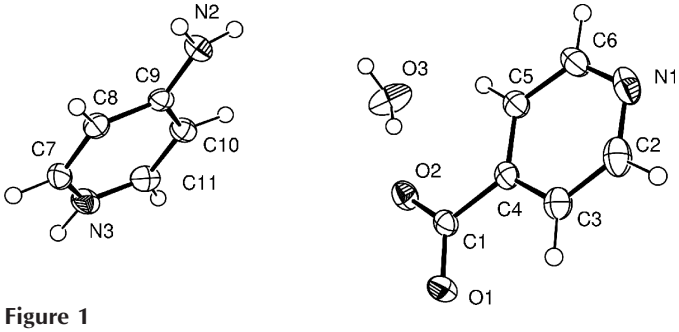


Figure 1
Asymmetric unit of (I), shown with 50% probability displacement ellipsoids.

chloroform solution of this oil after layering with diethyl ether (1.64 g, 53% yield). IR (KBr, cm^{-1}): 677, 769, 1204, 1373, 1542, 1603, 1650, 3415.

Crystal data

$C_5H_7N_2^+\cdot C_6H_4NO_2^-\cdot H_2O$	$Z = 2$
$M_r = 235.24$	$D_x = 1.351$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 6.7128$ (3) Å	Cell parameters from 2294 reflections
$b = 6.7911$ (2) Å	$\theta = 1.0$–$26.4°$
$c = 13.6379$ (8) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 75.830$ (3)°	$T = 123$ (2) K
$\beta = 75.999$ (2)°	Cut plate, colourless
$\gamma = 78.326$ (3)°	0.45 × 0.37 × 0.10 mm
$V = 578.08$ (5) Å^3	

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.030$
ω and φ scans	$\theta_{max} = 26.4°$
Absorption correction: none	$h = -8 \rightarrow 8$
9253 measured reflections	$k = -8 \rightarrow 8$
2348 independent reflections	$l = -17 \rightarrow 17$
1848 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.1136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.090$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
2348 reflections	Extinction correction: *SHELXL97*
207 parameters	Extinction coefficient: 0.046 (11)
All H-atom parameters refined	

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3N···N1^{i}	0.957 (19)	1.854 (19)	2.7978 (16)	167.9 (16)
N2—H2N···O3^{ii}	0.921 (18)	1.911 (18)	2.8313 (18)	175.8 (14)
N2—H1N···O1^{iii}	0.890 (18)	1.938 (19)	2.8283 (16)	177.5 (15)
O3—H1W···O2	0.89 (2)	1.86 (2)	2.7369 (15)	172.1 (18)
O3—H2W···O1^{iii}	0.85 (2)	1.92 (2)	2.7635 (15)	173 (2)

Symmetry codes: (i) $x, y, z+1$; (ii) $x+1, y, z$; (iii) $x, y+1, z$.

All H-atom parameters were refined freely; C—H distances are in the range 0.953 (16)–0.993 (16) Å.

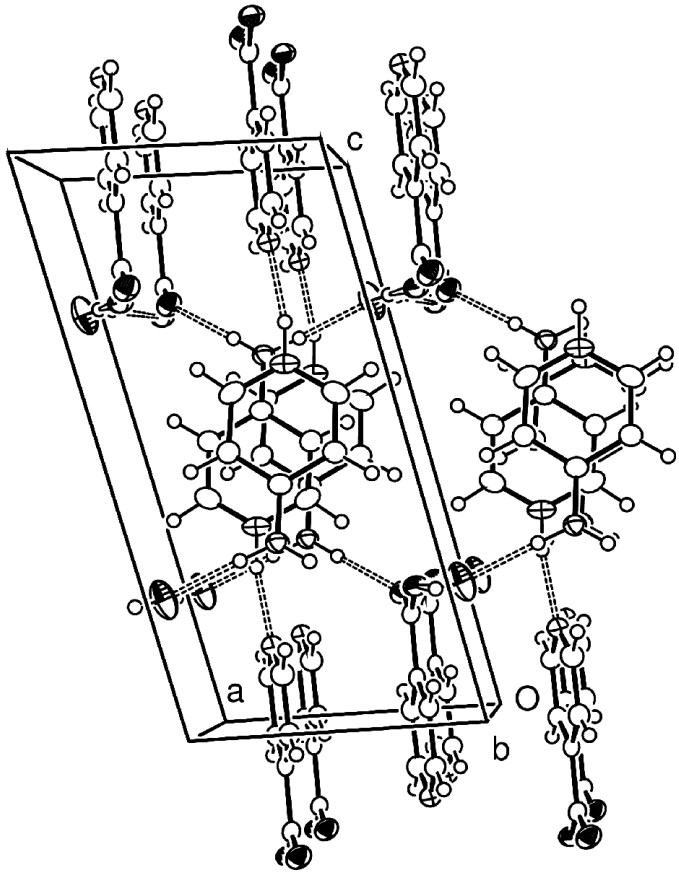


Figure 2
Packing diagram of (I), viewed down the b axis. Dashed lines indicate hydrogen bonds.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1988); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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$V = 578.08$ (5) Å^3
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$F(000) = 248$
$D_x = 1.351$ Mg m^{-3}
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Cell parameters from 2294 reflections
$\theta = 1.0$–$26.4°$
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Cut plate, colourless
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Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
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9253 measured reflections
2348 independent reflections
1848 reflections with $I > 2\sigma(I)$
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$\theta_{max} = 26.4°$, $\theta_{min} = 1.6°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.090$
$S = 1.04$
2348 reflections
207 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.1136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.046 (11)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.22409 (15)	0.15150 (13)	0.22438 (7)	0.0316 (3)
O2	0.14675 (14)	0.48046 (14)	0.23744 (7)	0.0290 (3)
O3	−0.04150 (18)	0.87519 (19)	0.24467 (10)	0.0483 (3)
N1	0.30325 (18)	0.5187 (2)	−0.14614 (9)	0.0343 (3)
N2	0.5281 (2)	0.90081 (17)	0.33110 (9)	0.0261 (3)
N3	0.35573 (19)	0.65430 (17)	0.63958 (9)	0.0301 (3)
C1	0.20050 (19)	0.34213 (19)	0.18639 (10)	0.0233 (3)
C2	0.3330 (2)	0.3211 (2)	−0.09781 (11)	0.0345 (4)
C3	0.3025 (2)	0.2581 (2)	0.00823 (11)	0.0281 (3)
C4	0.23968 (18)	0.40528 (19)	0.06936 (10)	0.0221 (3)
C5	0.2115 (2)	0.6099 (2)	0.01998 (10)	0.0251 (3)
C6	0.2442 (2)	0.6593 (2)	−0.08700 (11)	0.0303 (3)
C7	0.5595 (2)	0.64381 (19)	0.59471 (11)	0.0280 (3)
C8	0.6208 (2)	0.72207 (18)	0.49221 (10)	0.0242 (3)
C9	0.4716 (2)	0.81926 (17)	0.43125 (10)	0.0220 (3)
C10	0.2598 (2)	0.82558 (19)	0.48123 (10)	0.0254 (3)
C11	0.2077 (2)	0.7433 (2)	0.58388 (11)	0.0295 (3)
H3N	0.320 (3)	0.604 (3)	0.7125 (15)	0.051 (5)*
H2	0.378 (2)	0.219 (2)	−0.1425 (12)	0.040 (4)*
H1W	0.030 (3)	0.752 (3)	0.2392 (15)	0.060 (6)*
H2N	0.668 (3)	0.898 (2)	0.3041 (12)	0.037 (4)*
H3	0.325 (2)	0.109 (2)	0.0397 (12)	0.037 (4)*
H2W	0.048 (3)	0.953 (3)	0.2359 (16)	0.067 (6)*
H1N	0.433 (3)	0.977 (3)	0.2965 (13)	0.042 (5)*
H5	0.167 (2)	0.718 (2)	0.0595 (11)	0.024 (3)*
H6	0.225 (2)	0.800 (2)	−0.1230 (12)	0.037 (4)*
H7	0.659 (2)	0.578 (2)	0.6396 (12)	0.032 (4)*
H8	0.765 (2)	0.712 (2)	0.4621 (11)	0.027 (4)*
H10	0.153 (2)	0.889 (2)	0.4410 (12)	0.032 (4)*
H11	0.067 (2)	0.744 (2)	0.6204 (12)	0.034 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0368 (6)	0.0263 (5)	0.0301 (6)	−0.0058 (4)	−0.0126 (4)	0.0035 (4)
O2	0.0330 (5)	0.0318 (5)	0.0212 (5)	−0.0023 (4)	−0.0058 (4)	−0.0055 (4)
O3	0.0302 (6)	0.0324 (6)	0.0791 (9)	−0.0057 (5)	0.0027 (6)	−0.0182 (6)
N1	0.0254 (6)	0.0570 (8)	0.0208 (6)	−0.0095 (5)	−0.0047 (5)	−0.0060 (5)
N2	0.0269 (7)	0.0265 (6)	0.0216 (6)	−0.0016 (5)	−0.0040 (5)	−0.0014 (5)
N3	0.0437 (7)	0.0282 (6)	0.0175 (6)	−0.0076 (5)	−0.0033 (5)	−0.0040 (5)

C1	0.0192 (6)	0.0276 (7)	0.0227 (7)	−0.0048 (5)	−0.0067 (5)	−0.0010 (5)
C2	0.0286 (8)	0.0504 (9)	0.0271 (8)	−0.0049 (7)	−0.0039 (6)	−0.0155 (7)
C3	0.0237 (7)	0.0334 (8)	0.0281 (8)	−0.0029 (6)	−0.0059 (6)	−0.0087 (6)
C4	0.0152 (6)	0.0295 (7)	0.0220 (7)	−0.0045 (5)	−0.0051 (5)	−0.0036 (5)
C5	0.0208 (7)	0.0296 (7)	0.0244 (7)	−0.0055 (5)	−0.0053 (5)	−0.0027 (6)
C6	0.0249 (7)	0.0397 (8)	0.0238 (7)	−0.0092 (6)	−0.0067 (6)	0.0035 (6)
C7	0.0391 (8)	0.0228 (7)	0.0254 (7)	−0.0045 (6)	−0.0132 (6)	−0.0048 (5)
C8	0.0273 (7)	0.0211 (6)	0.0253 (7)	−0.0036 (5)	−0.0060 (6)	−0.0064 (5)
C9	0.0294 (7)	0.0157 (6)	0.0215 (7)	−0.0034 (5)	−0.0040 (5)	−0.0058 (5)
C10	0.0280 (7)	0.0220 (6)	0.0244 (7)	−0.0013 (5)	−0.0045 (6)	−0.0044 (5)
C11	0.0336 (8)	0.0264 (7)	0.0261 (8)	−0.0049 (6)	0.0014 (6)	−0.0081 (5)

Geometric parameters (Å, º)

O1—C1	1.2640 (15)	C3—C4	1.3924 (18)
O2—C1	1.2486 (15)	C3—H3	0.993 (16)
O3—H1W	0.89 (2)	C4—C5	1.3844 (18)
O3—H2W	0.85 (2)	C5—C6	1.3873 (19)
N1—C6	1.3370 (19)	C5—H5	0.971 (14)
N1—C2	1.341 (2)	C6—H6	0.961 (16)
N2—C9	1.3342 (16)	C7—C8	1.3610 (19)
N2—H2N	0.921 (18)	C7—H7	0.981 (16)
N2—H1N	0.890 (18)	C8—C9	1.4129 (19)
N3—C11	1.3516 (19)	C8—H8	0.954 (15)
N3—C7	1.3520 (19)	C9—C10	1.4171 (19)
N3—H3N	0.957 (19)	C10—C11	1.3614 (19)
C1—C4	1.5192 (18)	C10—H10	0.975 (16)
C2—C3	1.380 (2)	C11—H11	0.953 (16)
C2—H2	0.987 (16)		
H1W—O3—H2W	106.0 (19)	C4—C5—H5	120.6 (8)
C6—N1—C2	117.13 (12)	C6—C5—H5	120.2 (8)
C9—N2—H2N	117.4 (10)	N1—C6—C5	123.35 (13)
C9—N2—H1N	119.6 (11)	N1—C6—H6	116.0 (9)
H2N—N2—H1N	121.7 (15)	C5—C6—H6	120.7 (9)
C11—N3—C7	120.86 (12)	N3—C7—C8	120.80 (13)
C11—N3—H3N	121.0 (11)	N3—C7—H7	116.8 (9)
C7—N3—H3N	118.1 (11)	C8—C7—H7	122.4 (9)
O2—C1—O1	125.12 (12)	C7—C8—C9	120.31 (13)
O2—C1—C4	118.15 (11)	C7—C8—H8	119.3 (9)
O1—C1—C4	116.73 (11)	C9—C8—H8	120.4 (9)
N1—C2—C3	123.37 (13)	N2—C9—C8	121.35 (12)
N1—C2—H2	116.2 (9)	N2—C9—C10	121.65 (12)
C3—C2—H2	120.4 (9)	C8—C9—C10	117.00 (12)
C2—C3—C4	119.18 (13)	C11—C10—C9	120.09 (13)
C2—C3—H3	119.7 (9)	C11—C10—H10	120.8 (9)
C4—C3—H3	121.1 (9)	C9—C10—H10	119.1 (9)
C5—C4—C3	117.80 (12)	N3—C11—C10	120.93 (13)

C5—C4—C1	121.38 (12)	N3—C11—H11	116.3 (9)
C3—C4—C1	120.81 (11)	C10—C11—H11	122.8 (9)
C4—C5—C6	119.16 (13)		
C6—N1—C2—C3	1.1 (2)	C2—N1—C6—C5	−0.5 (2)
N1—C2—C3—C4	−0.7 (2)	C4—C5—C6—N1	−0.3 (2)
C2—C3—C4—C5	−0.27 (19)	C11—N3—C7—C8	−0.23 (18)
C2—C3—C4—C1	178.83 (12)	N3—C7—C8—C9	1.17 (18)
O2—C1—C4—C5	−1.76 (18)	C7—C8—C9—N2	178.61 (12)
O1—C1—C4—C5	177.80 (11)	C7—C8—C9—C10	−1.56 (17)
O2—C1—C4—C3	179.18 (11)	N2—C9—C10—C11	−179.09 (12)
O1—C1—C4—C3	−1.26 (17)	C8—C9—C10—C11	1.08 (18)
C3—C4—C5—C6	0.74 (18)	C7—N3—C11—C10	−0.26 (19)
C1—C4—C5—C6	−178.35 (11)	C9—C10—C11—N3	−0.19 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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