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4-Aminopyridinium isonicotinate monohydrate

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Key indicators

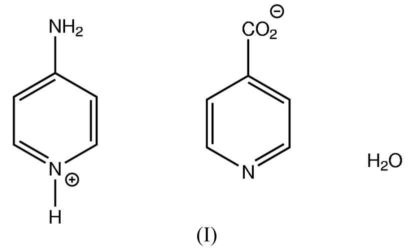
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.090
Data-to-parameter ratio = 11.3

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

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

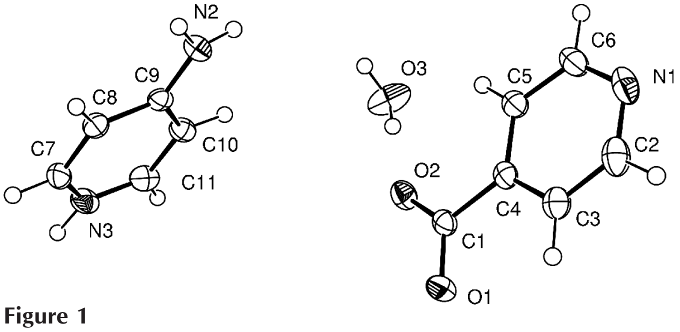


Figure 1
Asymmetric unit of (I), shown with 50% probability displacement ellipsoids.

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

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

Data collection

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

Refinement

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*N*···N1^{i}	0.957 (19)	1.854 (19)	2.7978 (16)	167.9 (16)
N2—H2*N*···O3^{ii}	0.921 (18)	1.911 (18)	2.8313 (18)	175.8 (14)
N2—H1*N*···O1^{iii}	0.890 (18)	1.938 (19)	2.8283 (16)	177.5 (15)
O3—H1*W*···O2	0.89 (2)	1.86 (2)	2.7369 (15)	172.1 (18)
O3—H2*W*···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.

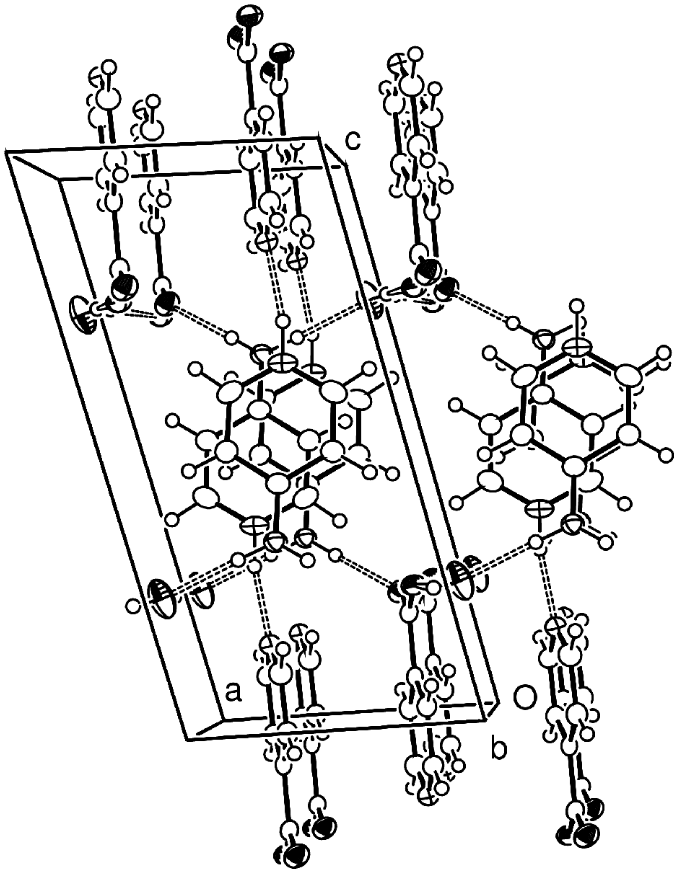


Figure 2
Packing diagram of (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

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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