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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.120
Data-to-parameter ratio = 14.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-Amino-3-methylpyridinium acetate

The title compound, $\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{C}_2\text{H}_3\text{O}_2^-$, contains eight- and sixteen-membered hydrogen-bonded rings involving 2-amino-3-methylpyridinium and acetate ions. The 2-amino-3-methylpyridinium and acetate ions are linked into zigzag chains by $\text{C}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. The dihedral angle between the 2-amino-3-methylpyridinium ring and the hydrogen-bonded acetate ion is $6.63(6)^\circ$. The heterocycle is fully protonated, enabling amine-imine tautomerization.

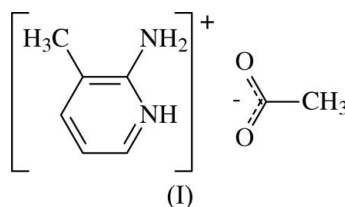
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Comment

Hydrogen bonding plays a key role in molecular recognition (Goswami & Ghosh, 1997) and crystal engineering research (Goswami *et al.*, 1998). The design of highly specific solid-state compounds is of considerable significance in organic chemistry due to the important applications of these compounds in the development of new optical, magnetic and electronic systems (Lehn, 1992). 2-Aminopyridine and its derivatives are used in the manufacture of pharmaceuticals, hair dyes and other dyes. The present work is part of a structural study of compounds of 2-amino-3-methylpyridinium systems with hydrogen-bond donors and we report here the structure of 2-amino-3-methylpyridinium acetate, (I) (Fig. 1).



In (I), the 2-amino-3-methylpyridinium ions are linked to the acetate ions through $\text{N1}-\text{H1}\cdots\text{O1}$ and $\text{N2}-\text{H2A}\cdots\text{O2}$ hydrogen bonds, resulting in the formation of eight-membered hydrogen-bonded rings (Fig. 1 and Table 2). The eight-membered hydrogen-bonded rings are linked by $\text{N2}-\text{H2B}\cdots\text{O2}$ and $\text{C5}-\text{H5}\cdots\text{O1}$ hydrogen bonds, forming a two-dimensional network. The hydrogen-bonded planes (two-dimensional network) are arranged so that $\text{C6}-\text{H6A}\cdots\text{O1}^{\text{iii}}$ hydrogen bonds form $R3_4^4[16]$ rings, resulting in a three-dimensional network (Fig. 2; symmetry code as in Table 2).

The 2-aminopyridine-carboxylic acid system has been the subject of theoretical (Inuzuka & Fujimoto, 1990) and spectroscopic (Inuzuka & Fujimoto, 1986) amine-imine tautomerization studies. 2-Aminopyridine and derivatives, like other organic bases, are protonated in acidic solution. The bonding of the H atom to the ring N atom of 2-aminopyridine rather than the amine N atom gives an ion for which an additional resonance structure can be written. As this mono-

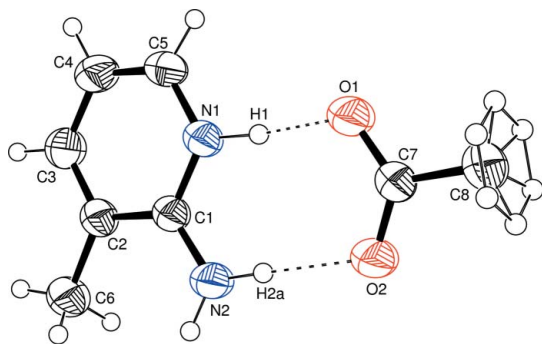


Figure 1

A view of the ion pair of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. Both disorder components are shown.

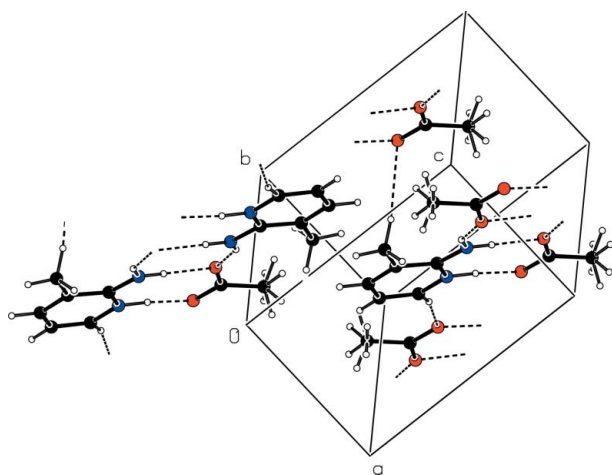


Figure 2

A packing diagram of the title compound, showing the hydrogen-bonding scheme (dashed lines).

cation has more resonance energy (additional ionic resonance) than 2-aminopyridine itself, 2-aminopyridine is a strong base, like amidines (Acheson, 1967).

The present investigation, like our previous work (Büyükgüngör & Odabaşoğlu, 2002, 2003; Odabaşoğlu, Büyükgüngör & Lönnecke, 2003; Odabaşoğlu, Büyükgüngör, Turgut *et al.*, 2003; Büyükgüngör *et al.*, 2004), clearly shows that the positive charge in the 2-aminopyridinium ion is on the amine group. Our investigations also show that the 2-amino-3-methylpyridinium cation is present in the crystal structure in a similar form and the methyl H atoms in the acetate show rotational disorder.

The C1–N2 bond length is approximately equal to that of a C=N double bond (Shanmuga Sundara Raj, Fun, Lu *et al.*, 2000), indicating that atom N2 of the amine group must also be sp^2 hybridized. This is also supported by the C1–N2–H2A angle of 117.2 (11)° (Table 1). Similar bond distances and angles have been observed in 2-aminopyridinium succinate succinic acid (Büyükgüngör & Odabaşoğlu, 2002), 2-aminopyridinium adipate monoacidic acid dihydrate (Odabaşoğlu, Büyükgüngör, Turgut *et al.*, 2003), bis(2-aminopyridinium) maleate (Büyükgüngör & Odabaşoğlu, 2003), 2-amino-

pyridinium fumarate fumaric acid (Büyükgüngör *et al.*, 2004) and in some 2-aminopyridine-containing molecules (Yang *et al.*, 1995; Grobelny *et al.*, 1995; Shanmuga Sundara Raj, Fun, Zhao *et al.*, 2000).

Experimental

The title compound was prepared by mixing 3-methyl-2-aminopyridine and acetic acid in a 1:1 molar ratio in water at 353 K. Crystals of (I) were obtained by slow evaporation of the solvent (m.p. 370–372 K).

Crystal data

$C_6H_9N_2^+ \cdot C_2H_3O_2^-$
 $M_r = 168.20$
 Triclinic, $P\bar{1}$
 $a = 7.0451$ (8) Å
 $b = 8.0502$ (10) Å
 $c = 8.5061$ (10) Å
 $\alpha = 65.756$ (9)°
 $\beta = 86.505$ (9)°
 $\gamma = 85.326$ (9)°
 $V = 438.21$ (10) Å³

$Z = 2$
 $D_x = 1.275$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 7421 reflections
 $\theta = 2.6$ – 28.0 °
 $\mu = 0.09$ mm⁻¹
 $T = 296$ (2) K
 Thick plate, colourless
 $0.64 \times 0.49 \times 0.24$ mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 7421 measured reflections
 2054 independent reflections
 1646 reflections with $I > 2\sigma(I)$

$R_{int} = 0.073$
 $\theta_{max} = 27.7$ °
 $h = -9 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.121$
 $S = 1.04$
 2054 reflections
 145 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.0553P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.19$ e Å⁻³
 $\Delta\rho_{min} = -0.17$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|-------------|--------------|
| C1–N2 | 1.3258 (16) | C7–O2 | 1.2385 (15) |
| C1–N1 | 1.3491 (15) | C7–O1 | 1.2532 (15) |
| C5–N1 | 1.3536 (16) | | |
| N2–C1–N1 | 117.94 (10) | O2–C7–O1 | 124.41 (12) |
| N2–C1–C2 | 123.09 (11) | | |
| N2–C1–C2–C3 | 178.99 (13) | N2–C1–N1–C5 | −179.15 (12) |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-----------------------------------|----------|--------------|--------------|----------------|
| N2–H2A \cdots O2 | 0.91 (2) | 1.89 (2) | 2.7992 (15) | 179 (2) |
| N2–H2B \cdots O2 ⁱ | 0.90 (2) | 2.03 (2) | 2.8426 (16) | 150 (2) |
| N1–H1 \cdots O1 | 1.01 (2) | 1.64 (2) | 2.6390 (14) | 174 (2) |
| C5–H5 \cdots O1 ⁱⁱ | 0.95 (2) | 2.42 (2) | 3.3566 (16) | 166 (1) |
| C6–H6A \cdots O1 ⁱⁱⁱ | 1.01 (2) | 2.60 (2) | 3.605 (2) | 172 (2) |

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

Refined C–H distances are in the range 0.94 (2)–0.98 (2) Å and U_{iso} values for H atoms are in the range 0.056 (4)–0.097 (7) Å². The H

atoms bounded to C8 were refined as an idealized disordered methyl group (two positions, each of site occupancy 0.5) in their calculated positions, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ of the parent atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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