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2-Aminopyridinium–fumarate–fumaric acid (2/1/1)

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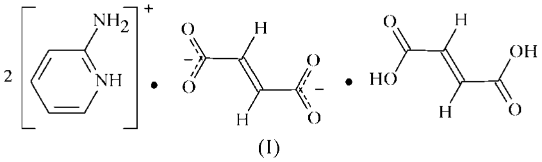
The title complex, $2C_5H_7N_2^+\cdot C_4H_2O_4^{2-}\cdot C_4H_4O_4$, contains cyclic eight-membered hydrogen-bonded rings involving 2-aminopyridinium and fumarate ions. The fumaric acid molecules and fumarate ions lie on inversion centers and are linked into zigzag chains by O—H···O hydrogen bonds. The dihedral angle between the pyridinium ring and the hydrogen-bonded fumarate ion is 7.60 (4)°. The fumarate anion is linked to the pyridinium cations by intermolecular N—H···O hydrogen bonds. The heterocycle is fully protonated, thus enabling amine–imine tautomerization.

Comment

The title complex was obtained from the reaction of 2-aminopyridine (used in the manufacture of pharmaceuticals, hair dyes and other dyes) and fumaric acid. 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). The present work is part of a structural study of complexes of 2-aminopyridinium systems with hydrogen-bond donors and we report here the structure of 2-aminopyridinium–fumarate–fumaric acid (2/1/1), (I) (Fig. 1).

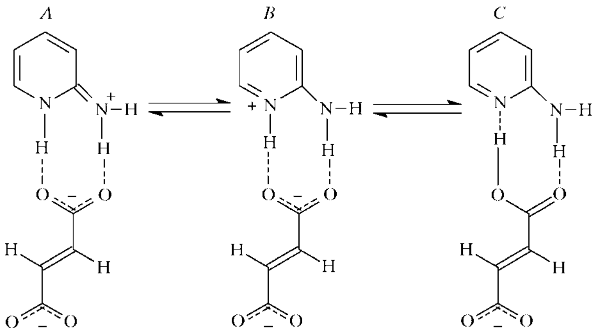


(I)

In (I), the 2-aminopyridinium ions are linked to the fumarate ions through N1—H1···O4 and N2—H11···O3 hydrogen bonds, resulting in the formation of cyclic eight-membered hydrogen-bonded rings (Fig. 1 and Table 2). The 2-aminopyridinium–fumarate–fumaric acid units are arranged so that N1—H1···O4, N2—H11···O3 and O1—H10···O4 hydrogen bonds form a two-dimensional network, with the networks connected *via* N2—H12···O3 hydrogen bonds, resulting in a three-dimensional network with a dihedral angle of 79.0 (2)° between the 2-aminopyridinium ions (Fig. 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, like other organic bases, is 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 monocation 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 *et al.*, 2003), clearly shows that the positive charge in the 2-aminopyridinium ions of (I) is on the amine group. Our investigations also show that the 2-aminopyridinium cation is present in the crystal lattice as the *A* tautomeric form (see scheme below).



The C1—N2 bond is approximately equal to a C═N double-bond length (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—H11 angle of 121.00 (13)° and by the fact that atoms C1, N2, H11 and H12 lie in the pyridine plane, with a maximum deviation of 0.018 (7) Å for atom N2 (Table 1). Similar bond distances and angles have been observed in 2-aminopyridinium succinate–succinic acid (Büyükgüngör & Odabaşoğlu, 2002) and 2-aminopyridinium adipate monoadipic acid dihydrate (Odabaşoğlu *et al.*, 2003), bis(2-aminopyridinium) maleate (Büyükgüngör & Odabaşoğlu, 2003) and in some 2-aminopyridine-containing molecules (Yang *et al.*, 1995; Grobelny *et al.*, 1995; Shanmuga Sundara Raj, Fun, Zhao *et al.*, 2000).

The C═C bond length [1.311 (3) Å] of the fumaric acid molecule is somewhat shorter than the C═C bond length [1.319 (3) Å] of the fumarate ion. A similar bond length [1.323 (3) Å] was found in the maleate anion of bis(2-aminopyridinium) maleate (Büyükgüngör & Odabaşoğlu, 2003). The average C—O distances in the carboxylate groups that form intermolecular hydrogen bonds are 1.32 (2) Å for the

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hydroxyl C—OH bond and 1.21 (3) Å for the carbonyl C=O bond (Borthwick, 1980); the value for the carboxylate anion has been reported as 1.25 Å (Borthwick, 1980) (Table 1).

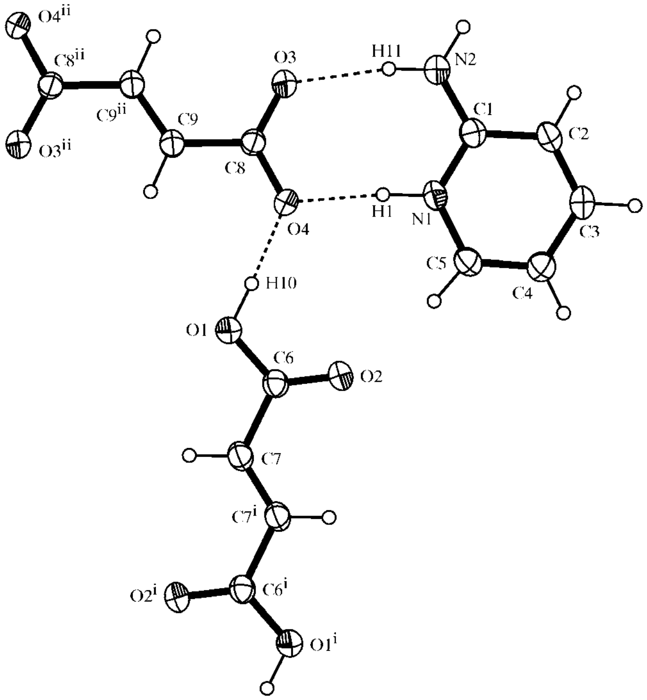

Figure 1
A view of the (I), with the atom-numbering scheme and 50% probability displacement ellipsoids [symmetry code: (i) $-x$, $-y$, $-z$].

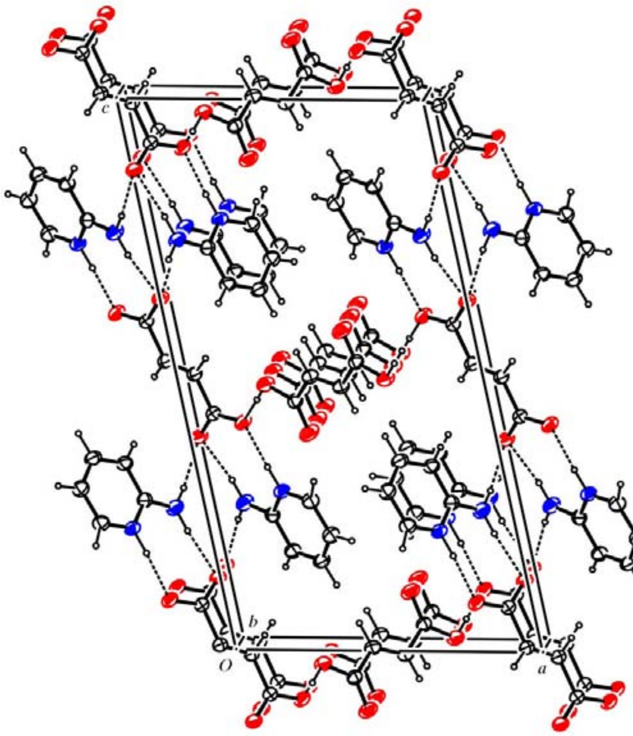

Figure 2
A packing diagram of (I), viewed along the *b* axis.

Experimental

The title compound was prepared by mixing 2-aminopyridine and fumaric 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. 456–458 K).

Crystal data

$2C_5H_7N_2^+\cdot C_4H_4O_4^{2-}\cdot C_4H_2O_4$
$M_r = 420.38$
Monoclinic, $P2_1/c$
$a = 10.4012\ (15)$ Å
$b = 4.9254\ (7)$ Å
$c = 19.162\ (3)$ Å
$\beta = 102.484\ (3)^\circ$
$V = 958.5\ (2)$ Å^3
$Z = 2$
$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 580 reflections
$\theta = 2.2$–25.5°
$\mu = 0.12$ mm^{-1}
$T = 210\ (2)$ K
Prism, light yellow
0.40 × 0.35 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.955$, $T_{\max} = 0.977$
4856 measured reflections
1868 independent reflections
1639 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 26.0^\circ$
$h = -12 \rightarrow 12$
$k = -5 \rightarrow 6$
$l = -17 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 1.08$
1868 reflections
176 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.2244P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C6	1.3182 (18)	N1—C5	1.363 (2)
O2—C6	1.2118 (19)	N2—C1	1.334 (2)
O3—C8	1.2482 (17)	C7—C7$^{\rm i}$	1.311 (3)
O4—C8	1.2771 (17)	C9—C9$^{\rm ii}$	1.319 (3)
N1—C1	1.3479 (19)		
O2—C6—O1	124.50 (14)	O3—C8—O4	123.61 (13)
C5—N1—C1—N2	−177.97 (14)	O3—C8—C9—C9$^{\rm ii}$	−4.5 (3)
O2—C6—C7—C7$^{\rm i}$	3.9 (3)	O4—C8—C9—C9$^{\rm ii}$	175.54 (18)
O1—C6—C7—C7$^{\rm i}$	−175.69 (19)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4	0.97 (2)	1.79 (2)	2.7533 (16)	174.2 (17)
N2—H11···O3	0.89 (2)	2.00 (2)	2.8643 (18)	163.2 (19)
N2—H12···O3$^{\rm iii}$	0.93 (2)	2.01 (2)	2.9211 (19)	166.0 (17)
O1—H10···O4	0.97 (2)	1.64 (3)	2.6004 (15)	175 (2)

Symmetry code: (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Refined C—H distances are in the range 0.94 (2)–0.98 (2) Å and $U_{\rm iso}$ values for H atoms are in the range 0.035 (5)–0.063 (7) Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1480). Services for accessing these data are described at the back of the journal.

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