

2,6-Diaminopyridinium hydrogen fumarate

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Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(C-C) = 0.003$ Å
 R factor = 0.028
 wR factor = 0.070
Data-to-parameter ratio = 6.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

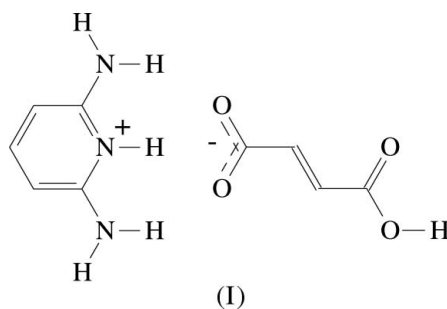
The title compound, $C_5H_8N_3^+ \cdot C_4H_3O_4^-$, contains edge-fused [$R_2^1(6)R_2^2(8)R_2^3(8)R_2^4(26)R_2^5(6)$] motifs involving 2,6-diaminopyridinium and hydrogen fumarate ions. In these motifs, 2,6-diaminopyridinium and hydrogen fumarate ions are connected by $N-H \cdots N$, $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds.

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Comment

The title compound, (I), was obtained by the reaction of 2,6-diaminopyridine and fumaric acid. The copper(II) complexes of aminopyridinium carboxylates have important applications in pharmaceuticals, as fungicides, as oxygen transfer, oxidative addition, homogenous hydrogenation and gas occlusion compounds, and in solvent extraction processes (Lah *et al.*, 2001; Yang *et al.*, 1995). Intermolecular interactions are responsible for crystal packing and gaining an understanding of them allows us to comprehend collective properties and permits the design of new crystals with specific physical and chemical properties (Lam & Mak, 2000). We have been interested in hydrogen-bonded systems formed by organic amines and carboxylic acids (Büyükgüngör & Odabaşoğlu, 2002, 2003, 2006; Odabaşoğlu, Büyükgüngör & Lönnecke, 2003; Odabaşoğlu, Büyükgüngör, Turgut *et al.*, 2003; Büyükgüngör *et al.*, 2004; Odabaşoğlu & Büyükgüngör, 2006*a,b*). The present work is part of a structural study of compounds of organic ammonium systems with hydrogen-bond donors and we report here the structure of 2,6-diaminopyridinium hydrogen fumarate, (I) (Fig. 1).



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. As for mono-aminopyridinium fumarate fumaric acid (Büyükgüngör *et al.*, 2003) and in some 2-aminopyridine-containing molecules (Yang *et al.*, 1995; Grobelny *et al.*, 1995; Shanmuga

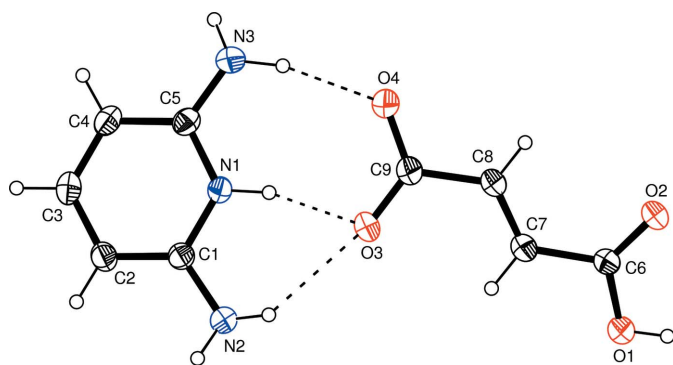


Figure 1
A view of the structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed lines indicate hydrogen bonds.

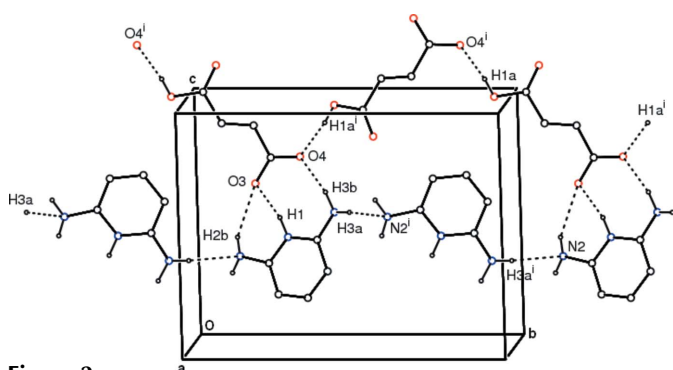


Figure 2
Part of the crystal structure of (I), showing the formation of two hydrogen-bonded (dashed lines) ring motifs. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry code: (i) $x + \frac{2}{3}, y + \frac{1}{2}, 1 - z$].

Sundara Raj *et al.*, 2000), 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.

In (I), the 2,6-diaminopyridinium ions are linked to the hydrogen fumarate ions through N—H···N, N—H···O and O—H···O hydrogen bonds and generate edge-fused [$R_2^1(6)R_2^2(8)R_2^3(8)R_6^5(26)R_1^2(6)$] motifs (Fig. 2 and Table 1). In these motifs, 2,6-diaminopyridinium and hydrogenfumarate ions are connected by N—H···N [C(6) chain] and O—H···O [C(7)chain] hydrogen bonds, respectively (Fig. 2). These hydrogen-bonded rings are linked into a complex three-dimensional framework by a combination of N—H···N, N—H···O and O—H···O hydrogen bonds (Fig. 3). The dihedral angles between the pyridinium ring and the H1A/O1/O2/C6/C7 and C8/C9/O3/O4 planes in the hydrogen fumarate ion are 30.13 (7) and 11.87 (10)°, respectively.

Experimental

Compound (I) was prepared by mixing 2,6-diaminopyridine and fumaric acid in a 1:1 molar ratio in 50 ml of water at 323–333 K. Crystals of (I) were obtained by slow evaporation of the solvent (m.p. 371–372 K).

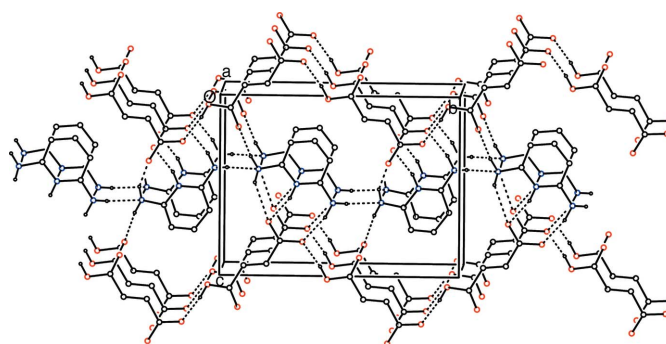


Figure 3
The packing of (I). Dashed lines indicate hydrogen bonds and H atoms not involved in the motifs shown have been omitted.

Crystal data

$C_5H_8N_3^+ \cdot C_4H_3O_4^-$
 $M_r = 225.21$
Monoclinic, $P2_1$
 $a = 3.7834$ (3) Å
 $b = 13.3967$ (13) Å
 $c = 10.0703$ (8) Å
 $\beta = 97.635$ (6)°
 $V = 505.89$ (8) Å³

$Z = 2$
 $D_x = 1.479$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 296$ K
Prism, colourless
 $0.60 \times 0.29 \times 0.06$ mm

Data collection

Stoe IPDS-2 diffractometer
 ω scans
Absorption correction: integration
(*X-RED32*; Stoe & Cie, 2002)
 $T_{\min} = 0.960$, $T_{\max} = 0.993$

5811 measured reflections
1045 independent reflections
951 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.070$
 $S = 1.10$
1045 reflections
165 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.0356P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.09$ e Å⁻³
 $\Delta\rho_{\min} = -0.15$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|----------|--------------|--------------|----------------|
| O1—H1A···O4 ⁱⁱ | 0.82 | 1.72 | 2.530 (2) | 172 |
| N1—H1···O3 | 0.87 (3) | 1.87 (3) | 2.704 (3) | 161 (3) |
| N2—H2A···O2 ⁱⁱⁱ | 0.92 (3) | 2.00 (3) | 2.913 (3) | 171 (3) |
| N2—H2B···O3 | 0.84 (4) | 2.32 (3) | 3.009 (3) | 138 (3) |
| N3—H3A···N2 ^{iv} | 0.86 (4) | 2.28 (4) | 3.129 (3) | 175 (3) |
| N3—H3B···O4 | 0.93 (4) | 2.00 (4) | 2.908 (3) | 164 (3) |

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

All C- and O-bound H atoms were refined using the riding-model approximation, with C—H = 0.93 Å [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and O—H = 0.82 Å [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The amino and ring N—H H atoms were located in a difference Fourier map and refined freely with an isotropic displacement parameter. In the absence of significant anomalous scattering, the Flack (1983) parameter was indeterminate; the Friedel equivalents were merged prior to the final least-squares

refinement cycles. The absolute configuration was deduced from that of the starting material.

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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