

4-Aminopyridinium hydrogen maleate

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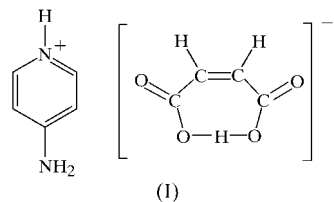
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The title compound, $C_5H_7N_2^+ \cdot C_4H_3O_4^-$, crystallizes in space group $P2_1$ with one ion pair in the asymmetric unit. The hydrogen maleate anion possesses nearly planar geometry and displays an extremely short intramolecular O—H...O hydrogen bond, with an O...O distance of 2.4198 (19) Å. Classical N—H...O hydrogen bonds, together with short C—H...O contacts, generate an extensive hydrogen-bonding network.

Comment

The structures of the hydrogen-bonded adducts of polycarboxylic acids with organoamines have received considerable attention in crystal-engineering research (Bowes *et al.*, 2003; Zakaria *et al.*, 2003; Farrell *et al.*, 2002). The maleic acid anion can exist in the fully deprotonated form or as hydrogen maleate, with one of the carboxylic acid groups protonated. Bis(2-aminopyridinium) maleate has recently been structurally investigated (Büyükgüngör & Odabaşoğlu, 2003). We report here the structure of 4-aminopyridinium hydrogen maleate, (I), and compare its hydrogen-bonding interactions with those in the structure of 2-aminopyridinium maleate.



A view of the ion pair of (I) with the atomic numbering scheme is depicted in Fig. 1. The hydrogen maleate anion possesses a short intramolecular O—H...O hydrogen bond, with an O...O distance of 2.4198 (19) Å, which forms a nearly planar seven-membered ring structure, as typically found in other hydrogen maleate anions (Madsen & Larsen, 1998, and references therein). The position of the H atom is asymmetrical, with O1—H11 = 1.17 (3) Å and O3—H11 = 1.26 (4) Å. Both cation and anion possess almost planar geometry and are parallel to each other [dihedral angle = 1.35 (5)°].

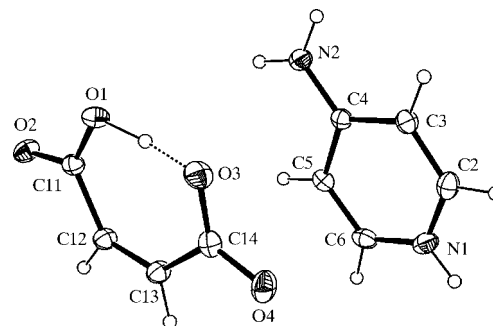


Figure 1

A view of the ion pair of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

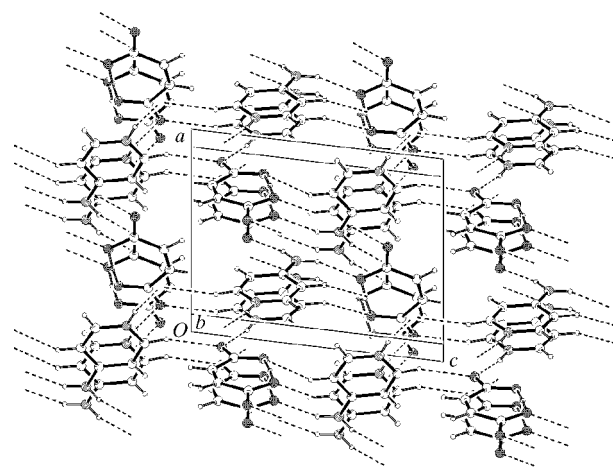


Figure 2

A packing diagram of (I), showing the hydrogen-bonding contacts as dashed lines.

In the structure of (I), the cations and anions are linked together by N—H...O hydrogen bonds. One of the amino-group H atoms forms a contact with one of the O atoms of a neighbouring anion [atom O3(1 - x, y - 1/2, 1 - z)], which is also involved in the formation of an intramolecular hydrogen bond. The second amino-group H atom connects atom N2 with atom O4(x, y - 1, z). The protonated endocyclic pyridine N atom is in contact with atom O2(x - 1, y + 1, z) of a neighbouring anion. One of the hydrogen maleate carboxylate groups is also involved in two short contacts to the pyridine H atoms of two different neighbouring cations, with C3...O1(1 - x, y + 1/2, 1 - z) = 3.332 (2) and C6...O2(1 - x, y + 1/2, -z) = 3.327 (2) Å. Thus, by a combination of classical and non-classical hydrogen-bond interactions, an extensive bonding scheme is created (Fig. 2); details of the hydrogen bonding are listed in Table 2.

In the structure of bis(2-aminopyridinium) maleate, two eight-membered rings are formed within the asymmetric unit through N—H...O contacts between both carboxylic acid O atoms and an H atom of the amino group and the H atom on the endocyclic pyridine N atom. The remaining H atom of the

amino group in the structure of 2-aminopyridinium maleate is involved in the formation of an intermolecular hydrogen bond with one of the O atoms of a neighbouring maleate ion.

Experimental

For the preparation of (I), equimolar quantities of 4-aminopyridine and maleic acid were dissolved in a water solution containing ZnSO₄. On standing at room temperature, small colourless crystals of (I) formed.

Crystal data

C ₅ H ₇ N ₂ ⁺ ·C ₄ H ₃ O ₄ ⁻	$D_x = 1.463 \text{ Mg m}^{-3}$
$M_r = 210.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1293 reflections
$a = 8.0029 (10) \text{ \AA}$	$\theta = 1.02\text{--}31.51^\circ$
$b = 5.4952 (5) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 10.9280 (15) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.840 (5)^\circ$	Prismatic, colourless
$V = 477.17 (10) \text{ \AA}^3$	$0.15 \times 0.15 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{\text{int}} = 0.017$
φ and ω scans	$\theta_{\text{max}} = 27.1^\circ$
2048 measured reflections	$h = -10 \rightarrow 10$
1161 independent reflections	$k = -7 \rightarrow 6$
1095 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 0.0693P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
1161 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
177 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.102 (17)

All H atoms were found in a difference Fourier map and were refined freely. The value of the Flack parameter [0.4 (9); Flack, 1983] was inconclusive (Flack & Bernardinelli, 2000), so the Friedel equivalents were merged prior to the final refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C11	1.2824 (19)	N1—C6	1.344 (3)
O2—C11	1.239 (2)	N1—C2	1.347 (2)
O3—C14	1.291 (2)	C2—C3	1.359 (3)
O4—C14	1.233 (2)	C3—C4	1.412 (2)
C11—C12	1.492 (2)	C4—N2	1.335 (2)
C12—C13	1.333 (3)	C4—C5	1.417 (2)
C13—C14	1.492 (2)	C5—C6	1.353 (3)
O2—C11—O1	122.77 (16)	N1—C2—C3	121.40 (17)
O2—C11—C12	117.00 (13)	C2—C3—C4	119.71 (15)
O1—C11—C12	120.22 (16)	N2—C4—C3	121.74 (14)
C13—C12—C11	131.13 (15)	N2—C4—C5	121.04 (16)
O4—C14—O3	123.34 (17)	C3—C4—C5	117.21 (15)
O4—C14—C13	117.79 (16)	C6—C5—C4	119.66 (16)
O3—C14—C13	118.86 (17)	N1—C6—C5	121.68 (16)
C6—N1—C2	120.33 (17)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 \cdots O3	1.17 (3)	1.26 (4)	2.4198 (19)	174 (2)
N1—H1 \cdots O2 ⁱ	0.88 (2)	1.87 (2)	2.740 (2)	168.2 (19)
N2—H2A \cdots O4 ⁱⁱ	0.93 (2)	1.98 (2)	2.885 (2)	164.2 (19)
N2—H2B \cdots O3 ⁱⁱⁱ	0.92 (2)	2.02 (2)	2.9042 (19)	160.3 (17)
C3—H3 \cdots O1 ^{iv}	1.002 (19)	2.49 (2)	3.332 (2)	141.4 (17)
C6—H6 \cdots O2 ^v	0.963 (18)	2.403 (19)	3.327 (2)	160.8 (16)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1655). Services for accessing these data are described at the back of the journal.

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