

Bis(2-aminopyridinium) maleate

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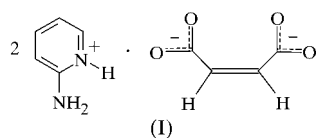
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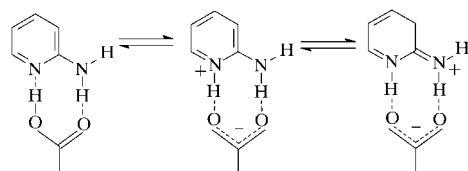
Two cyclic eight-membered hydrogen-bonded rings exist in the title compound, $2\text{C}_5\text{H}_7\text{N}_2^+ \cdot \text{C}_4\text{H}_2\text{O}_4^{2-}$, involving the 2-aminopyridinium and maleate ions. The dihedral angle between the two pyridinium rings hydrogen bonded to the maleate ion is $74.80(4)^\circ$. The maleate anion lies on a twofold axis and is linked to the pyridinium cations by intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The heterocycle is fully protonated, which enables amino-imino tautomerization.

Comment

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 bis(2-aminopyridinium) maleate, (I). A similar series of complexes formed from 2-aminopyridine and carboxylate have been reported recently (Büyükgüngör & Odabaşoğlu, 2002; Odabaşoğlu *et al.*, 2003).



A view of (I) is shown in Fig. 1. The complex owes its formation to two hydrogen-bond pairs, one between atoms O1 and O2 of the maleate ions and hydrogen-bond donors N1—H1 and N2—H2A, and the other between their symmetry-related pairs. There are two eight-membered rings in the structure, formed as a result of these $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. Furthermore, there is also an intermolecular hydrogen bond in (I) (Table 2).



The average C—O distances in carboxylate groups that form intermolecular hydrogen bonds are $1.32(2) \text{ \AA}$ for the

hydroxyl C—OH bond and $1.21(3) \text{ \AA}$ for the carbonyl C=O bond (Borthwick, 1980). The value for the carboxylate anion is also reported as 1.25 \AA (Borthwick, 1980). The O1—C11 and O2—C11 bond lengths in (I) thus fall into the category of a normal COO^- group (Table 1).

The C—N—C angle of pyridines is very sensitive to protonation (Jin, Pan, Xu & Xu, 2000; Jin *et al.*, 2002). In comparison with 2-amino-6-methylpyridinium neoabietate (Jin, Pan, Liu & Xu, 2000), the complete protonation of the heterocycle in (I) is indicated by the enlarged C1—N1—C5 angle [$122.69(15)^\circ$] and the reduced N1—C1—C2 angle [$117.47(16)^\circ$]. The 2-aminopyridine-carboxylic acid system has been the subject of theoretical (Inuzuka & Fujimoto, 1990) and spectroscopic (Inuzuka & Fujimoto, 1986) amino-imino tautomerization studies. The main features of amino-imino tautomerization (see Scheme 1) are demonstrated in the structure of (I) by the bond lengths and angles of the

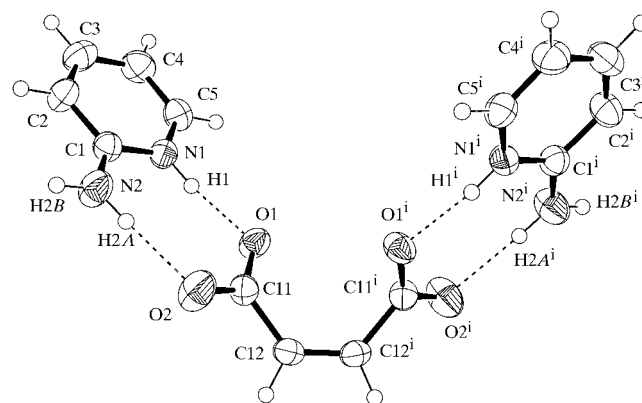


Figure 1

A view of the moieties of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$].

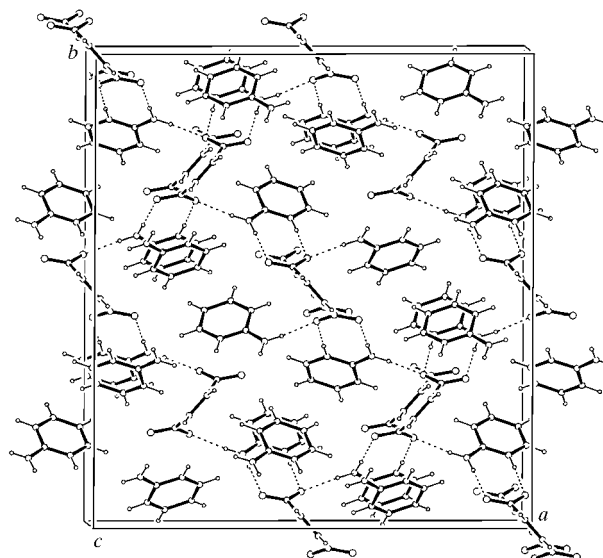


Figure 2

A packing diagram for (I), viewed along the *c* axis.

heterocycle and the maleate anion, respectively. The present investigation, like our previous work (Büyükgüngör & Odabaşoğlu, 2002; Odabaşoğlu *et al.*, 2003), clearly shows that the positive charge in the 2-aminopyridinium ions of (I) is on the amino group.

Experimental

The title compound was prepared by dissolving 2-aminopyridine and maleic acid in a 2:1 molar ratio in water at 373 K. Crystals of (I) were obtained by slow evaporation of the solvent at the room temperature.

Crystal data

$2\text{C}_5\text{H}_7\text{N}_2^+\cdot\text{C}_4\text{H}_2\text{O}_4^{2-}$	Mo $K\alpha$ radiation
$M_r = 304.30$	Cell parameters from 161 reflections
Orthorhombic, <i>Fdd2</i>	$\theta = 2.6\text{--}12.7^\circ$
$a = 21.756 (5) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 23.531 (5) \text{ \AA}$	$T = 153 (2) \text{ K}$
$c = 5.6280 (11) \text{ \AA}$	Rectangular, light yellow
$V = 2881.2 (11) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$Z = 8$	
$D_x = 1.403 \text{ Mg m}^{-3}$	

Data collection

Siemens P4 diffractometer	$h = -27 \rightarrow 5$
ω scans	$k = -30 \rightarrow 0$
1564 measured reflections	$l = -6 \rightarrow 7$
873 independent reflections	1 standard reflection
814 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{\text{int}} = 0.016$	intensity decay: <2%
$\theta_{\text{max}} = 27^\circ$	

Table 1

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

N1—C1	1.3434 (19)	O1—C11	1.264 (2)
N1—C5	1.354 (2)	O2—C11	1.2310 (19)
N2—C1	1.318 (2)	C11—C12	1.500 (2)
C1—C2	1.412 (3)	C12—C12 ⁱ	1.323 (3)
C1—N1—C5	122.69 (15)	N1—C1—C2	117.47 (16)

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

Table 2

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

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1 \cdots O1	0.88	1.78	2.6557 (18)	172
N2—H2A \cdots O2	0.88	1.96	2.837 (2)	177
N2—H2B \cdots O1 ⁱ	0.88	1.97	2.832 (2)	168

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.5722P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
873 reflections	$\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
101 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0048 (6)

Although space group *Cc* gave a chemically reasonable and computationally stable refinement, the correct space group was found to be *Fdd2*. Refinement of the absolute structure parameter was meaningless because of its large s.u. (1.2), and so Friedel-pair reflections were averaged before the final refinement. All H atoms were treated using a riding model, with C—H distances of 0.95 \AA and N—H distances of 0.88 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Sheldrick, 1990); 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: *WinGX* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1408). Services for accessing these data are described at the back of the journal.

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