

# Strong symmetrical intramolecular hydrogen bonds in diprotonated piperazinium bis(hydrogenmaleate)

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## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

$R$  factor = 0.042

$wR$  factor = 0.102

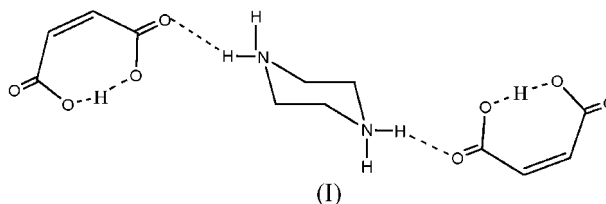
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title salt,  $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{C}_4\text{H}_3\text{O}_4^-$ , the diprotonated piperazine cation links to two hydrogen maleate anions through  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds. An H atom is approximately centered in an extremely short intramolecular hydrogen bond of the  $\text{O} \cdots \text{H} \cdots \text{O}$  type in each of the hydrogen maleate anions.

## Comment

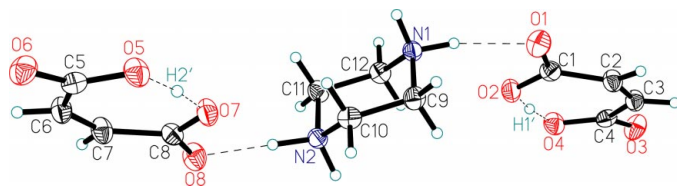
Maleic acid may bind to cations in either the monoanionic or dianionic form, displaying a plethora of interesting structures. Piperazine is a strongly basic amine, able to form a dication, in which all four  $\text{N}-\text{H}$  bonds are generally active in hydrogen-bond formation (Coupar *et al.*, 1996; Ferguson *et al.*, 1998; Loehlin *et al.*, 1994). Many cases of symmetrical intramolecular hydrogen bonds have been observed in the hydrogen maleate anion, with an H atom centered in an extremely short  $\text{O} \cdots \text{H} \cdots \text{O}$  intramolecular hydrogen bond (Darlow, 1961; Darlow & Cochran, 1961; Fillaux *et al.*, 1999). In this work, the combination of piperazine and maleic acid has been chosen to explore the special hydrogen-bond pattern.



The crystal structure shows a local pseudocenter of symmetry at  $x = 0.887(3)$ ,  $y = 0.757(9)$ ,  $z = 0.384(5)$ . Adopting a normal chair conformation, as reported previously (Bois, 1970; Kuppayee *et al.*, 1999; Jin *et al.*, 2001), the dication of the title salt, (I), links to two anions through  $\text{N1}-\text{H} \cdots \text{O1}$  and  $\text{N2}-\text{H} \cdots \text{O8}$  hydrogen bonds, where the H atoms are equatorial.

In (I), two hydrogen maleate anions each hold an H atom at the approximate center of the extremely short intramolecular hydrogen bonds  $\text{O2} \cdots \text{H1}' \cdots \text{O4}$  and  $\text{O7} \cdots \text{H2}' \cdots \text{O5}$ . With the centered H atoms in the intramolecular hydrogen bonds, atoms O2, O4, O5 and O7 are both hydrogen donors and acceptors. The  $\text{O2}-\text{C1}$ ,  $\text{O4}-\text{C4}$ ,  $\text{O5}-\text{C5}$  and  $\text{O7}-\text{C8}$  distances are longer than those of  $\text{O1}-\text{C1}$ ,  $\text{O3}-\text{C4}$ ,  $\text{O6}-\text{C5}$  and  $\text{O8}-\text{C8}$ , showing differences between the  $\text{C}-\text{O}$  and  $\text{C}=\text{O}$  bond types of the carboxylic acid group (Borthwick, 1980).

Supramolecular layers of the title salt (Fig. 2) are formed parallel to the  $ac$  plane by  $\text{N1}-\text{H} \cdots \text{O1}$ ,  $\text{N2}-\text{H} \cdots \text{O8}$ ,  $\text{N1}-\text{H} \cdots \text{O3}^i$  and  $\text{N2}-\text{H} \cdots \text{O6}^{ii}$  hydrogen bonds (see Table 2).



**Figure 1**  
The molecular structure of the title salt, showing 35% probability displacement ellipsoids; hydrogen bonds are illustrated by dashed lines.

Furthermore, these layers are stabilized by C10—H···O4<sup>i</sup> and C12—H···O5<sup>ii</sup> hydrogen bonds. There are no hydrogen bonds between these layers.

## Experimental

Crystals of the title salt were obtained from a 1:2 aqueous solution of piperazine and maleic acid by slow concentration for a week.

### Crystal data

$C_4H_{12}N_2^{2+} \cdot 2C_4H_3O_4^-$	$D_x = 1.490 \text{ Mg m}^{-3}$
$M_r = 318.28$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 22 reflections
$a = 10.735 (2) \text{ \AA}$	$\theta = 4.0\text{--}12.6^\circ$
$b = 11.603 (2) \text{ \AA}$	$\mu = 0.13 \text{ mm}^{-1}$
$c = 11.843 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 105.87 (1)^\circ$	Prism, colorless
$V = 1418.9 (4) \text{ \AA}^3$	$0.46 \times 0.30 \times 0.20 \text{ mm}$
$Z = 4$	

### Data collection

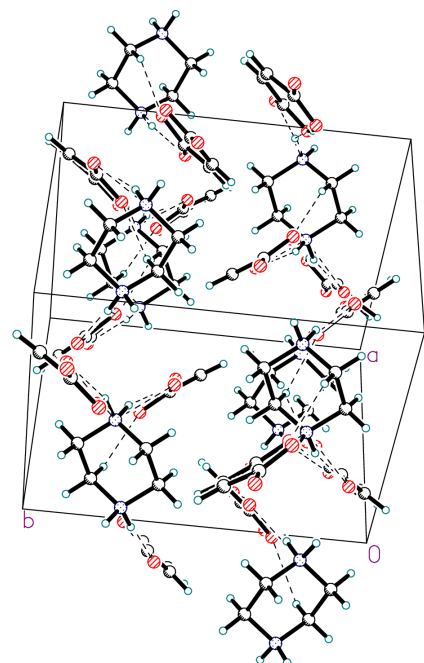
Siemens P4 diffractometer	$h = 0 \rightarrow 13$
$\omega$ scans	$k = 0 \rightarrow 14$
2775 measured reflections	$l = -14 \rightarrow 13$
2631 independent reflections	3 standard reflections
1500 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.028$	intensity decay: 1.3%
$\theta_{\text{max}} = 25.5^\circ$	

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.102$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.91$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
2631 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
200 parameters	Extinction correction: <i>SHELXTL</i>
H atoms: see below	Extinction coefficient: 0.0156 (16)

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O1—C1	1.232 (3)	O2—C1	1.281 (3)
O3—C4	1.226 (3)	O4—C4	1.281 (3)
O6—C5	1.230 (3)	O5—C5	1.285 (3)
O8—C8	1.230 (3)	O7—C8	1.279 (3)
O1—C1—O2	122.0 (2)	O4—C4—C3	119.8 (2)
O1—C1—C2	118.0 (2)	O6—C5—O5	122.4 (2)
O2—C1—C2	119.9 (2)	O6—C5—C6	117.9 (2)
O8—C8—O7	122.6 (2)	O5—C5—C6	119.6 (2)
O8—C8—C7	117.8 (2)	C3—C2—C1	130.2 (2)
O7—C8—C7	119.7 (2)	C6—C7—C8	130.8 (2)
O3—C4—O4	122.5 (2)	C2—C3—C4	130.5 (2)
O3—C4—C3	117.6 (2)	C7—C6—C5	130.9 (2)



**Figure 2**  
A three-dimensional view of the supramolecular layer of the title salt; hydrogen bonds are illustrated by dashed lines.

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H1'···O4	1.21	1.22	2.419 (2)	171
O7—H2'···O5	1.19	1.23	2.420 (2)	171
N1—H1B···O1	0.98	1.90	2.842 (2)	161
N2—H2B···O8	1.04	1.73	2.757 (2)	169
N1—H1A···O3 <sup>i</sup>	0.92	1.94	2.813 (3)	157
N2—H2A···O6 <sup>ii</sup>	0.96	1.84	2.770 (3)	162
C10—H10B···O4 <sup>i</sup>	0.97	2.46	3.356 (3)	153
C12—H12A···O5 <sup>ii</sup>	0.97	2.50	3.357 (3)	148

Symmetry codes: (i)  $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$ .

The H atoms involved in O—H···O and N—H···O hydrogen bonds were found in difference Fourier maps and were not incorporated in the refinement. All other H atoms were positioned geometrically and included in the refinement as riding, with  $U_{\text{iso}}$  values equal to  $1.2U_{\text{eq}}$  of the carrier atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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