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The 2:1 complex of maleic acid and 1,4-diazabicyclo[2.2.2]octane: hydrogen-bonded sheets linked by C–H···O hydrogen bonds

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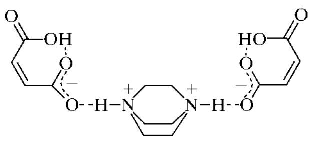
In the title complex, 1,4-diazoniabicyclo[2.2.2]octane bis(hydrogen maleate), $C_6H_{14}N_2^{2+}\cdot 2C_4H_3O_4^-$, the $C_4H_3O_4^-$ and $C_6H_{14}N_2^{2+}$ ions, derived from maleic acid and 1,4-diazabicyclo[2.2.2]octane, respectively, are disordered across a mirror plane in space group $Cmc2_1$, and they are linked by two nearly linear N—H···O hydrogen bonds, with N···O distances of 2.662 (3) and 2.614 (4) Å, and N—H···O angles of 173°. The crystal structure consists of sheets with reticulations of 3.3792 (4) Å in stratum and 7.3892 (8) Å in width. The sheets are linked by C—H···O hydrogen bonds.

Comment

Supramolecular aggregate design is an active field (Zaworotko, 2001). Some examples have been reported which use 1,4-diazabicyclo[2.2.2]octane (DABCO) as one of the building blocks (Ferguson *et al.*, 1997; Glidewell *et al.*, 1999) in a supramolecular architecture in two and three dimensions. We have used two simple building blocks, DABCO and maleic acid (MA), to synthesize the title complex, (I), and report here its sheet-type structure.



(I)

In the structure of (I) (Fig. 1), the $C_4H_3O_4^-$ and $C_6H_{14}N_2^{2+}$ ions are linked by two nearly linear hydrogen bonds (Table 2). Hydrogen maleate anions, $C_4H_3O_4^-$, have been reported with both symmetric and asymmetric intramolecular hydrogen bonds (Fillaux *et al.*, 1999; James & Williams, 1974). Complex (I) contains two distinct hydrogen maleate ions, each involved in an asymmetric intramolecular hydrogen bond (Table 2), with O···O distances intermediate between those typical of symmetric (2.437 Å; Fillaux *et al.*, 1999) and asymmetric [2.502 (1) Å; James & Williams, 1974] examples.

Viewed approximately along [100] (Fig. 2), the geometrical arrangement of (I) is characterized by a sheet-like structure of MA anions and DABCO cations enclosing spaces measuring 3.3792 (4) × 7.3892 (8) Å. Atoms N1, N2, C1 and C2 of the DABCO cation, and the whole MA anion, exhibit small deviations from the mirror plane and form a continuous sheet.

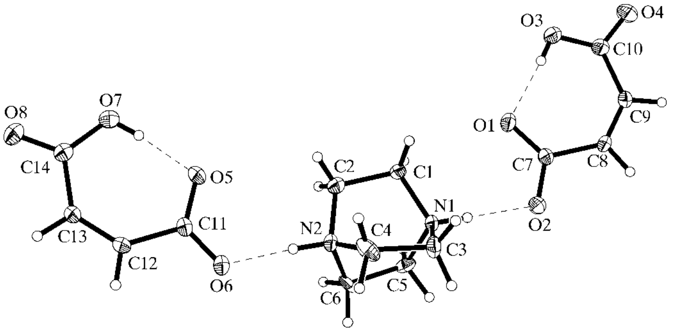


Figure 1
A view of the cation and anion units of (I), showing the atom labelling and 50% probability displacement ellipsoids. Hydrogen bonds are illustrated as thin dashed lines. For the sake of clarity, only one orientation of each component is shown.

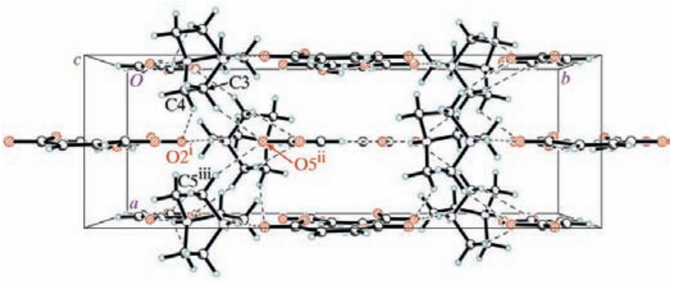


Figure 2
An illustration of the unit-cell packing of (I), viewed along the *c* axis. Hydrogen bonds are shown by thin dashed lines [symmetry codes: (i) $\frac{1}{2}-x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x+\frac{1}{2}, \frac{3}{2}-y, z+\frac{1}{2}$; (iii) $x+1, y, z$]. For the sake of clarity, only one orientation of each component is shown.

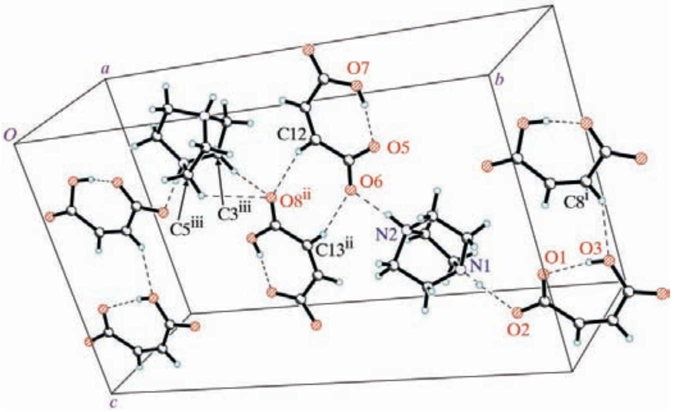


Figure 3
Part of the crystal structure of (I), showing the continuous sheets parallel to (100). Hydrogen bonds are shown by thin dashed lines [symmetry codes: (i) $x, 1-y, z-\frac{1}{2}$; (ii) $-x, 2-y, z+\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, z-\frac{1}{2}$].

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The C—H···O hydrogen bonds in (I) (Table 2) play an important role in linking the sheets. As seen in Fig. 3, the zigzag sheets of MA anions are linked by C12—H12···O8($-x$, $-y+2$, $z+\frac{1}{2}$) and C13—H13···O6($-x$, $-y+2$, $z-\frac{1}{2}$) hydrogen bonds, while straight sheets of MA anions are linked by C8—H8···O3($-x$, $-y+1$, $z+\frac{1}{2}$) hydrogen bonds. The methylene groups of the DABCO cations take part in other C—H···O hydrogen bonds to reinforce the structure. Zigzag and straight sheets in the same layer are coplanar with each other, forming the observed continuous structure.

The DABCO cation and some of the atoms of the MA anion (O1, O3, C8 and C9, and their associated H atoms) were disordered across pairs of sites slightly removed from the mirror plane at $x = 0$. The remaining atoms lie on the mirror plane. It may be noted here that DABCO has been observed disordered across a centre of inversion in the 1:1 complex with 4,4′-biphenol (Ferguson *et al.*, 1998) and perchloric acid (Katrusiak, 2000).

Experimental

1,4-Diazabicyclo[2.2.2]octane (0.01 mol) and maleic acid (0.02 mol) were dissolved in water by heating until a clear solution was obtained. Single crystals of the title complex, (I), were formed by allowing the resulting solution to stand overnight at 293 K.

Crystal data

$C_6H_{14}N_2^{2+}\cdot 2C_4H_3O_4^-$
$M_r = 344.32$
Orthorhombic, $Cmc2_1$
$a = 6.7584$ (8) Å
$b = 20.145$ (4) Å
$c = 11.255$ (2) Å
$V = 1532.3$ (4) Å^3
$Z = 4$
$D_x = 1.493$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4.3$–15.0°
$\mu = 0.12$ mm^{-1}
$T = 289$ (2) K
Prism, colourless
0.46 × 0.38 × 0.36 mm

Data collection

Siemens *P*4 diffractometer
ω scans
1194 measured reflections
1044 independent reflections
845 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\rm max} = 28°$

$h = 0 \rightarrow 8$
$k = 0 \rightarrow 26$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.078$
$S = 0.96$
1044 reflections
178 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.257 (6)	O8—C14	1.212 (4)
O2—C7	1.257 (4)	N1—C5	1.493 (4)
O3—C10	1.315 (6)	N1—C3	1.493 (4)
O4—C10	1.215 (4)	N1—C1	1.500 (3)
O5—C11	1.273 (4)	N2—C6	1.486 (4)
O6—C11	1.235 (4)	N2—C4	1.487 (4)
O7—C14	1.319 (4)	N2—C2	1.494 (3)
N1—C1—C2—N2	10 (2)	N1—C5—C6—N2	12.6 (15)
N1—C3—C4—N2	14.0 (17)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.91	1.76	2.662 (3)	174
N2—H2···O6	0.91	1.71	2.614 (4)	173
O3—H3···O1	0.82	1.72	2.484 (7)	154
O7—H7···O5	0.82	1.64	2.440 (4)	164
C3—H3*A*···O5$^{\rm i}$	0.97	2.34	3.27 (2)	160
C4—H4*B*···O2$^{\rm ii}$	0.97	2.58	3.395 (19)	141
C12—H12···O8$^{\rm iii}$	0.93	2.56	3.452 (4)	161
C13—H13···O6$^{\rm iv}$	0.93	2.49	3.382 (4)	161
C3—H3*B*···O8$^{\rm v}$	0.97	2.47	3.288 (2)	141
C8—H8···O3$^{\rm vi}$	0.93	2.40	3.213 (7)	145
C5—H5*A*···O8$^{\rm v}$	0.97	2.70	3.341 (2)	124
C5—H5*B*···O5$^{\rm vii}$	0.97	2.46	3.332 (4)	149

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

H atoms were placed in calculated positions, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ of their parent atoms, and with N—H = 0.91 Å, O—H = 0.82 Å and C—H = 0.93–0.97 Å. In the absence of significant anomalous scattering, Friedel pairs were merged; the absolute structure could not be determined.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1226). Services for accessing these data are described at the back of the journal.

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