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Hydrogen-bonded sheets in benzylmethylammonium hydrogen maleate

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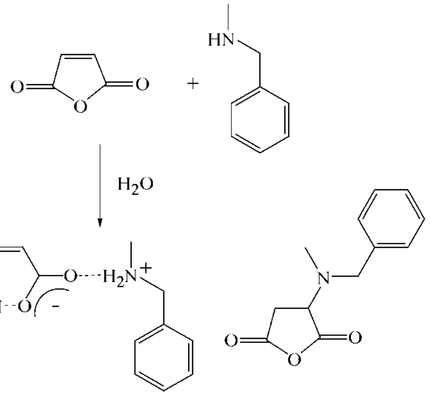
In the title compound, $C_8H_{12}N^+\cdot C_4H_3O_4^-$, there is a short and almost linear but asymmetric O—H···O hydrogen bond in the anion. The ions are linked into $C_2^2(6)$ chains by two short and nearly linear N—H···O hydrogen bonds and the chains are further weakly linked into sheets by a single C—H···O hydrogen bond.

Comment

We report here the molecular and supramolecular structure of benzylmethylammonium hydrogen maleate, (I), and we briefly compare the supramolecular aggregation in (I) with that in hydrogen maleate salts of some other secondary amines. The compound was obtained during an attempt to prepare α-(benzylmethylamino)succinic anhydride, (II) (see scheme), for use as an intermediate in the synthesis of new fused heterocyclic systems. Synthetic targets potentially accessible from intermediates of type (II) include amino-substituted phthalazines, which show activity as inhibitors of specific enzymes, such as human liver aldehyde oxidase (Beedham *et al.*, 1995) and superoxide dismutase (Rodriguez-Ciria *et al.*, 2007), as well as activity against seizures induced by electroshock (Sivakumar *et al.*, 2002), and fused 1,3-diazepines, which show activity against the hepatitis-B and hepatitis-C viruses (Zhang *et al.*, 2005). The intended synthesis of (II) involved a Michael-type reaction between benzylmethylamine and maleic anhydride, but evidently hydrolysis occurred during this procedure so that compound (I) was obtained instead, albeit in low yield. A quantitative yield of compound (I) was subsequently obtained from the direct reaction of benzylmethylamine and maleic acid.

In the cation of (I), the exocyclic chain adopts an almost planar extended-chain conformation, with the aryl ring almost orthogonal to this plane, as shown by the torsion angles (Table 1). The dihedral angle between the planes of atoms C11–C16 and C17/N17/C18 is 80.07 (13)°, and the dihedral angle between the C11–C16 plane and the best plane through atoms C11/C17/N17/C18 is 81.41 (13)°.



(I) (II)

There is a short and nearly linear O—H···O hydrogen bond within the anion of (I) (Table 2) and the C—O distances are fully consistent with the location of the H atom in this hydrogen bond, as deduced from difference maps. It is interesting to compare the location of the hydrogen-bonded H atom in the anion in salt (I) with that in some related hydrogen maleate salts derived from simple amines, such as the methylammonium and dimethylammonium salts (Madsen & Larsen, 1998), the dicyclohexylammonium salt (Ng *et al.*, 1991), the tetramethylammonium salt (Drobež *et al.*, 1985) and the salts derived from some heteroaromatic diamines (Bowes *et al.*, 2003).

For methylammonium hydrogen maleate, the systematic absences permitted a choice of space group, *viz*. *Pna*2$_1$ or *Pnam* (a nonstandard setting of *Pnma*). The sites of all of the non-H atoms were consistent with *Pnam* and the only atoms whose positions could deviate from *Pnam* were the hydrogen-bonded H atoms in the two independent anions; the preferred model, in space group *Pnam*, had each of these H atoms

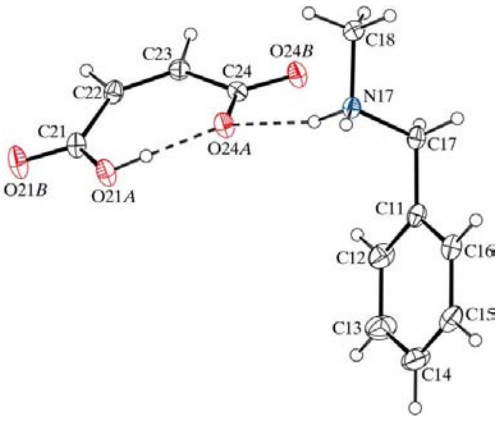


Figure 1
The independent ionic components in compound (I), showing the atom-labelling scheme and the hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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located in off-centre sites of 0.5 occupancy in each of the anions, which both lie across mirror planes (Madsen & Larsen, 1998).

The unique H atom could not be located in the dicyclohexylammonium salt, and it was fixed at the mid-point of the two close O atoms (Ng *et al.*, 1991); this seems a reasonable assignment in view of the C—O distances in this compound. In tetramethylammonium hydrogen maleate (Drobež *et al.*, 1985), the O—H distances were found to be 1.09 (4) and 1.32 (4) Å, with an O—H···O angle of 174 (3)° and an O···O distance of 2.403 (4) Å; although the precision of the O—H distances does not permit a firm distinction between a centred and a close-bound H atom, the associated C—O distances support the centred model.

The location of the H atom closely bonded to just one of the O atoms found here for compound (I) is consistent with the locations of this atom found in a number of hydrogen maleate salts of heteroaromatic diamines (Bowes *et al.*, 2003). Despite the presence of the short O—H···O hydrogen bond in compound (I), the anion is not completely planar and the C—C—C angles at C22 and C23 are both *ca* 130°.

The ionic components in (I) are linked into chains by two strong N—H···O hydrogen bonds (Table 2). Atom N17 in the cation at (x, y, z) acts as hydrogen-bond donor to atom O24*A* in the anion also at (x, y, z), and to atom O24*B* in the anion at (x, $-1 + y$, z), so generating by translation a $C_2^2(6)$ chain (Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 2). These chains are further weakly linked by a single C—H···O hydrogen bond (Table 2). Methylene atom C17 at (x, y, z) acts as hydrogen-bond donor to carboxyl atom O21*A* at (x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$), so forming a $C_3^2(7)$ chain running parallel to the [001] direction and generated by the *c*-glide plane at $y = \frac{1}{4}$. The combination of the [100] and [001] chains generates a sheet of $S(7)$ and $R_7^6(23)$ rings parallel to (100) (Fig. 3). Two sheets of this type, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent sheets.

The formation of the chain of N—H···O hydrogen bonds in compound (I) utilizes two O atoms from a single carboxylate group. This may be contrasted with the chains formed by N—H···O hydrogen bonds in the hydrogen maleate salts of other simple aliphatic diamines. In the dimethylammonium (Madsen & Larsen, 1998) and dicyclohexylammonium (Ng *et al.*, 1991) salts, the two O atoms utilized in the chain formation form parts of different carboxyl groups, so that these chains are both of the $C_2^2(9)$ type, as opposed to $C_2^2(6)$ in compound (I). By contrast, in the 1:2 hydrogen maleate salts derived from 4,4′-bipyridyl and 1,2-di-4-pyridylethane, the N—H···O hydrogen bonds generate three-component aggregates, *viz.* anion–cation–anion, which lie across twofold rotation axes and inversion centres, respectively. The incorporation of these aggregates into supramolecular structures of higher dimensionality, twofold interwoven frameworks in the case of the 4,4′-bipyridyl salt and a sheet in the case of 1,2-di-4-pyridylethane, depends solely on multiple C—H···O hydrogen bonds (Bowes *et al.*, 2003).

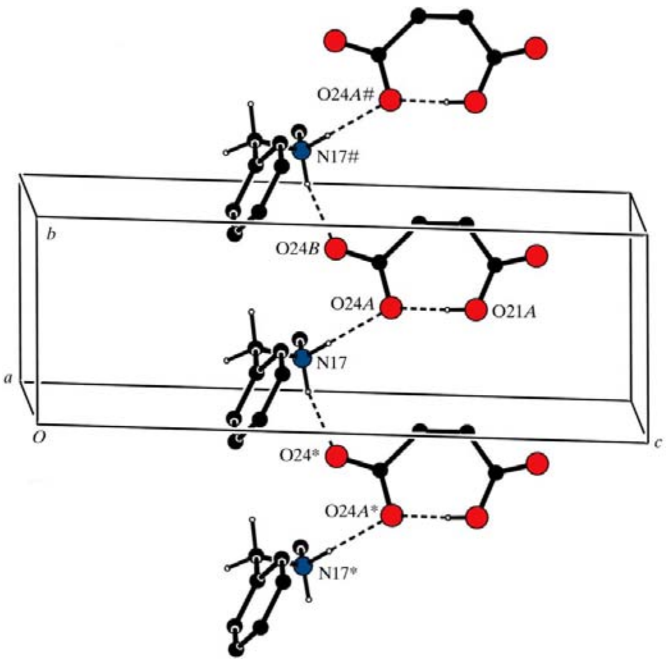

Figure 2
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C_2^2(6)$ chain parallel to [010]. For the sake of clarity, H atoms bonded to C atoms which play no role in the supramolecular aggregation have been omitted. Atoms marked with an asterisk (*) or a hash symbol (#) are at the symmetry positions (x, $-1 + y$, z) and (x, $1 + y$, z), respectively.

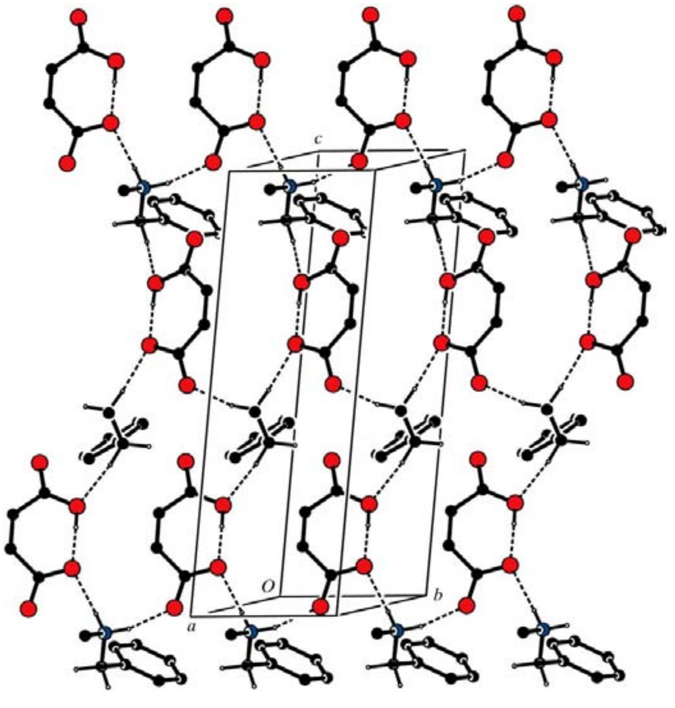

Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to (100). For the sake of clarity, H atoms bonded to C atoms which play no role in the supramolecular aggregation have been omitted.

Experimental

A mixture of maleic anhydride (0.826 mmol) and benzylmethylamine (0.833 mmol) was dissolved in undistilled ethyl acetate (2 ml) and stirred at room temperature for 1 h. The resulting white solid, compound (I), was collected by filtration and washed with cold ethyl acetate (yield 10%, m.p. 384 K). IR (KBr, ν, cm^{-1}): 3499, 3359, 2932, 2835, 2785, 2698, 1666, 1583, 1489, 1367, 754, 700; MS (70 eV): *m*/*e* (%) 236 (0.6, $M - 1$), 192 (17), 120 (54), 91 (100). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethyl acetate. The identical product was obtained in quantitative yield by stirring an equimolar mixture of maleic acid and benzylmethylamine in ethyl acetate at ambient temperature.

Crystal data

$C_8H_{12}N^+\cdot C_4H_3O_4^-$
$M_r = 237.25$
Monoclinic, $P2_1/c$
$a = 13.1084$ (10) Å
$b = 5.6177$ (2) Å
$c = 17.6911$ (13) Å
$\beta = 113.566$ (7)°
$V = 1194.13$ (15) Å^3
$Z = 4$
Mo *Kα* radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
0.40 × 0.31 × 0.15 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.969$, $T_{max} = 0.985$
28597 measured reflections
2748 independent reflections
1768 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.133$
$S = 1.07$
2748 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C21—O21*A*	1.313 (2)	C24—O24*A*	1.280 (2)
C21—O21*B*	1.219 (2)	C24—O24*B*	1.240 (2)
C21—C22—C23	130.70 (18)	C22—C23—C24	130.61 (18)
C11—C17—N17—C18	172.90 (15)	C12—C11—C17—N17	82.1 (2)
O21*A*—C21—C22—C23	8.2 (3)	O24*A*—C24—C23—C22	−17.2 (3)
O21*B*—C21—C22—C23	−172.5 (2)	O24*B*—C24—C23—C22	163.4 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21*A*—H21*A*···O24*A*	0.84	1.63	2.464 (2)	177
N17—H17*C*···O24*A*	0.92	1.99	2.882 (2)	164
N17—H17*D*···O24*B*^{i}	0.92	1.90	2.802 (2)	166
C17—H17*A*···O21*A*^{ii}	0.99	2.52	3.474 (2)	162

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

The $P2_1/c$ space group was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with distances C—H = 0.95 (aromatic and alkenic), 0.98 (CH$_3$) or 0.99 Å (CH$_2$), N—H = 0.92 Å and O—H = 0.84 Å, and with U_{iso}(H) = kU_{eq}(carrier), where $k = 1.5$ for the hydroxyl and methyl groups and 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3098). Services for accessing these data are described at the back of the journal.

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