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Crystal Structure at 110 K of (*R*)-1-Phenylethylammonium Hydrogen Maleate–Water (1/0.25), and a Study of the Conformation of 1-Phenylethylammonium Ions

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The title compound crystallizes in the orthorhombic space group *C*2 with $a = 39.191(4)$, $b = 5.624(2)$, $c = 11.247(2)$ Å and $\beta = 95.750(11)°$, $Z = 8$. Using 3182 reflections the structure was refined to $R = 0.027$ and $R_w = 0.032$. A short asymmetric intramolecular hydrogen bond is observed in both crystallographically independent anions; the two O–O distances are 2.42 and 2.44 Å. One of the hydrogen maleate ions displays a significant twist of the carboxylic groups relative to the double bond. The two (*R*)-1-phenylethylammonium ions are virtually identical. The water molecule links one of the cations to one of the anions. Based on a search of the Cambridge Structural Database the conformations of 1-phenylethylammonium ions in different salts have been investigated. This showed that three preferred orientations of the phenyl group exist for the ion.

Very short hydrogen bonds with O ··· O distances in the range 2.4–2.5 Å are frequently found in acid salts of dicarboxylic acids. Speakman[1] was the first to perform a thorough investigation of these salts. He found that the crystallographic symmetry often makes the carboxylate and carboxylic acid groups equivalent. Many acidic salts of maleic acid have been characterized structurally. The carboxylate and carboxylic acid groups in the hydrogen maleate salts interact through an intramolecular hydrogen bond. A search of the Cambridge Structural Database[2] showed that a symmetric hydrogen bond was found in approximately half of the hydrogen maleate structures determined with *R*-values less than 0.07. The hydrogen bond was classified to be asymmetric if the difference between the two C–O distances is larger than 0.01 Å rather than using the position of the hydrogen atom, as this may not be well determined in X-ray diffraction studies.

In optical resolution through diastereomeric salt formation 1-phenylethylamine is used widely as a resolving agent for racemic acids. In order to investigate the effect of a chiral cation on the short hydrogen bond in the hydrogen maleate salts we have undertaken a structure determination for the acidic maleate salt of the (*R*)-1-phenylethylammonium ion. As part of this investigation we have also analyzed the stereochemistry of the 1-phenylethylammonium ion in different crystalline environments.

Experimental

Preparation. 1.16 g maleic acid and 1.21 g (*R*)-1-phenylethylamine were dissolved in 5 cm^3 methanol. The white residue obtained after evaporation of the solvent was recrystallized from ethylacetate to give white colourless needles suitable for the X-ray diffraction study. $[\alpha]_D = 7.75$ (*c* 0.5; EtOH), m.p. 100–102°C.

X-Ray crystallography. A crystal of dimensions 0.05 × 0.10 × 0.45 mm was selected for the X-ray diffraction study. Intensity data were collected with a CAD4 diffractometer using graphite-monochromated Cu*K*α radiation. The crystal was cooled to ca. 110 K during the experiment by an Enraf-Nonius gas flow low-temperature device. The temperature measured with a thermocouple in the exhaust pipe was constant within 1 K.

The unit cell dimensions were determined from a refinement of the setting angles for 21 reflections with $16 < \Theta < 44°$. Based on an analysis of reflection profiles, the scan range and the ω-2Θ scan mode were selected. The maximum scan time was 60 s. Intensities of three standard reflections were recorded every 10 000 s, and the orienta-

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† Deceased.

Table 1. Crystal data and a summary of data collection and structure refinement results.

Formula	$(C_8H_{11}N^+)(CH_3O_4^-)\cdot 1/4H_2O$
Formula weight/g mol^{-1}	241.76
Space group	$C2$
Radiation; wavelength/Å	Cu$K\alpha$; 1.541 84
Temperature/K	110 ± 1
Cell dimensions:	
a/Å	39.191(4)
b/Å	5.624(2)
c/Å	11.247(2)
β/Å	95.750(11)
V/Å^3	2466(2)
Z	8
d_{cal}/g cm^{-3}	1.302
μ/cm^{-1}	7.89
$\Delta\omega$/°	$0.8+0.15\tan\Theta$
Θ-range/° (octants measured)	1–75($\pm h\ k\pm l$) 1–40($h-k\pm l$)
No. of measured reflections	6485
No. of unique reflections	3632
R_{int}	0.023
No. of contributing reflections, n, $[\lvert F\rvert^2>(\sigma^2(F)]$	3182
w^{-1}	$\sigma_6^2(F)+4\times10^{-4}\lvert F\rvert^2$
No. of variables, m	404
R	0.027
R_w	0.032
$S=\{\Sigma w\Delta F^2/(n-m)\}^{1/2}$	1.07

Table 2. Positional parameters and B_{iso}.

Atom	x	y	z	B_{iso}
O1A	0.296 92(3)	0.1986(2)	0.3831(1)	2.18(2)
O2A	0.339 75(3)	−0.0518(2)	0.3726(1)	1.90(2)
O3A	0.399 31(3)	−0.0320(2)	0.3352(1)	2.08(2)
O4A	0.437 19(3)	0.2488(2)	0.3091(1)	2.40(2)
C1A	0.326 20(4)	0.1592(3)	0.3587(1)	1.60(3)
C2A	0.346 33(4)	0.3577(3)	0.3132(2)	1.78(3)
C3A	0.379 66(4)	0.3691(3)	0.2963(2)	1.87(3)
C4A	0.407 31(4)	0.1853(3)	0.3158(1)	1.78(3)
NA	0.196 65(3)	0.4828(3)	0.3869(1)	1.62(2)
C5A	0.247 81(4)	0.7121(3)	0.3483(2)	2.24(3)
C6A	0.227 14(4)	0.4903(3)	0.3155(1)	1.65(3)
C7A	0.215 13(4)	0.4701(3)	0.1841(1)	1.67(3)
C8A	0.193 77(5)	0.6417(3)	0.1259(2)	2.08(3)
C9A	0.183 28(5)	0.6199(4)	0.0054(2)	2.61(4)
C10A	0.193 91(5)	0.4273(4)	−0.0586(2)	2.95(4)
C11A	0.215 15(5)	0.2576(4)	−0.0021(2)	2.93(4)
C12A	0.225 64(5)	0.2779(3)	0.1186(2)	2.23(3)
O1B	0.471 59(3)	0.4446(2)	0.5886(1)	2.59(2)
O2B	0.428 88(3)	0.2056(2)	0.6184(1)	2.25(2)
O3B	0.367 55(3)	0.2440(2)	0.6360(1)	2.19(2)
O4B	0.329 48(3)	0.5311(2)	0.6407(1)	2.31(2)
C1B	0.441 11(4)	0.4155(3)	0.5977(1)	1.75(3)
C2B	0.417 76(4)	0.6240(3)	0.5844(1)	1.67(3)
C3B	0.384 21(4)	0.6444(3)	0.5947(1)	1.72(3)
C4B	0.358 78(4)	0.4622(3)	0.6255(1)	1.68(3)
NB	0.467 08(3)	0.6982(3)	0.3137(1)	1.97(3)
C5B	0.505 10(5)	0.9109(3)	0.1882(2)	2.35(3)
C6B	0.482 69(4)	0.6926(3)	0.1966(1)	2.02(3)
C7B	0.454 36(5)	0.6668(3)	0.0963(1)	2.24(3)
C8B	0.429 58(5)	0.8400(4)	0.0731(2)	2.65(4)
C9B	0.402 71(6)	0.8096(5)	−0.0154(2)	3.94(5)
C10B	0.401 18(7)	0.6063(5)	−0.0839(2)	5.28(6)
C11B	0.426 01(9)	0.4359(5)	−0.0649(2)	6.07(7)
C12B	0.452 44(7)	0.4658(4)	0.0246(2)	4.15(5)
OW	0.500	0.000	0.500	2.07(3)

tion of the crystal was checked after every 300 reflections. These measurements showed that no mis-setting or deterioration of the crystal had occurred during the data collection. The data reduction included corrections for background, Lorentz and polarization effects, and the reflections were averaged according to the symmetry of the crystal class. The structure was solved by direct methods (SHELX-86)[3] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o|-|F_c|)^2$. After anisotropic displacement parameters were introduced a difference density map showed clearly the positions of all the hydrogen atoms in the structure. A fixed isotropic displacement parameter of 2.5 Å^2 was used for the hydrogen atoms and their positional parameters included in the refinement. After the final cycle the maximum shift was 0.4σ. The final difference density was featureless with values in the range -0.2 to 0.2 e Å^{-3}. Additional details concerning data collection and structure refinement are given in Table 1. Apart from the structure determination, all the crystallographic computations were performed with the SDP-system.[4] Scattering factors were from Ref. 5 and used as contained in the program.

The final positional parameters for the non-hydrogen atoms are listed in Table 2. Anisotropic displacement parameters, parameters for the hydrogen atoms and lists of observed and calculated structure amplitudes can be obtained from one of the authors (S.L.).

Discussion

The crystal structure determination revealed that the compound is a hydrate. The oxygen atom of the water molecule is found on a crystallographic twofold axis. With two independent cations and anions in the asymmetric unit this corresponds to $1/4H_2O$ per ion pair. First we give a description of the entities in the crystal, followed by a discussion of their intermolecular interactions.

The hydrogen maleate ions. The molecular geometry of the two anions is illustrated in Fig. 1 and the bond lengths and angles in Table 3. An inspection of the table reveals that the two anions are virtually identical; the bond lengths and angles agree within experimental error, only differing in their conformation. The anion labelled B is almost planar. The two carboxylate groups in the ion labelled A are twisted significantly from the plane defined by the C1–C2–C3–C4 fragment. This is surprising, as the strong intramolecular hydrogen bond in the hydrogen maleate ion should stabilize the planar conformation of the ion.

An examination of hydrogen maleate salts in the Cambridge Structural Database shows that in most cases the ion is found in a planar conformation. Deviations from planarity comparable to those observed in anion A, as large as 12°, have previously only been observed in a few of the investigated hydrogen maleates;[6–8] in these cases they were also salts of large organic chiral cations.

Comparative studies of the geometry of the hydrogen

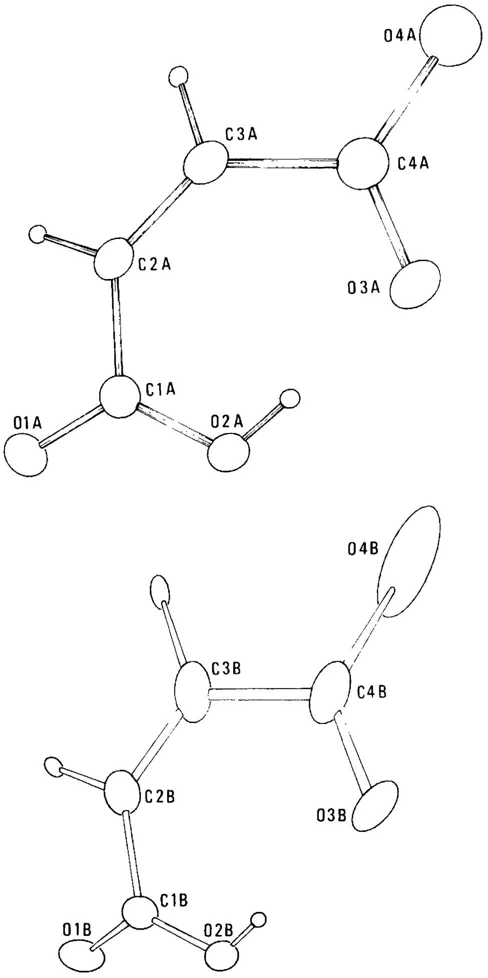

Fig. 1. ORTEP[15] drawings of the two hydrogen maleate anions. The thermal ellipsoids are scaled to enclose 50% probability. The hydrogen atoms are drawn as spheres with a fixed radius.

Table 3. Bond lengths (in Å), bond and torsion angles (in °) in the hydrogen maleate ions.

	A	B
C1–O1	1.226(2)	1.220(2)
C1–O2	1.303(2)	1.303(2)
C1–C2	1.487(3)	1.486(3)
C2–C3	1.340(3)	1.336(2)
C3–C4	1.498(3)	1.494(2)
C4–O3	1.286(2)	1.276(2)
C4–O4	1.234(2)	1.240(2)
O1–C1–O2	121.1(2)	121.1(2)
O1–C1–C2	118.8(2)	119.0(2)
O2–C1–C2	120.1(2)	119.9(2)
C1–C2–C3	130.0(2)	131.3(2)
C2–C3–C4	130.3(2)	130.2(2)
C3–C4–O3	119.7(2)	120.1(2)
C3–C4–O4	118.0(2)	117.8(2)
O3–C4–O4	122.3(2)	122.1(2)
O2–C1–C2–C3	−9.9(3)	3.3(3)
C1–C2–C3–C4	−1.0(3)	1.2(3)
C2–C3–C4–O3	11.8(3)	−6.4(3)

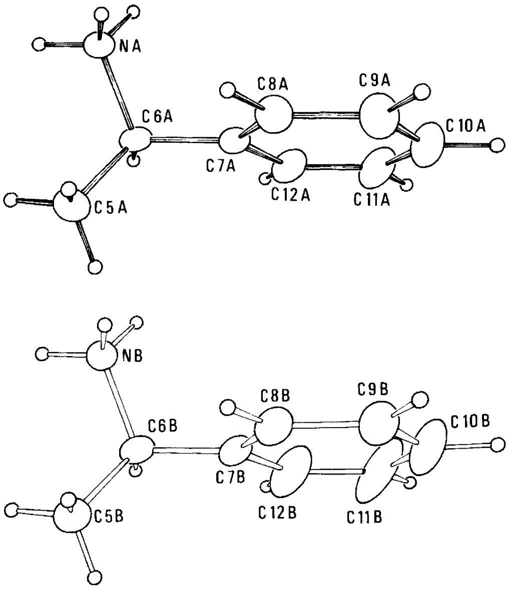

Fig. 2. ORTEP[15] drawings of the two independent cations. The thermal ellipsoids are scaled to enclose 50% probability and the hydrogen atoms as spheres with a fixed radius.

maleate ion have been performed by Olovsson *et al.*[9] and by Popeliver *et al.*[10]

From the refined positions of the hydrogen atoms and from the difference in bond lengths in the two carboxy moieties we conclude that the intramolecular hydrogen bonds in the anions are asymmetric.

(R)-*1-Phenylethylammonium ions.* The two independent cations are depicted in Fig. 2. Both these diagrams and

Table 4. Bond lengths (in Å), bond and torsion angles (in °) in the (*R*)-1-phenylethylammonium ions.

	A	B
N–C6	1.506(2)	1.508(3)
C6–C5	1.513(3)	1.518(3)
C6–C7	1.510(2)	1.508(3)
C7–C8	1.397(3)	1.382(3)
C8–C9	1.381(3)	1.386(3)
C9–C10	1.388(3)	1.377(4)
C10–C11	1.379(3)	1.367(5)
C11–C12	1.383(3)	1.381(4)
C12–C7	1.394(3)	1.386(3)
N–C6–C5	109.1(2)	109.0(2)
N–C6–C7	109.5(2)	108.8(2)
C5–C6–C7	114.2(2)	114.8(2)
C6–C7–C8	121.4(2)	121.6(2)
C6–C7–C12	119.8(2)	120.4(2)
C8–C7–C12	118.8(2)	118.0(2)
C7–C8–C9	120.3(2)	121.2(2)
C8–C9–C10	120.2(2)	119.5(3)
C9–C10–C11	120.0(2)	120.3(3)
C10–C11–C12	120.1(2)	119.9(3)
C11–C12–C7	120.6(2)	121.1(3)
N–C6–C7–C8	62.2(2)	63.6(2)
C5–C6–C7–C8	−60.3(2)	−58.7(2)

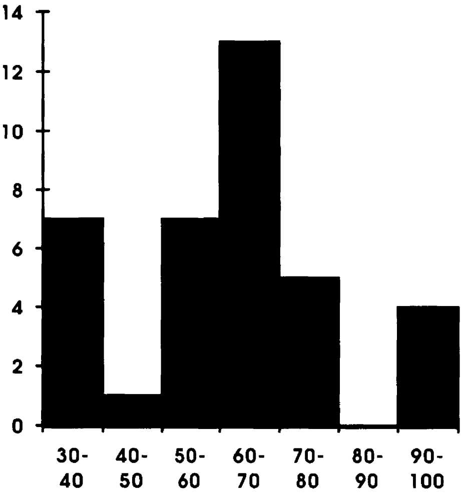

Fig. 3. A histogram drawn a 10° intervals for the torsion angle N–C6–C7–C8 of the (*R*)-1-phenylethylammonium ion.

the bond lengths and angles listed in Table 4 show that the two cations are virtually identical even with respect to their conformation. As this similarity cannot be caused by intramolecular hydrogen bonding, we have made use of the Cambridge Structural Database to investigate the variation in conformation of the (*R*)-1-phenylethylammonium ions described by the relative orientation of the phenyl group. A search resulted in 39 unique 1-phenylethylammonium salts. Structural information was available for 28 salts, containing 32 independent 1-phenylethylammonium ions. The relative orientation of the phenyl group described by the torsion angle N–C6–C7–C8 was calculated for these ions using the GSTAT program. To define the torsion angle uniquely, C8 was selected as the carbon atom in the benzene ring, which gave opposite signs for the two torsion angles N–C6–C7–C8 and C5–C6–C7–C8 and a positive sign for the N–C6–C7–C8 angle. The signs of the torsion angles for (*S*)-1-phenylethylammonium salts were inverted to make all torsion angles refer to the (*R*)-1-phenylethylammonium ion. In the analysis of the conformation of the ions, we also included results from recently published structure determinations from our group[11,12] as well as those reported here. The distribution of the torsion angle N–C6–C7–C8 for (*R*)-1-phenylethylammonium ions is illustrated by the histogram in Fig. 3, showing three maxima in the distribution. Most of the torsion angles are found in a rather narrow (30°) interval around 60°, but the distribution also has two almost symmetrical maxima

Table 5. Geometrical characterisation of the hydrogen bonds.

D–H---A	D–A/Å	∠D–H–A/°	H–A/Å
O2A–HO2A–O3A	2.416(2)	174(2)	1.31(2)
O2B–HO2B–O3B	2.441(2)	177(2)	1.39(2)
NA–HNA1–O1A[a]	2.846(2)	147(2)	1.99(2)
NA–HNA2–O3B[a]	2.902(2)	154(2)	1.99(2)
NA–HNA3–O4B[b]	2.745(2)	174(2)	1.82(2)
NB–HNB1–OW[c]	2.897(2)	133(2)	2.17(2)
NB–HNB1–O1B[d]	2.914(2)	123(2)	2.30(2)
NB–HNB2–O3A[c]	3.089(2)	154(2)	2.26(2)
NB–HNB3–O4A	2.784(2)	169(2)	1.88(3)
OW–HW1–O1B[d]	2.950(2)	151(2)	2.22(3)

[a](1/2–*x*, 1/2+*y*, 1–*z*). [b](1/2–*x*, *y*–1/2, 1–*z*). [c](*x*, *y*+1, *z*). [d](1–*x*, *y*, 1–*z*).

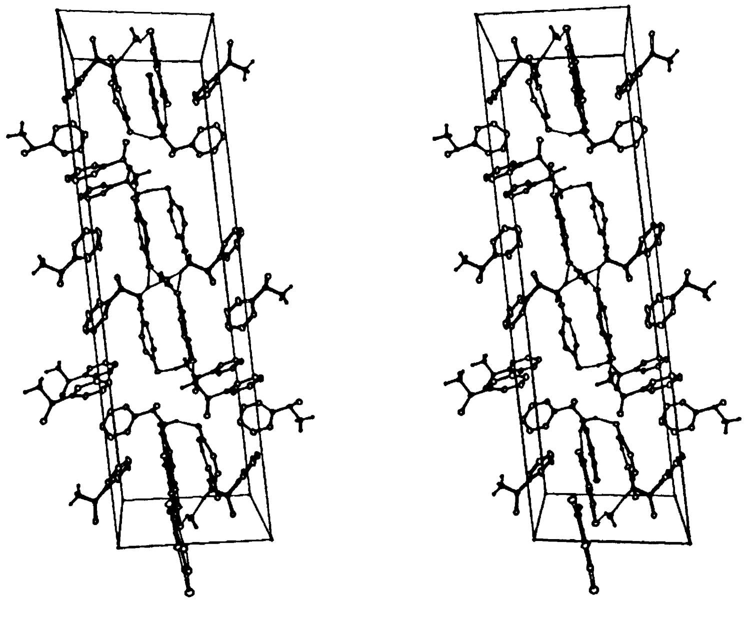

Fig. 4. A stereo diagram illustrating the crystal packing seen along the *b*-axis. The cations and anions are depicted in the same way as in Figs. 1 and 2. The hydrogen bonds are drawn as thin lines.

for torsion angles around 30 and 100°, corresponding to conformations in which the benzene carbon atom is close to either the NH_3^+ or the CH_3 group. The histogram indicates that the 1-phenylethylammonium ion has three preferred conformations; in the one with lowest energy the torsion angle N–C2–C3–C4 is 60°. Two other conformations symmetrically related around the first conformation with N–C6–C7–C8 values of ca. 30 and ca. 100° also appear to be stable conformations with slightly higher energy.

Recently a similar investigation was performed for mandelate salts.[11] The relative orientation of the phenyl group varied much more in these compounds, which have two functional groups that may interact through an intramolecular hydrogen bond.

In the 1-phenylethylammonium hydrogen succinate salt, the anion adopts a highly unusual conformation[13] that is totally different from the usual extended conformation found in other hydrogen succinate salts,[14] but the cation is found in a conformation similar to that observed for the two independent cations in the present structure determination. It suggests that the conformational energy for the 1-phenylethylammonium ion has well defined minima. The bond lengths and angles listed in Table 4 agree well with those observed in other structures containing this cation.

Crystal packing. The hydrogen bonds are listed in Table 5. They play an important role for the crystal packing as illustrated on the stereo pair shown in Fig. 3. All possible donor and acceptor atoms take part in the hydrogen bonding.

The independent ions are involved in slightly different hydrogen-bond interactions. As shown in Table 4 the three carboxy oxygen atoms O1, O3 and O4 accept three protons from three different ammonium groups, but in addition O1 in ion B accepts a proton from a water molecule. One of the hydrogen atoms of cation B's NH_3^+ group is involved in bifurcated hydrogen bonds to O1B and OW. The water molecule seems to play an essential role in the crystal packing, linking one of the cations (B) to the almost planar anion labelled B. It should be noted that the compound is prepared from a non-aqueous medium, so the presence of water seems to be essential for stabilization of the crystal packing.

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