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β-Alaninium maleate

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Key indicators

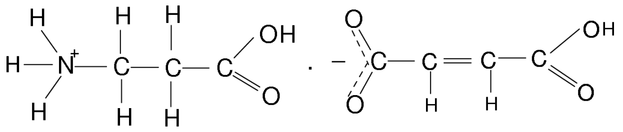
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.190
Data-to-parameter ratio = 12.3

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

In the title compound, $C_3H_8NO_2^+ \cdot C_4H_3O_4^-$, the β-alanine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in the mono-ionized state. In the semi-maleate ion, the intramolecular hydrogen bond between atoms O3 and O5 is found to be asymmetric. There are no direct hydrogen-bonded interactions between the semi-maleate anions. The nature of interactions between individual molecules is different from those observed in L-alaninium maleate.

Comment

Structural data for complexes of organic acids with amino acids seem to be very limited. Among organic acids, simple carboxylic acids, which are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971), form crystalline complexes with amino acids. X-ray studies on many such compounds are being carried out in our laboratory with the aim of studying the nature of intermolecular interactions and characteristic aggregation patterns, at atomic resolution. Recently, the crystal structures of glycinium maleate (Rajagopal *et al.*, 2001) and L-alaninium maleate (Alagar *et al.*, 2001) have been reported. The present study reports the crystal structure of β-alaninium maleate, (I), a complex of β-alanine with maleic acid. β-Alanine is the only naturally occurring β-amino acid and is a constituent of the dipeptides carnosine and anserine.



(I)

Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The β-alanine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in the mono-ionized state. The semi-maleate ion is essentially planar as observed in the crystal structures of similar complexes. In the semi-maleate ion, the intramolecular hydrogen bond between atoms O3 and O5 is found to be asymmetric, as in the crystal structures of maleic acid (James & Williams, 1974), glycinium maleate and L-alaninium maleate. However, in the crystal structures of complexes of maleic acid with DL- and L-arginine (Ravishankar *et al.*, 1998) and L-histidine and L-lysine (Pratap *et al.*, 2000), this intramolecular hydrogen bond between the carboxylic acid and

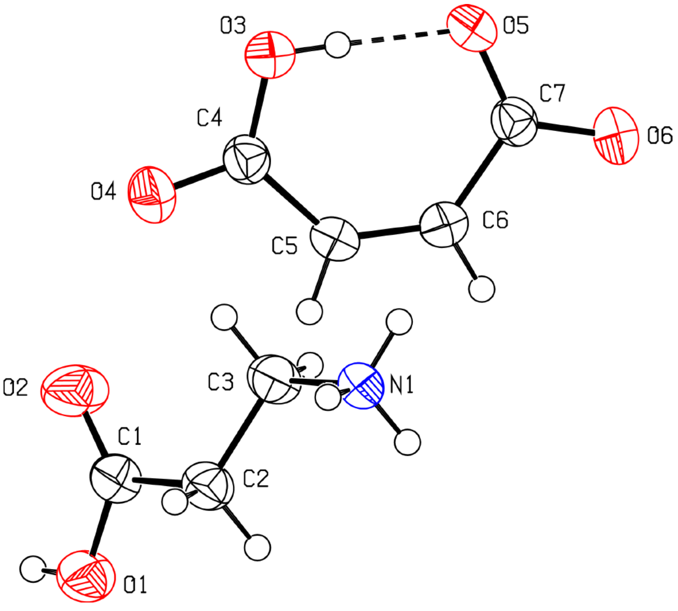


Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

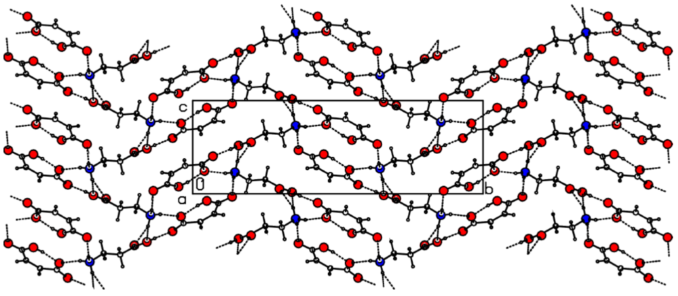


Figure 2
Packing of the molecules of (I) viewed down the *a* axis.

carboxylate groups is symmetric with an H atom shared between the respective O atoms. A common feature observed among the crystal structures of amino acid–maleic acid complexes is that the shortest cell dimension in all of them is close to 5.4 Å, with the exception of lysine–maleic acid complex. It is interesting to note that the shortest cell dimension in almost all the crystal structures of amino acids themselves lies in the neighborhood of 5.4 Å (Suresh & Vijayan, 1983).

Fig. 2 shows the packing of the molecules of (I) viewed down the *a* axis. The *β*-alaninium and semi-maleate ions form alternate columns parallel to the axis of intermediate length, as in L-alaninium maleate. The semi-maleate ions do not have direct hydrogen-bonded interactions among themselves. They link the *β*-alaninium ions into a linear chain running parallel to the longer axis. A head-to-tail hydrogen bond is observed between the *n*-glide related *β*-alaninium ions. Strikingly, the cell lengths of (I) are similar to those in L-alaninium maleate. However, in (I), *β*-alaninium interacts with the semi-maleate anion through the ionized carboxylate group, as in glycinium maleate, whereas in L-alaninium maleate the interaction is through the carboxylic acid group. Such differences in the nature of interaction between individual molecules is reflected in the packing mode. The zigzag packing of molecules observed in (I) is distinctly different from those observed in the crystal structures of other amino acid–maleic acid complexes. The crystal packing is also characterized by the presence of two C—H···O hydrogen bonds.

Experimental

Colorless needle-shaped single crystals of (I) were grown from a saturated aqueous solution containing *β*-alanine and maleic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_3H_8NO_2^+ \cdot C_4H_3O_4^-$
$M_r = 205.17$
Monoclinic, $P2_1/n$
$a = 5.4186$ (11) Å
$b = 22.951$ (5) Å
$c = 7.4518$ (15) Å
$\beta = 99.730$ (16)°
$V = 913.4$ (3) Å^3
$Z = 4$
$D_x = 1.492$ Mg m^{-3}
$D_m = 1.51$ Mg m^{-3}
D_m measured by flotation in mixture of xylene and carbon tetrachloride
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 6$–17°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.35 × 0.30 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.97$, $T_{\max} = 0.99$
1775 measured reflections
1600 independent reflections
1344 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 27$
$l = -8 \rightarrow 8$
2 standard reflections every 200 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.190$
$S = 1.16$
1600 reflections
130 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1299P)^2 + 0.1847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.047 (14)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.301 (3)	O6—C7	1.250 (3)
O2—C1	1.209 (3)	C1—C2	1.509 (3)
N1—C3	1.484 (3)	C2—C3	1.501 (3)
O3—C4	1.295 (3)	C4—C5	1.487 (3)
O4—C4	1.222 (3)	C5—C6	1.330 (3)
O5—C7	1.262 (3)	C6—C7	1.492 (3)
O2—C1—O1	124.2 (2)	O3—C4—C5	120.7 (2)
O2—C1—C2	123.4 (2)	C6—C5—C4	131.5 (2)
O1—C1—C2	112.5 (2)	C5—C6—C7	130.3 (2)
C3—C2—C1	111.7 (2)	O6—C7—O5	124.0 (2)
N1—C3—C2	111.3 (2)	O6—C7—C6	115.1 (2)
O4—C4—O3	120.4 (2)	O5—C7—C6	120.9 (2)
O4—C4—C5	118.8 (2)		
O2—C1—C2—C3	24.6 (4)	O3—C4—C5—C6	1.4 (4)
O1—C1—C2—C3	−155.8 (2)	C4—C5—C6—C7	−1.3 (5)
C1—C2—C3—N1	−177.4 (2)	C5—C6—C7—O6	178.3 (2)
O4—C4—C5—C6	−177.7 (3)	C5—C6—C7—O5	−2.0 (4)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O1-H1\cdots O6^{i}}$	0.82	1.71	2.522 (3)	172
$\mathrm{N1-H1}A\cdots\mathrm{O5^{ii}}$	0.89	2.00	2.880 (3)	170
$\mathrm{N1-H1}B\cdots\mathrm{O2^{iii}}$	0.89	2.23	3.012 (3)	146
$\mathrm{N1-H1}C\cdots\mathrm{O4^{iv}}$	0.89	1.99	2.823 (3)	155
$\mathrm{O3-H3\cdots O5}$	0.82	1.66	2.481 (2)	173
$\mathrm{C2-H2}B\cdots\mathrm{O2^{iii}}$	0.97	2.67	3.421 (3)	134
$\mathrm{C6-H6\cdots O6^{v}}$	0.93	2.61	3.477 (3)	156

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

All the H-atom positions were generated geometrically and the H atoms were allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and displacement parameters. The torsion angles about the C—O bonds of the two hydroxyl groups were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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