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L-Alaninium maleate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.106
Data-to-parameter ratio = 7.9

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

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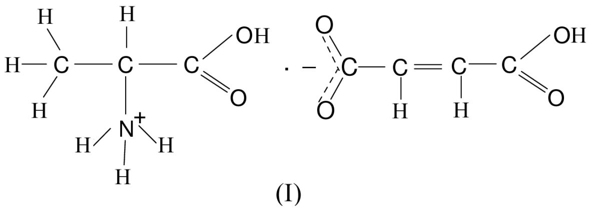
In the title compound, $C_3H_8NO_2^+ \cdot C_4H_3O_4^-$, the alanine molecule exists in the cationic form and the maleic acid molecule in the mono-ionized state. A head-to-tail hydrogen bond is observed between the amino acid molecules. There are no direct hydrogen-bonded interactions between the semimaleate anions. The overall aggregation pattern is similar to that observed in the L-alanine-oxalic acid complex.

Comment

X-ray studies on crystalline complexes of amino acids with simple carboxylic acids, which are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971), are expected to throw light on the nature of intermolecular interactions and biomolecular aggregation patterns (Vijayan, 1988; Prasad & Vijayan, 1993). The crystal structures of complexes of oxalic acid with glycine (Subha Nandhini *et al.*, 2001*a*), sarcosine (Krishnakumar *et al.*, 1999), L-alanine (Subha Nandhini *et al.*, 2001*b*) and DL-alanine (Subha Nandhini *et al.*, 2001*c*) were elucidated recently. The present report on the crystal structure of L-alaninium maleate is part of a series of investigations on amino acid–carboxylic acid complexes.



(I)

Fig. 1 shows the molecular structure with the numbering scheme. The 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 (*i.e.* as a semimaleate). A common feature observed among the crystal structures of L-alaninium oxalate, DL-alaninium oxalate and (I) is that their cell dimensions are very similar. However, the crystals of the racemate are monoclinic and those of the isomers are orthorhombic. The semimaleate ion is essentially planar and the intramolecular hydrogen bond between atoms O3 and O5 is found to be asymmetric, as in the crystal structure of maleic acid (James & Williams, 1974).

Fig. 2 shows the packing of molecules of (I) viewed down the *a* axis. The alaninium and semimaleate ions form alternate columns parallel to the *b* axis. There are no direct hydrogen-bond interactions between the semimaleate anions. They link the alaninium ions into a linear chain running parallel to the

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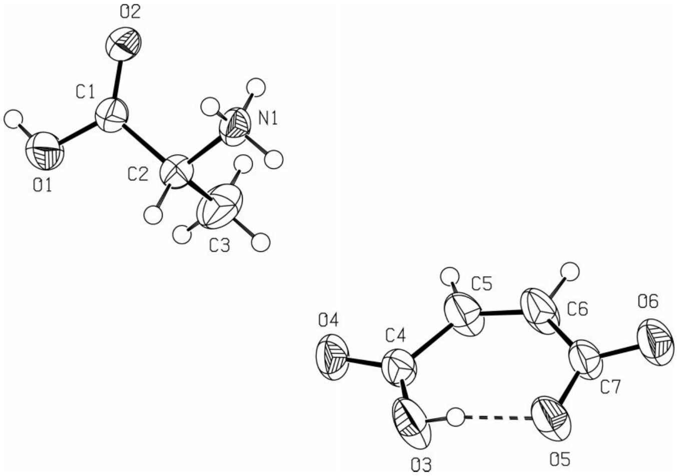

Figure 1
The molecular structure of (I) with atom-numbering scheme and 50% probability displacement ellipsoids.

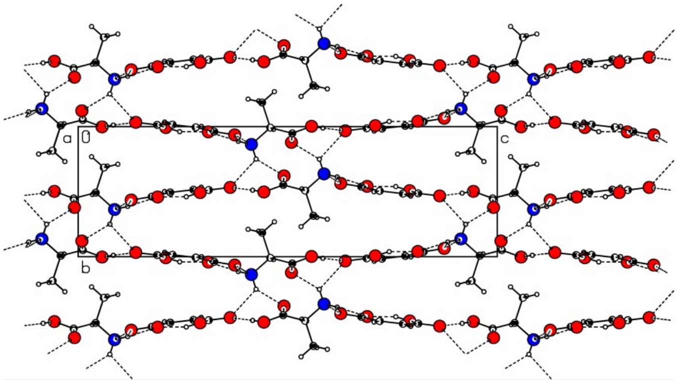

Figure 2
Packing diagram of the molecules of (I) viewed down the *a* axis.

longer *c* axis. The overall aggregation pattern is similar to that observed in the L-alanine–oxalic acid complex. A comparison of the crystal structure of (I) with those of complexes of maleic acid with glycine (Rajagopal *et al.*, 2001), DL- and L-arginine (Ravishankar *et al.*, 1998) and L-histidine and L-lysine (Pratap *et al.*, 2000) shows that the intrinsic aggregation properties of individual molecules in a particular amino acid–carboxylic acid complex seem to largely depend on the nature of the amino acid.

Experimental

Colorless single crystals of (I) were grown as transparent needles, from a saturated aqueous solution containing L-alanine and maleic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_3H_8O_2N^+ \cdot C_4H_3O_4^-$
$M_r = 205.17$
Orthorhombic, $P2_12_12_1$
$a = 5.5873 (11)$ Å
$b = 7.3864 (17)$ Å
$c = 23.688 (3)$ Å
$V = 977.6 (3)$ Å^3
$Z = 4$
$D_x = 1.394$ Mg m^{-3}
$D_m = 1.40 (2)$ Mg m^{-3}
D_m measured by flotation in a liquid mixture of xylene and bromoform
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18$–27°
$\mu = 1.08$ mm^{-1}
$T = 293 (2)$ K
Needle, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.76$, $T_{\max} = 0.90$
1024 measured reflections
1024 independent reflections
977 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 67.9°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 25$
2 standard reflections every 200 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.106$
$S = 1.10$
1024 reflections
130 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.1453P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.018 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.303 (3)	N1—C2	1.485 (3)
O2—C1	1.209 (3)	C1—C2	1.509 (3)
O3—C4	1.267 (3)	C2—C3	1.527 (3)
O4—C4	1.230 (3)	C4—C5	1.474 (3)
O5—C7	1.281 (3)	C5—C6	1.326 (4)
O6—C7	1.228 (3)	C6—C7	1.475 (4)
O2—C1—O1	124.8 (2)	O4—C4—C5	117.6 (2)
O2—C1—C2	122.3 (2)	O3—C4—C5	120.8 (2)
O1—C1—C2	112.8 (2)	C6—C5—C4	130.4 (2)
N1—C2—C1	108.28 (18)	C5—C6—C7	131.4 (2)
N1—C2—C3	109.2 (2)	O6—C7—O5	121.8 (2)
C1—C2—C3	110.3 (2)	O6—C7—C6	119.2 (2)
O4—C4—O3	121.6 (2)	O5—C7—C6	119.0 (2)
O2—C1—C2—N1	27.4 (3)	O3—C4—C5—C6	−1.8 (6)
O1—C1—C2—N1	−155.8 (2)	C4—C5—C6—C7	−0.1 (8)
O2—C1—C2—C3	−92.0 (3)	C5—C6—C7—O6	−175.9 (5)
O1—C1—C2—C3	84.8 (3)	C5—C6—C7—O5	3.7 (7)
O4—C4—C5—C6	178.7 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4$^{\rm i}$	0.82	1.78	2.593 (2)	174
O3—H3···O5	0.82	1.63	2.425 (3)	164
N1—H1A···O5$^{\rm ii}$	0.89	2.00	2.887 (3)	175
N1—H1B···O2$^{\rm iii}$	0.89	2.17	2.881 (2)	137
N1—H1B···O4$^{\rm iv}$	0.89	2.43	2.996 (3)	122
N1—H1C···O6$^{\rm v}$	0.89	1.96	2.828 (3)	165
C5—H5···O3$^{\rm vi}$	0.93	2.45	3.264 (3)	146
C6—H6···O5$^{\rm vi}$	0.93	2.51	3.419 (3)	165

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

The absolute configuration of L-alaninium maleate was not established by the analysis but is known from the configuration of the starting reagents. The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms with *HFIX* instructions using *SHELXL*97 (Sheldrick, 1997) defaults.

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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