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DL-Valinium maleate at 150 K

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.134
Data-to-parameter ratio = 14.9

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

In the title compound, $C_5H_{12}NO_2^+ \cdot C_4H_3O_4^-$, the amino acid exists in the cationic form and the maleic acid molecule in the mono-ionized state. The intramolecular hydrogen bond observed between atoms O3 and O5 in the semimaleate anion is found to be asymmetric. The non-polar side chains of the DL-valinium cations form alternating hydrophobic columns down the *a* axis. The crystal structure is stabilized by O—H···O and N—H···O hydrogen bonds.

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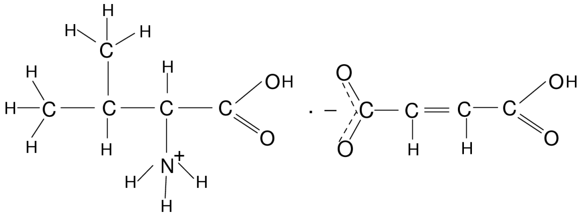
Comment

Valine [$(CH_3)_2CH–CH(NH_2)–COOH$, 2-amino-3-methylbutanoic acid] is one of the amino acids required in human and animal diet for the maintenance of nitrogen equilibrium. It is also glucogenic. Being hydrophobic with a non-polar hydrocarbon chain, it plays a vital role in the stabilization of the structures of protein molecules. Though crystal structures of complexes of valine with a few inorganic acids are known, structural data on the crystalline complexes of valine with organic acids are scarce. The present study on a complex of DL-valine with maleic acid forms part of a series of investigations being carried out in our laboratory on crystalline amino acid–carboxylic acid complexes. The crystal structures of glycinium maleate (Rajagopal *et al.*, 2001) and L-alaninium maleate (Alagar, Krishnakumar, Subha Nandhini & Natarajan, 2001) have been reported recently.



(I)

Fig. 1 shows the molecular structure with the atom-numbering scheme. The DL-valinium molecule exists in the cationic form with a protonated 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. The angle between the planes of the half-molecule, O3/O4/C6/C7 and O5/O6/C8/C9, is 8.1 (1)°. This value is somewhat larger than that found in L-phenylalaninium maleate [3.5 (1)°; Alagar, Krishnakumar & Natarajan, 2001], where the intramolecular hydrogen bond between atoms O3 and O5 is symmetric. The larger value observed in (I) may be attributed to the asymmetric nature of the intramolecular

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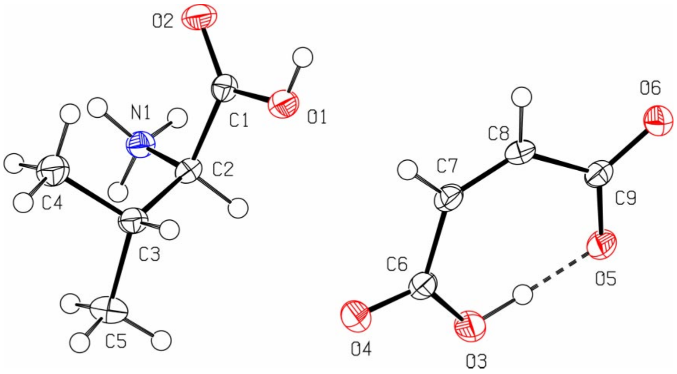

Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

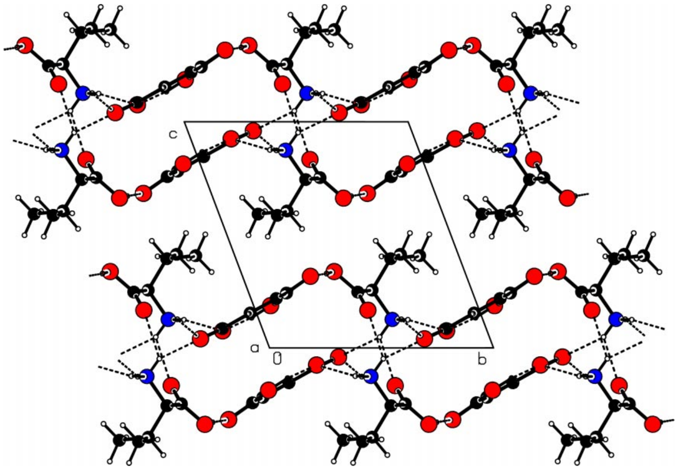

Figure 2
Packing of the molecules of (I), viewed down the *a* axis.

hydrogen bond. An asymmetric intramolecular hydrogen bond is observed in the crystal structures of maleic acid (James & Williams, 1974), glycinium maleate and L-alaninium maleate; it is found to be symmetric 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) with an H atom shared between the respective O atoms.

Fig. 2 shows the packing of the molecules of (I), viewed down the *a* axis. The semi-maleate ions do not have direct hydrogen-bonded interactions among themselves except for a weak C—H···O hydrogen bond which links them to form an infinite one-dimensional chain down the *a* axis. There is a head-to-tail hydrogen bond among the centrosymmetrically-related amino acid molecules leading to the formation of a dimer. The non-polar side chains of the DL-valinium cations form alternating hydrophobic columns down the *a* axis. The crystal packing is characterized by O—H···O and N—H···O hydrogen bonds. However, considering the presence of many strong O—H···O and N—H···O bonds, it seems unlikely that weak hydrogen bonds of the type C—H···O play a role in determining the packing modes of the molecules. The aggregation pattern has some similarities with that observed in L-phenylalaninium maleate, but is distinctly different from glycinium maleate and L-alaninium maleate.

Experimental

Colorless prismatic single crystals of (I) were grown from a saturated aqueous solution containing DL-valine and maleic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_5H_{12}NO_2^+ \cdot C_4H_3O_4^-$
$M_r = 233.22$
Triclinic, $P\overline{1}$
$a = 6.1830\ (12)$ Å
$b = 9.6480\ (19)$ Å
$c = 10.534\ (2)$ Å
$\alpha = 104.92\ (3)^\circ$
$\beta = 106.32\ (3)^\circ$
$\gamma = 104.40\ (3)^\circ$
$V = 546.71\ (19)$ Å^3
$Z = 2$
$D_x = 1.417$ Mg m^{-3}
$D_m = 1.42$ Mg m^{-3}
D_m measured by flotation in a mixture of xylene and carbon tetrachloride
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
$\theta = 2.2$–26.3°
$\mu = 0.12$ mm^{-1}
$T = 150\ (2)$ K
Prismatic, colorless
0.3 × 0.3 × 0.3 mm

Data collection

BRUKER SMART diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1998)
$T_{\min} = 0.968$, $T_{\max} = 0.968$
5585 measured reflections
2225 independent reflections
1991 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 26.4^\circ$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 11$
$l = -13 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.134$
$S = 1.09$
2225 reflections
149 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0837P)^2 + 0.1505P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3170 (18)	C1—C2	1.5236 (19)
O2—C1	1.2117 (17)	C2—C3	1.539 (2)
O3—C6	1.2932 (19)	C3—C5	1.5289 (19)
O4—C6	1.2343 (19)	C3—C4	1.532 (2)
O5—C9	1.2812 (17)	C6—C7	1.4963 (19)
O6—C9	1.2386 (17)	C7—C8	1.336 (2)
N1—C2	1.4967 (18)	C8—C9	1.502 (2)
O2—C1—O1	125.43 (13)	O4—C6—O3	122.39 (14)
O2—C1—C2	122.63 (13)	O4—C6—C7	117.28 (13)
O1—C1—C2	111.93 (11)	O3—C6—C7	120.33 (13)
N1—C2—C1	106.47 (11)	C8—C7—C6	130.46 (13)
N1—C2—C3	113.72 (11)	C7—C8—C9	130.42 (13)
C1—C2—C3	111.40 (11)	O6—C9—O5	123.48 (13)
C5—C3—C4	111.08 (12)	O6—C9—C8	116.58 (12)
C5—C3—C2	111.31 (12)	O5—C9—C8	119.94 (12)
C4—C3—C2	112.87 (12)		
O2—C1—C2—N1	−15.48 (17)	C1—C2—C3—C4	−63.27 (15)
O1—C1—C2—N1	165.83 (11)	O4—C6—C7—C8	173.59 (15)
O2—C1—C2—C3	109.03 (15)	O3—C6—C7—C8	−6.5 (2)
O1—C1—C2—C3	−69.66 (15)	C6—C7—C8—C9	−0.2 (3)
N1—C2—C3—C5	−68.65 (15)	C7—C8—C9—O6	−176.16 (15)
C1—C2—C3—C5	171.02 (11)	C7—C8—C9—O5	4.0 (2)
N1—C2—C3—C4	57.05 (16)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.84	1.76	2.5963 (15)	178
O3—H3···O5	0.84	1.60	2.4330 (17)	174
N1—H1*A*···O6^{ii}	0.91	1.99	2.8323 (17)	154
N1—H1*B*···O5^{iii}	0.91	2.07	2.9572 (18)	166
N1—H1*C*···O2^{iv}	0.91	2.21	2.8542 (17)	127
N1—H1*C*···O6^{v}	0.91	2.07	2.828 (2)	140
C2—H2···O4^{vi}	1.00	2.48	3.453 (2)	164
C7—H7···O1^{vi}	0.95	2.51	3.458 (2)	172
C8—H8···O3^{vii}	0.95	2.54	3.4229 (19)	155

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

All the H atoms were positioned geometrically and were allowed to ride on their parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and displacement parameters.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); 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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