

DL-Valine-fumaric acid (2/1)

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.058

wR factor = 0.154

Data-to-parameter ratio = 13.7

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

In the title compound, $\text{C}_5\text{H}_{11}\text{NO}_2 \cdot 0.5\text{C}_4\text{H}_4\text{O}_4$, the valine molecule exists as a zwitterion and the fumaric acid molecule in the unionized state, forming an adduct, a feature uncommon in similar crystal structures. The fumaric acid molecule has a centre of symmetry and is planar with a *trans* configuration about the central $\text{C}=\text{C}$ bond. The fumaric acid molecules have no hydrogen-bonded interactions among themselves and only mediate interactions between DL-valine layers, leading to a three-dimensional network of molecules.

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Comment

Fumaric acid, a key intermediate in organic acid biosynthesis, is known to readily form adducts/complexes with other organic molecules. Valine, an essential amino acid, is hydrophobic with a non-polar hydrocarbon chain and plays a vital role in the stabilization of protein molecules. A determination of the present crystal structure, (I), was carried out to examine the stoichiometry and ionization states, and it appears to be the first of its kind involving fumaric acid and an amino acid. Moreover, the aggregation and the interaction patterns observed in amino acid–carboxylic acid complexes might possibly contribute to an understanding of the self-assembly processes that might have led to the emergence of primitive multimolecular systems. Recently, the crystal structures of complexes of DL-valine with maleic acid (Alagar *et al.*, 2001) and trichloroacetic acid (Rajagopal *et al.*, 2002) were reported from our laboratory.

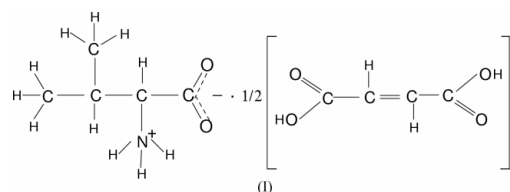


Fig. 1 shows the molecular structure of (I), with the adopted atom-numbering scheme. The valine molecule exists as a zwitterion, and the fumaric acid molecule in the unionized state, forming an adduct involving the two distinct species, a feature uncommon in similar crystal structures. Usually in the crystals of amino acid–carboxylic acid complexes, the amino acid molecule is expected to exist in the cationic state (with a neutral carboxylic acid group and a protonated amino group) and the dicarboxylic acid in the anionic state (with a neutral carboxylic acid group and a negatively charged carboxylate group), as a result of proton transfer. The observed zwitterionic form of DL-valine and the unionized state of fumaric acid in the present structure is due to a ‘break-down’ in the

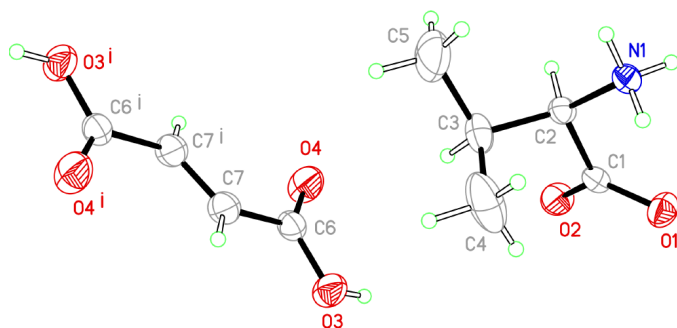


Figure 1
The molecular structure of (I), with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $-x, -y, -z$].

otherwise routine proton transfer observed in such complexes. The conformation of the valine molecule, determined by χ^{11} [$-58.9(2)^\circ$] and χ^{12} [$68.5(2)^\circ$], differs significantly from the values observed for the monoclinic form of DL-valine (Mallikarjunan & Rao, 1969) and for the triclinic form of DL-valine (Dalhus & Görbitz, 1996). However, the values agree well with those observed in DL-valinium maleate (Alagar *et al.*, 2001), in spite of the difference in the ionization states of the amino acid molecules. The fumaric acid molecule has a centre of symmetry, and is planar with a *trans* configuration about the central C=C bond.

The adduct formed by DL-valine and fumaric acid is held together by hydrogen-bonding interactions (Fig. 2). DL-valine molecules aggregate into layers parallel to the *bc* plane, in which glide- and screw-related head-to-tail hydrogen bonds are present between the amino acids. The fumaric acid molecules have no hydrogen-bonded interactions among themselves. They only mediate interactions between DL-valine layers through hydrogen bonds, leading to a three-dimensional network of molecules. The aggregation pattern of individual molecules is distinctly different from those observed in the complexes of DL-valine with maleic acid and trichloroacetic acid.

Experimental

Colourless single crystals of (I) were grown, as transparent needles, from a saturated aqueous solution containing DL-valine and fumaric acid in 1:1 stoichiometric ratio.

Crystal data

$C_5H_{11}NO_2 \cdot 0.5C_4H_4O_4$
 $M_r = 175.18$
 Monoclinic, $C2/c$
 $a = 24.417(4) \text{ \AA}$
 $b = 7.5713(10) \text{ \AA}$
 $c = 10.013(2) \text{ \AA}$
 $\beta = 109.268(10)^\circ$
 $V = 1747.4(5) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.332 \text{ Mg m}^{-3}$
 $D_m = 1.34(2) \text{ Mg m}^{-3}$

D_m , measured by flotation in xylene-bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 7\text{--}13^\circ$
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Plate, colourless
 $0.28 \times 0.22 \times 0.14 \text{ mm}$

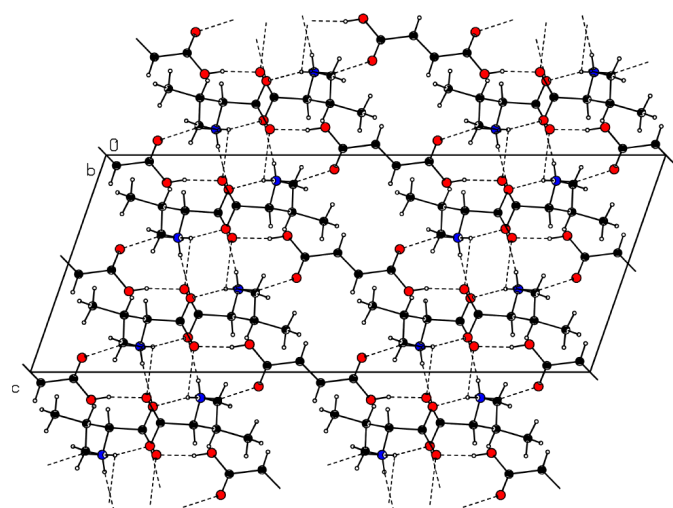


Figure 2
Packing diagram of the molecules of (I), viewed down the *b* axis.

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.88, T_{\max} = 0.98$
 2600 measured reflections
 1524 independent reflections
 1356 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.10$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 28$
 $k = -8 \rightarrow 8$
 $l = -11 \rightarrow 11$
 2 standard reflections
 every 100 reflections
 intensity decay: $<1\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.154$
 $S = 1.07$
 1524 reflections
 111 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 1.3337P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.007(2)

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

O1—C1	1.263(2)	C2—C3	1.541(3)
O2—C1	1.237(2)	C3—C4	1.507(3)
O3—C6	1.297(2)	C3—C5	1.529(3)
O4—C6	1.214(2)	C6—C7	1.496(2)
N1—C2	1.489(2)	C7—C7 ⁱ	1.322(4)
C1—C2	1.532(2)		
O2—C1—O1	126.24(16)	C4—C3—C2	112.48(16)
O2—C1—C2	116.59(14)	C5—C3—C2	111.04(19)
O1—C1—C2	117.17(15)	O4—C6—O3	125.38(16)
N1—C2—C1	109.74(12)	O4—C6—C7	122.61(16)
N1—C2—C3	113.11(14)	O3—C6—C7	112.01(16)
C1—C2—C3	111.48(15)	C7 ⁱ —C7—C6	121.3(2)
C4—C3—C5	112.7(2)		
O2—C1—C2—N1	-169.55(15)	N1—C2—C3—C4	-58.9(2)
O1—C1—C2—N1	10.6(2)	C1—C2—C3—C4	65.3(2)
O2—C1—C2—C3	64.3(2)	N1—C2—C3—C5	68.5(2)
O1—C1—C2—C3	-115.49(17)	C1—C2—C3—C5	-167.25(18)

Symmetry code: (i) $-x, -y, -z$.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3A \cdots O1 ⁱⁱ	0.82	1.68	2.4860 (18)	168
N1—H1A \cdots O4 ⁱⁱⁱ	0.89	2.03	2.8755 (19)	158
N1—H1B \cdots O2 ^{iv}	0.89	1.97	2.826 (2)	161
N1—H1C \cdots O2 ⁱⁱⁱ	0.89	2.05	2.9201 (19)	166
C2—H2 \cdots O3 ^v	0.98	2.47	3.233 (2)	135

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

The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (spek, 1999); software used to prepare material for publication: *SHELXL97*.

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