DL-Valine–succinic acid (2/1)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.133
Data-to-parameter ratio = 16.6

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

In the title compound, $2C_5H_{11}NO_2 \cdot C_4H_6O_4$, the DL-valine molecule exists in the zwitterionic form and the neutral succinic acid molecule lies across an inversion center. There are no direct hydrogen-bonding interactions between succinic acid molecules. Valine and succinic acid molecules form alternating columns parallel to the c axis and are interlinked through characteristic hydrogen bonds to form a three-dimensional network.

Comment

Valine, an essential amino acid, is required in human and animal diet for the maintenance of nitrogen equilibrium. It is hydrophobic with a non-polar hydrocarbon chain and plays a vital role in the stabilization of the structures of protein molecules. Carboxylic acids belong to an important class of organic molecules and are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971). Recently, carboxylic acids have also attracted the attention of 'crystal engineers' and are being used as suitable substrates for crystal engineering, owing to their ability to form predictable modes of hydrogen-bonding interactions among themselves. Crystal structures of complexes of amino acids with carboxylic acids have provided a wealth of information regarding stoichiometry, ionization states, hydrogen-bonding interactions and aggregation patterns of individual molecules. In this context, accurate determination of crystal structures of such complexes are being carried out in our laboratory, and recently the crystal structures of DL-valinium maleate (Alagar *et al.*, 2001), DL-valinium trichloroacetate (Rajagopal *et al.*, 2002) and DL-valine–fumaric acid (2/1) (Alagar *et al.*, 2003) have been reported.
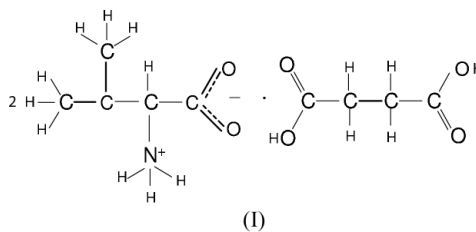

(I)

Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The asymmetric unit of (I) contains one valine and one-half of a succinic acid molecule. In the crystal structures of amino acid–dicarboxylic acid complexes, usually the amino acid molecule exists as a cation (with a positively charged amino group and a uncharged carboxylic acid group) and the carboxylic acid exists as an anion (doubly negatively charged) or as a semi-anion (singly negatively charged). In the
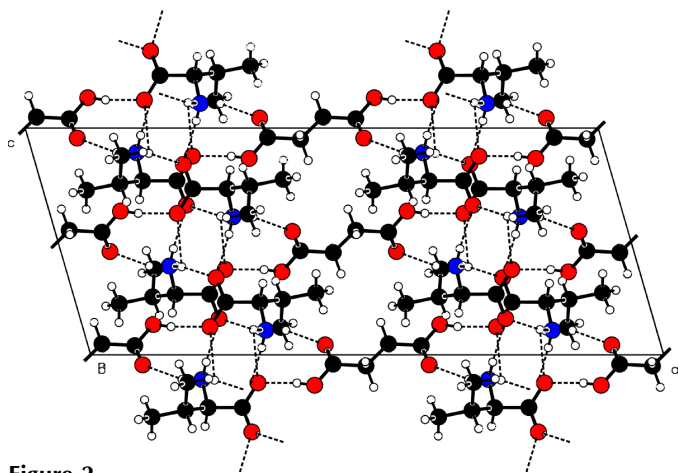
DOI: 10.1107/S1600536804011134 M. Alagar *et al.* · $2C_5H_{11}NO_2 \cdot C_4H_6O_4$ **o1009**
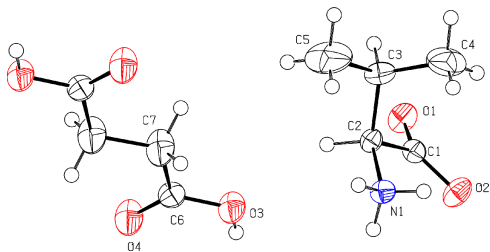
Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

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

title compound, (I), DL-valine exists as a zwitterion, as observed in the crystal structure of DL-proline with succinic acid (Prasad & Vijayan, 1993). However, the zwitterionic form of amino acids in similar crystal structures remains an uncommon feature. The carboxylate and the amino group are coplanar, with the former twisted by 10.7 (2)° from the plane, and this configuration is also evidenced from the values of ψ_1 [−169.3 (1)°] and ψ_2 [10.7 (2)°]. The conformation of the valine molecule described by χ^{11} [−59.9 (2)°] and χ^{12} [67.6 (2)°] differs significantly from that observed for the monoclinic form of DL-valine (Mallikarjunan & Rao, 1969) and the triclinic form of DL-valine (Dalhus & Görbitz, 1996). A comparison of χ^{11} and χ^{12}, ignoring the differences in the ionization states, with the complexes of DL-valinium trichloroacetate [−162.9 (1) and 70.9 (1)°], DL-valinium maleate [57.1 (2) and −63.3 (2)°] and DL-valine–fumaric acid (2/1) [−58.9 (2) and 68.5 (2)°] possibly indicates the identical nature of the influence of dicarboxylic acids on the conformation of DL-valine in these crystal structures.

The succinic acid molecule is quite planar and its dimensions in the present structure agree well with the values obtained for succinic acid itself using neutron diffraction (Leviel et al., 1981). The succinic acid molecule exhibits a variety of ionization states in forming complexes with amino acids viz. succinate ion, semisuccinate ion, neutral succinic acid and also as a complex dimeric species (Prasad & Vijayan, 1991). In the present structure, the neutral succinic acid molecule lies across an inversion centre, as observed in the DL-proline–succinic acid complex (Prasad & Vijayan, 1993). It is

interesting to note that, in DL-amino acid complexes, succinic acid prefers to lie across inversion centers, restricting the ionization states for succinic acid in such complexes to either the neutral succinic acid or the doubly negatively charged succinate anion. In the crystal structures of complexes of DL-amino acids with succinic acid, a singly negatively charged succinate anion (unsymmetrical semi-succinate anion) has not yet been found.

Fig. 2 shows the packing of the molecules of (I), viewed down the b axis. Characteristic glide-related head-to-tail hydrogen bonds between valine molecules form layers parallel to the bc plane. These layers are interlinked through succinic acid molecules, forming a three-dimensional network. There are no direct hydrogen-bonded interactions between succinic acid molecules. The aggregation pattern differs significantly from those observed in the cases of complexes of DL-valine with maleic acid and trichloroacetic acid. Interestingly, a comparison of the structural features of (I) with those of DL-valine–fumaric acid shows similarities in the unit-cell lengths and angles, ionization states of the molecules and aggregation patterns. Further investigations of crystal structures containing DL-amino acids with succinic and fumaric acids are expected to throw light on many of the interesting features these complexes/adducts possess.

Experimental

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

Crystal data

$2C_5H_{11}NO_2 \cdot C_4H_6O_4$	D_m measured by flotation in a
$M_r = 352.38$	mixture of xylene and bromoform
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 24.373$ (2) Å	Cell parameters from 1024
$b = 7.5744$ (6) Å	reflections
$c = 10.0284$ (9) Å	$\theta = 2.0$–23.0°
$\beta = 106.134$ (2)°	$\mu = 0.11$ mm^{-1}
$V = 1778.4$ (3) Å^3	$T = 293$ (2) K
$Z = 4$	Block, colorless
$D_x = 1.316$ Mg m^{-3}	$0.28 \times 0.22 \times 0.16$ mm
$D_m = 1.32$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1875 independent reflections
	1620 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan	$\theta_{max} = 28.0°$
(SADABS; Bruker, 1998)	$h = -30 \rightarrow 30$
$T_{min} = 0.96$, $T_{max} = 0.99$	$k = -9 \rightarrow 10$
5087 measured reflections	$l = -5 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.2632P]$
$wR(F^2) = 0.133$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1875 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
113 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2386 (19)	C2—C3	1.534 (2)
O2—C1	1.2543 (18)	C3—C4	1.506 (3)
O3—C6	1.299 (2)	C3—C5	1.522 (3)
O4—C6	1.209 (2)	C6—C7	1.501 (2)
N1—C2	1.4876 (18)	C7—C7^i	1.486 (4)
C1—C2	1.5331 (19)		
O1—C1—O2	126.64 (13)	C4—C3—C2	112.80 (14)
O1—C1—C2	116.18 (13)	C5—C3—C2	111.35 (15)
O2—C1—C2	117.18 (13)	O4—C6—O3	124.78 (14)
N1—C2—C1	109.55 (11)	O4—C6—C7	122.78 (15)
N1—C2—C3	113.25 (12)	O3—C6—C7	112.43 (14)
C1—C2—C3	111.11 (12)	C7^i—C7—C6	114.36 (19)
C4—C3—C5	112.42 (19)		
O1—C1—C2—N1	−169.28 (13)	N1—C2—C3—C5	67.6 (2)
O2—C1—C2—N1	10.68 (18)	C1—C2—C3—C5	−168.58 (17)
O1—C1—C2—C3	64.83 (17)	O4—C6—C7—C7^i	−4.7 (4)
O2—C1—C2—C3	−115.20 (15)	O3—C6—C7—C7^i	176.0 (3)
N1—C2—C3—C4	−59.87 (19)		

Symmetry code: (i) $-x, 2-y, 1-z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O3—H3$\cdots$O2^{ii}	0.82	1.70	2.5050 (15)	169
N1—H1$B\cdots$O4^{iii}	0.89	2.04	2.8814 (16)	158
N1—H1$C\cdots$O1^{iv}	0.89	1.95	2.8124 (16)	162
N1—H1$A\cdots$O1^{v}	0.89	2.04	2.9147 (17)	167

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

All the H atoms were positioned geometrically and were allowed to ride on their parent atoms, with N—H = 0.89 Å, O—H = 0.82 Å and C—H = 0.96–0.98 Å, and with $U_{iso} = 1.2U_{eq}$(C,N) or $1.5U_{eq}$(C,O).

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