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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.032
wR factor = 0.085
Data-to-parameter ratio = 6.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

L-Phenylalanine fumaric acid

In the title adduct, $\text{C}_9\text{H}_{11}\text{NO}_2 \cdot \text{C}_4\text{H}_4\text{O}_4$, the amino acid molecules exist as zwitterions and the fumaric acid molecules exist in the unionized state, a feature uncommon in similar crystal structures. The asymmetric unit is composed of two molecules of each species. The fumaric acid molecules are related to each other through a pseudo-inversion centre and are essentially planar. The phenylalanine and fumaric acid molecules form hydrogen-bonded double layers, linked together by hydrogen bonds and extending along [001]. These double layers are flanked, on either side, by the hydrophobic side chains of phenylalanine, leading to alternating hydrophilic and hydrophobic zones.

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Comment

In view of the importance of non-covalent interactions in the aggregation and interaction patterns of biological molecules, we have been elucidating the X-ray crystal structures of simple complexes involving amino acids and dicarboxylic acids. Precise crystallographic data on such complexes are expected to provide useful insights into chemical evolution and self-assembly, processes that might have led to the emergence of primitive multi-molecular systems. Fumaric acid (*trans*-butenedioic acid) is among the organic compounds widely found in nature, and is a key intermediate in the biosynthesis of organic acids. X-ray investigations of amino acid complexes with fumaric acid seem to have been first initiated in our laboratory. Such investigations have provided some interesting data regarding the ionization states and stoichiometry of these molecules. Recently, we have reported the crystal structures of complexes of maleic acid (*cis*-butenedioic acid) with DL-phenylalanine (Alagar, Subha Nandhini *et al.*, 2003) and L-phenylalanine (Alagar *et al.*, 2001). The present study reports the crystal structure of a complex of L-phenylalanine with fumaric acid.

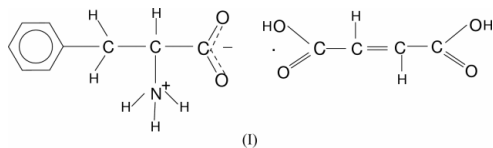


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. There are two molecules of phenylalanine and two molecules of fumaric acid in the asymmetric unit. The ionization state exhibited in this structure is uncommon in similar crystal structures. The amino acid molecules exist as zwitterions and the two fumaric acid molecules exist in the unionized state. Usually, in the crystal structures of amino acid-carboxylic acid complexes, the amino acid molecules prefer the cationic state and the carboxylic acids the anionic

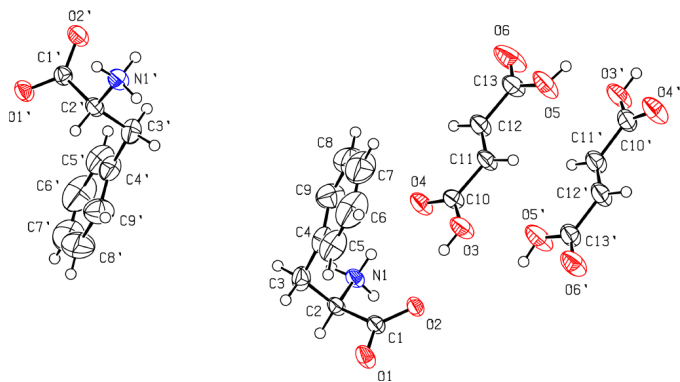


Figure 1
The molecular structure of the asymmetric unit of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

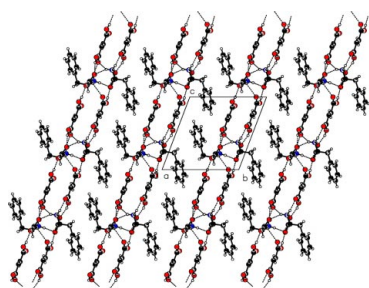


Figure 2
Packing diagram of the molecules of (I), viewed down the *a* axis.

state, either as carboxylate(2⁻) or semicarboxylate(1⁻) anions. The two fumaric acid molecules in the asymmetric unit are related to each other through a pseudo-inversion centre, and are essentially planar.

Interestingly, if we exclude the N and O atoms, then the two independent amino acid molecules are also related by a pseudo-inversion centre. This is evident from the torsion angles ψ^1 [-164.1 (2), -138.6 (3) $^\circ$], ψ^2 [17.8 (4), 41.1 (3) $^\circ$], χ^1 [-69.4 (3), 166.3 (3) $^\circ$], χ^{21} [-96.9 (4), 99.2 (4) $^\circ$], χ^{22} [83.2 (4), -79.1 (4) $^\circ$].

The phenylalanine and fumaric acid molecules form hydrogen-bonded double layers, linked together by N—H \cdots O and O—H \cdots O hydrogen bonds, and extending along [001]. These double layers are flanked, on either side, by the hydrophobic side chains of phenylalanine, leading to alternating hydrophilic and hydrophobic zones (Fig. 2). In addition to van der Waals interactions, a short carbonyl contact C1' \cdots O2 ($x+1, y, z-1$) = 2.998 (3) Å is also observed (Allen *et al.*, 1998).

In the present structure there are no direct hydrogen-bonded interactions between the fumaric acid molecules. This situation is also observed for the non-amino-acid components of the following complexes: L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992), L-phenylalaninium maleate (Alagar *et al.*, 2001), DL-phenylalaninium maleate (Alagar, Subha Nandhini *et al.*, 2003), DL-valine fumaric acid 2/1 (Alagar, Krishnakumar *et al.*, 2003), and DL-valinium maleate (Alagar *et al.*, 2001).

Experimental

Colourless, single crystals of (I) were grown as transparent prisms, from a saturated aqueous solution containing L-phenylalanine and fumaric acid in a 1:1 stoichiometric ratio. The density was measured by flotation in a mixture of xylene and bromoform.

Crystal data

C₉H₁₁NO₂·C₄H₄O₄
M_r = 281.26
 Triclinic, *P*1
a = 5.7016 (10) Å
b = 11.4864 (15) Å
c = 11.5542 (17) Å
 α = 67.953 (11) $^\circ$
 β = 81.158 (13) $^\circ$
 γ = 79.379 (15) $^\circ$
V = 686.37 (19) Å³
Z = 2

D_x = 1.361 Mg m⁻³
D_m = 1.35 (2) Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 2–7 $^\circ$
 μ = 0.11 mm⁻¹
T = 293 (2) K
 Prism, colorless
 0.28 × 0.23 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 T_{\min} = 0.960, T_{\max} = 0.975
 2541 measured reflections
 2540 independent reflections
 2154 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.013
 θ_{\max} = 25.0 $^\circ$
 $h = -6 \rightarrow 6$
 $k = 0 \rightarrow 13$
 $l = -12 \rightarrow 13$
 2 standard reflections every 100 reflections
 intensity decay: < 1%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 1.03$
 2410 reflections
 366 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.0393P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, $^\circ$).

O1—C1	1.245 (3)	O1'—C1'	1.249 (3)
O2—C1	1.247 (3)	O2'—C1'	1.257 (3)
N1—C2	1.488 (3)	N1'—C2'	1.488 (3)
C1—C2	1.521 (3)	C1'—C2'	1.533 (4)
C2—C3	1.539 (4)	C2'—C3'	1.526 (4)
C3—C4	1.508 (5)	C3'—C4'	1.506 (4)
O3—C10	1.318 (4)	O3'—C10'	1.315 (4)
O4—C10	1.214 (4)	O4'—C10'	1.199 (4)
O5—C13	1.307 (4)	O5'—C13'	1.313 (4)
O6—C13	1.200 (4)	O6'—C13'	1.209 (4)
O1—C1—O2	124.6 (2)	O1'—C1'—O2'	124.1 (3)
N1—C2—C1	110.2 (2)	N1'—C2'—C1'	110.4 (2)
N1—C2—C3	112.0 (2)	N1'—C2'—C3'	109.5 (2)
C1—C2—C3	111.1 (2)	C1'—C2'—C3'	111.8 (2)
O4—C10—O3	123.6 (3)	O4'—C10'—O3'	124.9 (3)
C12—C11—C10	120.1 (3)	C12'—C11'—C10'	122.1 (3)
O6—C13—O5	125.2 (3)	O6'—C13'—O5'	122.8 (3)
O1—C1—C2—N1	-164.1 (2)	O1'—C1'—C2'—N1'	-138.6 (2)
O2—C1—C2—N1	17.8 (4)	O2'—C1'—C2'—N1'	41.1 (3)
O1—C1—C2—C3	71.2 (3)	O1'—C1'—C2'—C3'	99.3 (3)
O2—C1—C2—C3	-106.9 (3)	O2'—C1'—C2'—C3'	-81.0 (3)
N1—C2—C3—C4	-69.4 (3)	N1'—C2'—C3'—C4'	166.3 (2)
C1—C2—C3—C4	54.3 (3)	C1'—C2'—C3'—C4'	-71.1 (3)
C2—C3—C4—C5	-96.9 (4)	C2'—C3'—C4'—C5'	99.2 (4)
C2—C3—C4—C9	83.2 (4)	C2'—C3'—C4'—C9'	-79.1 (4)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O2	0.82	1.83	2.633 (3)	168
O5—H5...O1 ⁱ	0.82	1.82	2.616 (3)	163
O3'—H3'...O1' ⁱⁱⁱ	0.82	1.86	2.659 (3)	166
O5'—H5'...O2' ⁱⁱⁱ	0.82	1.81	2.570 (3)	154
N1—H1A...O1 ^{iv}	0.89	1.88	2.730 (3)	160
N1—H1B...O1' ⁱⁱⁱ	0.89	2.02	2.882 (3)	162
N1—H1C...O4	0.89	2.05	2.880 (3)	156
N1'—H1'1...O2' ^v	0.89	2.16	3.032 (3)	165
N1'—H1'2...O2' ^{vi}	0.89	2.18	2.959 (3)	146
N1'—H1'2...O4' ^{vii}	0.89	2.42	2.894 (3)	113
N1'—H1'3...O6' ^{vi}	0.89	2.01	2.886 (3)	166

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

The absolute configuration of L-phenylalanine fumaric acid was not established by the analysis but is known from the configuration of the starting reagents. Friedel pairs were merged before the final cycles of refinement. The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms, with C—H = 0.96 Å, N—H = 0.89 Å, O—H = 0.82 Å and $U_{\text{iso}} = 0.05 \text{ \AA}^2$.

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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