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Key indicators

Single-crystal X-ray study
 $T = 150\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$
 R factor = 0.113
 wR factor = 0.269
Data-to-parameter ratio = 7.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

L-Phenylalanine nitrate (4/1)

The asymmetric unit of the title compound, L-phenylalaninium nitrate tris(L-phenylalanine), $\text{C}_9\text{H}_{12}\text{NO}_2^+ \cdot \text{NO}_3^- \cdot 3\text{C}_9\text{H}_{11}\text{NO}_2$, contains a nitrate anion and a peculiar sequence of four L-phenylalanine molecules. Three of them are present as zwitterions, while the last carries the positive charge and acts as donor in a $-\text{COOH} \cdots ^-\text{OOC}-$ hydrogen bond with an $\text{O} \cdots \text{O}$ distance of $2.443(9)\text{ \AA}$.

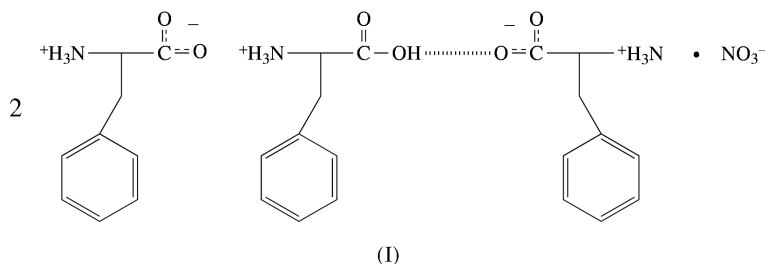
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Comment

The title compound, (I), was studied as part of a search for good crystallization conditions for various peptides. Several nice-looking crystals were obtained, but the diffraction patterns revealed that the structure was probably divided into layers that were misaligned along one axis. This made the unit-cell determination difficult, and only after testing several specimens was it possible to find the third axis, collect diffraction data and integrate them successfully.



As a result of the poor crystal quality, the final R factor is high for a small molecule structure. Nevertheless, the structure proved to be interesting in having an odd sequence of four phenylalanine molecules in the asymmetric unit in addition to the nitrate anion (Fig. 1). Three of the phenylalanines (*B*, *C* and *D*) are in the zwitterionic form. The positive charge most likely (see below) resides with the last amino acid molecule *A*, which is connected to molecule *B* by a very short $-\text{COOH} \cdots ^-\text{OOC}-$ hydrogen bond (Table 2). The shortness of this interaction can in part be attributed to the fact that the carboxylate group of molecule *B* participates in no other strong interactions, a most unusual situation. The COOH group of molecule *A* is furthermore involved in only one additional hydrogen bond with an $\text{H} \cdots \text{O}$ distance less than 2.50 \AA .

The molecular packing shown in Fig. 2 has, as suspected, thick hydrophobic layers of L-phenylalanine side chains, and also hydrophilic layers composed of two interconnected hydrogen-bonded sheets. This is a very persistent pattern, which occurs not only in the structure of phenylalanine itself (Weissbuch *et al.*, 1990) and its complexes with mandelic acid

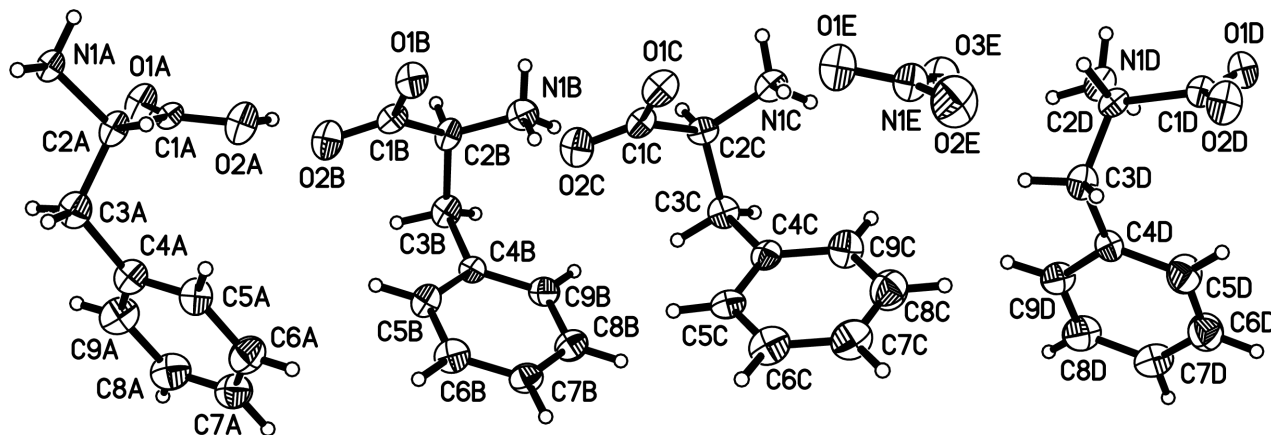


Figure 1

The structure of the title compound with the atomic numbering indicated. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

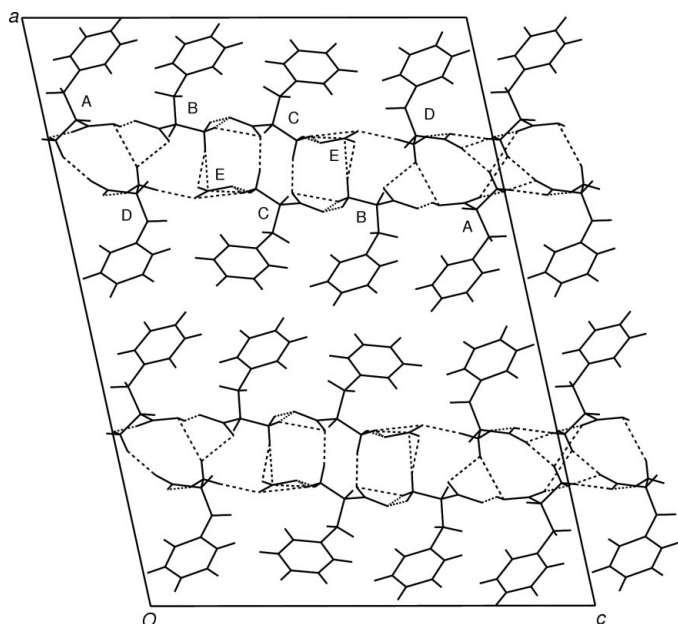


Figure 2

The unit cell and molecular packing viewed along the *b* axis. Hydrogen bonds are dashed.

(Okamura *et al.*, 1997), but also in other salts such as L-phenylalanine hydrochloride (Al-Karaghoul & Koetzle, 1975), L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992) and L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997). It is noteworthy that the latter two structures include one L-phenylalanine zwitterion and one L-phenylalaninium cation in the asymmetric unit, which are in both cases connected by a very short hydrogen bond like the one seen in the title structure.

Experimental

L-Phenylalanine was obtained from Sigma and used as received. Crystals in the shape of long flat needles were grown by slow evaporation of a dilute nitric acid solution of the amino acid at room temperature.

Crystal data

$4C_9H_{12}NO_2^+ \cdot 4NO_3^- \cdot 12C_9H_{11}NO_2$
 $M_r = 723.80$
 Monoclinic, C_2
 $a = 30.285$ (8) Å
 $b = 5.3022$ (13) Å
 $c = 22.317$ (6) Å
 $\beta = 102.263$ (4)°
 $V = 3501.9$ (15) Å³
 $Z = 4$

$D_x = 1.373$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3964 reflections
 $\theta = 1.9$ – 25.0 °
 $\mu = 0.10$ mm⁻¹
 $T = 150$ (2) K
 Flat needle, colourless
 $0.55 \times 0.20 \times 0.07$ mm

Data collection

Siemens SMART CCD diffractometer
 Sets of exposures each taken over 0.3° ω rotation scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{min} = 0.945$, $T_{max} = 0.993$
 9411 measured reflections

3450 independent reflections
 2777 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.100$
 $\theta_{max} = 25.0$ °
 $h = -36 \rightarrow 34$
 $k = -6 \rightarrow 6$
 $l = -24 \rightarrow 26$
 Intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.113$
 $wR(F^2) = 0.269$
 $S = 1.63$
 3450 reflections
 474 parameters
 H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 3.750P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.005$
 $\Delta\rho_{max} = 0.62$ e Å⁻³
 $\Delta\rho_{min} = -0.54$ e Å⁻³
 Extinction correction: SHELXTL
 Extinction coefficient: 0.0053 (14)

Table 1

Selected geometric parameters (Å, °).

O1A—C1A	1.219 (10)	O1C—C1C	1.298 (10)
O2A—C1A	1.271 (9)	O2C—C1C	1.230 (9)
N1A—C2A	1.494 (6)	N1C—C2C	1.489 (6)
O1B—C1B	1.247 (10)	O1D—C1D	1.261 (10)
O2B—C1B	1.265 (9)	O2D—C1D	1.250 (10)
N1B—C2B	1.490 (6)	N1D—C2D	1.491 (6)
O1A—C1A—O2A	127.3 (7)	O2C—C1C—O1C	124.9 (6)
O1A—C1A—C2A	118.2 (6)	O2C—C1C—C2C	118.1 (6)
O2A—C1A—C2A	114.5 (6)	O1C—C1C—C2C	117.0 (5)
O1B—C1B—O2B	125.4 (6)	O2D—C1D—O1D	125.9 (6)
O1B—C1B—C2B	118.5 (6)	O2D—C1D—C2D	117.5 (7)
O2B—C1B—C2B	115.8 (6)	O1D—C1D—C2D	116.5 (6)

O1A—C1A—C2A—N1A	−46.3 (8)	O1C—C1C—C2C—N1C	−10.3 (9)
N1A—C2A—C3A—C4A	167.2 (6)	N1C—C2C—C3C—C4C	55.8 (7)
C2A—C3A—C4A—C5A	61.0 (10)	C2C—C3C—C4C—C5C	96.2 (8)
O1B—C1B—C2B—N1B	12.4 (9)	O1D—C1D—C2D—N1D	−0.7 (9)
N1B—C2B—C3B—C4B	55.4 (7)	N1D—C2D—C3D—C4D	53.5 (7)
C2B—C3B—C4B—C5B	83.5 (8)	C2D—C3D—C4D—C5D	71.5 (10)

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

D—H...A	D—H	H...A	D...A	D—H...A
O2A—HO2A...O2B	1.00	1.49	2.443 (9)	158
N1A—H1A...O1D ⁱ	0.91	2.11	2.858 (8)	138
N1A—H1A...O1A ⁱⁱ	0.91	2.19	2.844 (10)	128
N1A—H2A...O2D ⁱⁱⁱ	0.91	1.97	2.837 (9)	159
N1A—H3A...O1D ^{iv}	0.91	1.95	2.785 (9)	152
N1A—H3A...O1A ^v	0.91	2.50	3.071 (8)	121
N1B—H1B...O2C ^{vi}	0.91	2.16	3.053 (10)	167
N1B—H2B...O2C	0.91	2.17	3.012 (10)	154
N1B—H3B...O2E ^{vii}	0.91	2.01	2.898 (10)	166
N1C—H1C...O1E ^{vi}	0.91	2.19	2.909 (10)	135
N1C—H2C...O1E	0.91	2.04	2.903 (10)	158
N1C—H3C...O1C ^{vii}	0.91	1.86	2.744 (9)	164
N1D—H1D...O3E ^{vi}	0.91	2.01	2.886 (10)	161
N1D—H2D...O2D ^{vi}	0.91	2.07	2.896 (9)	151
N1D—H3D...O1B ^{vii}	0.91	2.40	2.954 (9)	119
N1D—H3D...O2A ^{vii}	0.91	2.46	3.322 (10)	157

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

Three sets of exposures with the detector set at $2\theta = 29^\circ$, crystal-to-detector distance 4.98 cm. Constrained H-atom refinement with U_{iso} values set to $1.2U_{\text{eq}}$ of the carrier atom or $1.5U_{\text{eq}}$ for the amino groups. The H atom in the shortest hydrogen bond could not be found in difference Fourier maps. It could therefore not be established with certainty whether it is actually bonded to O2A or O2B (a centered position was considered to be less likely). A combined geometric and force-field calculation with the program *HYDROGEN* (Nardelli, 1999) showed, however, that the H atom is most likely associated with O2A, and it was thus named HO2A. For a 2.44 Å O...O distance, the

previously observed lengthening of the covalent O—H bond is about 0.15 Å (Steiner & Saenger, 1994). The HO2A position output by *HYDROGEN* was consequently adjusted so as to increase the O—H bond length from 0.85 (default) to 1.00 Å. Based on results from a survey of neutron diffraction structures with COOH groups from the Cambridge Structural Database (Allen & Kennard, 1993), the C—O—H angle was furthermore set to 111.5° and the the C—C—O—H torsion angle was increased to 175° (Görbitz, 2001). *SAME* restraints were used for the four phenylalanine side chains. The absolute structure could not be determined, and Friedel pairs were merged in the final refinements.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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