

L-Phenylalanine L-phenylalaninium dihydrogenphosphate

B. Ravikumar, B. Sridhar and R. K. Rajaram*

Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: sshiya@yahoo.com

Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.016\text{ \AA}$

R factor = 0.063

wR factor = 0.184

Data-to-parameter ratio = 9.1

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

In the title compound, $\text{C}_9\text{H}_{11}\text{NO}_2 \cdot \text{C}_9\text{H}_{12}\text{NO}_2^+ \cdot \text{H}_2\text{PO}_4^-$, the dihydrogenphosphate anion links the phenylalaninium and zwitterionic phenylalanine residues *via* strong $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. A three-centered hydrogen bond is observed in the phenylalaninium residue. This aggregation results in the formation of hydrophilic layers that are sandwiched between hydrophobic layers. Both *S2* and *Z1* head-to-tail sequences are observed.

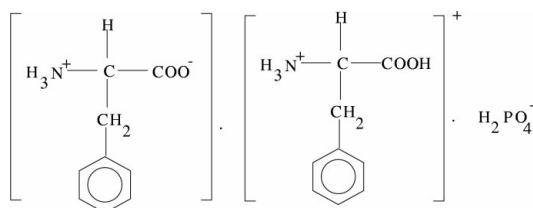
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Comment

The crystal structures of L-phenylalanine hydrochloride (Gurskaya & Vainshtein, 1963; Al-Karaghoulis & Koetzle, 1975), bis(L-phenylalaninium) sulfate monohydrate (Nagashima *et al.*, 1992) and L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992) are known. The related structures of L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), bis(DL-phenylalaninium) sulfate monohydrate (Srinivasan *et al.*, 2001a), L-phenylalanine–nitric acid (2/1) (Srinivasan *et al.*, 2001b), and DL-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2001) have been determined in our laboratories. The structure of the title compound, (I), was determined as a part of an on-going study into the structural chemistry of phenylalanine derivatives.



(I)

The asymmetric unit comprises two crystallographically independent L-phenylalanine residues and a dihydrogenphosphate anion (Fig. 1 and Table 1). One of the L-phenylalanine residues has been protonated, indicating proton transfer from the original orthophosphoric acid. The conformation angles ψ^1 for the residues I and II are -14.7 (11) and -14.1 (11) $^\circ$, respectively. The branched-side-chain conformation angle χ^1 is in a *gauche*-II form [-80.3 (11) $^\circ$] for the phenylalanine residue, whilst for the phenylalaninium residue, the side chain is in the *trans* form [-151.4 (8) $^\circ$]. The torsion angles χ^{21} and χ^{22} for both residues [89.5 (12) and -95.8 (12) $^\circ$, and 68.7 (13) and -114.4 (11) $^\circ$, respectively] indicate a folded conformation in each case.

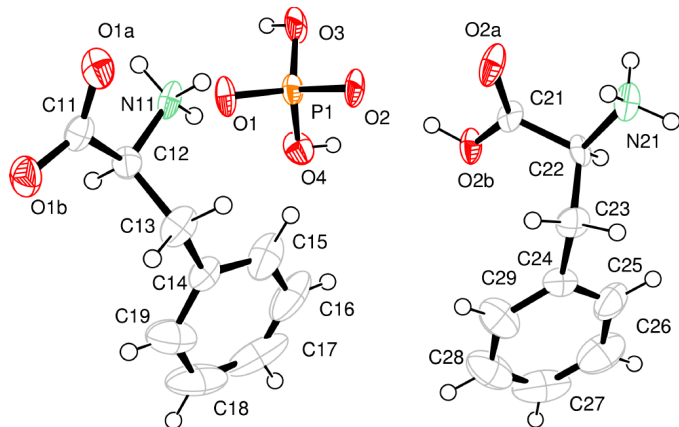


Figure 1

The molecular structures of the molecules comprising the asymmetric unit, showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

An examination of the derived interatomic parameters clearly distinguishes between the two forms of the phenylalanine residues. For the phenylalanine residue, the C—O distances [1.228 (10) and 1.235 (11) Å] and O—C—C angles [115.4 (9) and 116.6 (8)°] clearly indicate the zwitterionic nature of the molecule, whilst in the case of phenylalaninium residue, the carboxyl group [1.217 (10) and 1.305 (13) Å] is clearly protonated. Similarly, the P—O distances and angles within the phosphate group are consistent with an H₂PO₄ anion. The phosphate anion plays a vital role in stabilizing the structure (Table 2). The phenylalaninium residue, as a donor, forms a strong hydrogen bond with the phosphate anion [2.543 (9) Å]. The phosphate anion also forms a strong hydrogen bond with the phenylalanine residue [2.535 (9) Å] and a somewhat weaker hydrogen bond with a second phenylalaninium residue [2.938 (9) Å].

The O atoms of the phosphate anion form the expected N—H...O hydrogen bonding with both residues. Interestingly, the amino N atom of the phenylalanine residue associates only with the phosphate anion. The O1 atom of the phosphate anion links the amino N atom of the phenylalanine residue as a chain running along the *b* axis. A three-centered hydrogen-bonding scheme associated with the phenylalaninium residue is observed. This involves the amino N and the carboxyl atoms O2A and O2B. In the phenylalaninium residue, both straight (S2) and zigzag (Z1) head-to-tail sequences are observed (Vijayan, 1988).

From the packing diagram (Fig. 2), the aggregation of the hydrophilic zone along *c* = $\frac{1}{2}$ is such as to be sandwiched between two hydrophobic layers aligned along the *a* axis.

Experimental

The title compound, (I), was crystallized from an aqueous solution of L-phenylalanine and orthophosphoric acid (2:1) by slow evaporation.

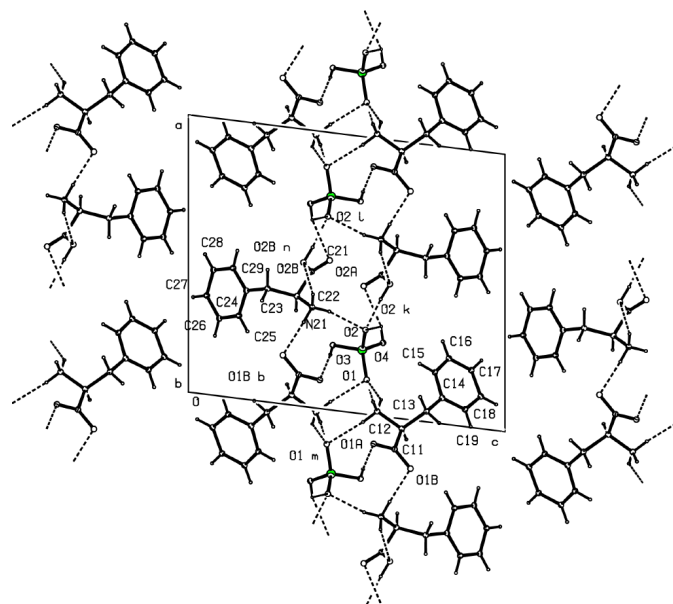


Figure 2

Packing diagram viewed down the *b* axis.

Crystal data

C₉H₁₁NO₂·C₉H₁₂NO₂⁺·H₂PO₄⁻
M_r = 428.37
 Monoclinic, *P*2₁
a = 13.441 (1) Å
b = 4.8760 (4) Å
c = 15.470 (2) Å
 β = 97.12 (1)°
V = 1006.06 (17) Å³
Z = 2
D_x = 1.414 Mg m⁻³
D_m = 1.41 Mg m⁻³

D_m, measured by flotation using a mixture of carbon tetrachloride and xylene
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 8.5–13.9°
 μ = 0.19 mm⁻¹
T = 293 (2) K
 Needle, colorless
 0.60 × 0.13 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 T_{\min} = 0.972, T_{\max} = 0.982
 2762 measured reflections
 2439 independent reflections
 1167 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.064
 θ_{\max} = 25.0°
 $h = -1 \rightarrow 15$
 $k = -1 \rightarrow 5$
 $l = -18 \rightarrow 18$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.063
wR(*F*²) = 0.184
S = 0.97
 2439 reflections
 267 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = -0.2 (4)

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.494 (5)	O1A—C11	1.235 (11)
P1—O2	1.528 (7)	O1B—C11	1.228 (10)
P1—O3	1.537 (7)	O2A—C21	1.217 (10)
P1—O4	1.560 (7)	O2B—C21	1.305 (13)
O1B—C11—O1A	128.0 (10)	O2A—C21—O2B	123.7 (9)
O1B—C11—C12	115.4 (9)	O2A—C21—C22	121.5 (10)
O1A—C11—C12	116.6 (8)	O2B—C21—C22	114.8 (8)
O1A—C11—C12—N11	−14.7 (11)	O2A—C21—C22—N21	−14.1 (11)
N11—C12—C13—C14	−80.3 (11)	N21—C22—C23—C24	−151.4 (8)
C12—C13—C14—C19	−95.8 (12)	C22—C23—C24—C25	68.7 (13)
C12—C13—C14—C15	89.5 (12)	C22—C23—C24—C29	−114.4 (11)

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...O1A ⁱ	0.82	1.74	2.535 (9)	164
O4—H4...O2A ⁱⁱ	0.82	2.15	2.938 (9)	162
N11—H11A...O1	0.89	2.23	3.022 (10)	148
N11—H11B...O1 ⁱⁱⁱ	0.89	1.95	2.834 (10)	176
N11—H11C...O1 ^{iv}	0.89	2.07	2.923 (8)	161
O2B—H2B...O2	0.87 (10)	1.68 (10)	2.543 (9)	172 (12)
N21—H21A...O1B ^v	0.89	1.90	2.736 (9)	156
N21—H21B...O2B ⁱⁱⁱ	0.89	2.15	3.017 (10)	165
N21—H21B...O2A ^{vi}	0.89	2.62	3.062 (9)	111
N21—H21C...O2 ^{vi}	0.89	2.02	2.896 (9)	167

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

Atom H2B of the carboxyl group of phenylalaninium residue II was located and refined. All other H atoms were included in the riding-model approximation. The crystal is weakly diffracting and hence nearly half of the unique reflections have $I < 2\sigma(I)$. Similarity restraints were employed for U_{ij} values of both phenyl rings, since some of the C-atom ADP max/min ratios were large.

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, 1997); 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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