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DL-Phenylalaninium nitrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.047
wR factor = 0.141
Data-to-parameter ratio = 12.9

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

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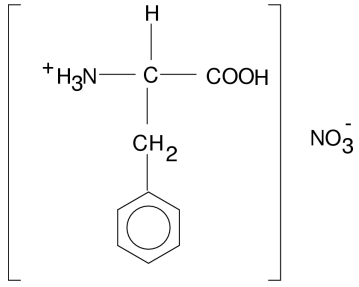
In the title compound, $C_9H_{12}NO_2^+\cdot NO_3^-$, the phenylalaninium residue adopts a folded conformation. It forms a strong O—H···O hydrogen bond with the nitrate anion and is also involved in a zigzag head-to-tail hydrogen-bonding sequence (*Z*1). In the crystal packing of the title compound, the aggregation of the hydrophobic layer about the $x = 0$ plane (parallel to the *ab* plane) is sandwiched between hydrophilic double layers at $x = -\frac{1}{2}$ and $x = \frac{1}{2}$.

Comment

Phenylalanine is an essential amino acid and one of the aromatic amino acids. As part of our ongoing research program studying hydrogen-bonding features and aggregation patterns of phenylalanine in the presence of various inorganic acids, a number of crystal structures have been reported, *viz*., L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), bis(DL-phenylalaninium) sulfate monohydrate (Srinivasan *et al.*, 2001*a*), L-phenylalanine nitric acid (2/1) (Srinivasan *et al.*, 2001*b*), DL-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2001) and L-phenylalanine L-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2002). In the present paper, the crystal structure of DL-phenylalaninium nitrate, (I), is described. The asymmetric unit contains one phenylalaninium residue and one nitrate anion (Fig. 1).



(I)

The bond distances and bond angles of the phenylalaninium residue are within the expected ranges. The conformation angle ψ^1 (O1*A*—C1—C2—N1) corresponds to the *cis* form [−34.0 (5)°], the deviation of the amino nitrogen from the mean carboxyl plane being 0.80 (6) Å. This tendency for the C—N bond to twist is found in various amino acids (Lakshminarayanan *et al.*, 1967). The angle between the carboxyl plane and phenyl ring plane is 51.2 (2)°. The branched side-chain conformation angle χ^1 (N1—C2—C3—C4) is −174.7 (3)°, indicating the *trans* form. The other

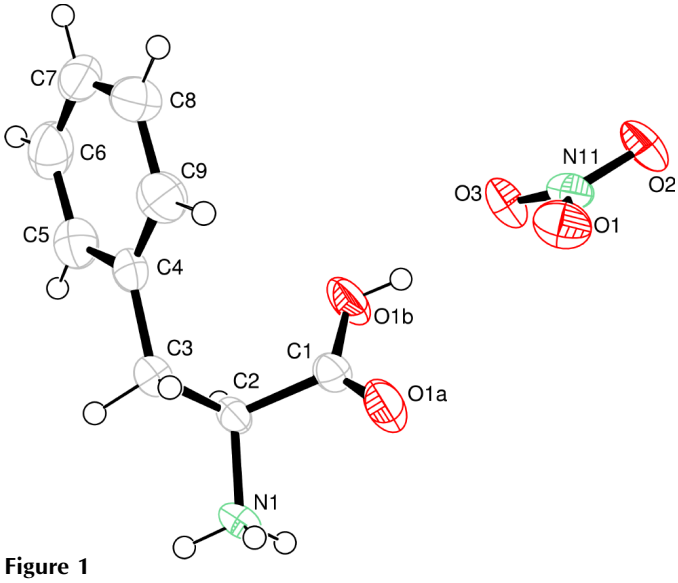


Figure 1
The phenylalaninium cation and the nitrate anion in the structure of the title compound, showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

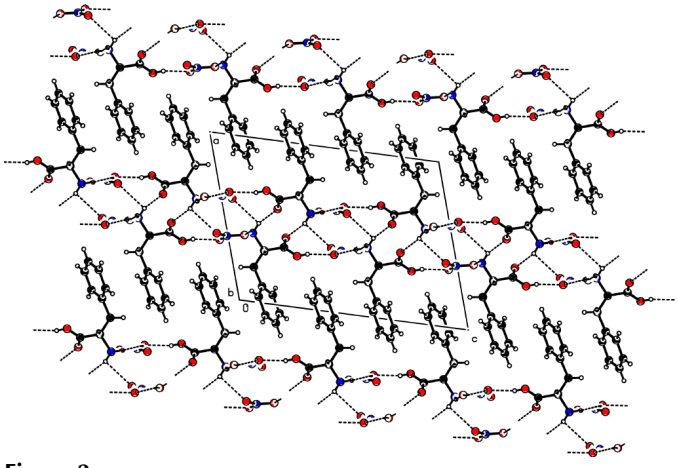


Figure 2
Packing diagram of the crystal of the title compound, viewed down the *b* axis.

conformation angles χ^{21} and χ^{22} (C2—C3—C4—C5 and C2—C3—C4—C9, respectively) are 81.2 (4) and −101.3 (5)°, and correspond to a folded conformation. The χ^{21} value lies within the expected range of 90±30° (Cotrait *et al.*, 1984).

The nitrate anion plays a vital role in hydrogen bonding. However, only two of the three O atoms take part in hydrogen bonds. The N—O distances involving these two O atoms [1.254 (4) and 1.256 (4) Å] are slightly longer than the third N—O bond [1.234 (4) Å].

The phenylalaninium residue forms a strong O—H···O hydrogen bond with the nitrate anion. The amino nitrogen of the phenylalaninium residue forms an N—H···O hydrogen bond with O atoms of the nitrate anion and the carboxyl O atom (O1*A*). There is a zigzag (*Z*1) head-to-tail hydrogen-bonding sequence involving the amino nitrogen and carboxyl O atoms (Table 2). The phenylalaninium cation in the title structure exhibits a hydrogen-bonding pattern with three two-centered hydrogen bonds [class I hydrogen-bonding pattern, according to Jeffrey & Saenger (1991)]. The zigzag (*Z*1) head-to-tail sequence implies hydrogen bonding between two 2_1-related amino acid molecules parallel to the *b* axis (Vijayan, 1988).

In the crystal packing of the title compound, the aggregation of the hydrophobic layer around the $x = 0$ plane (parallel to the *ab* plane) is sandwiched between hydrophilic double layers at $x = -\frac{1}{2}$ and $x = \frac{1}{2}$ (Fig. 2). Similar aggregation patterns are also observed in L-phenylalaninium formate (Görbitz & Etter, 1992), L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), L-phenylalanine nitric acid (2/1) (Srinivasan *et al.*, 2001*b*), DL-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2001) and L-phenylalanine L-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2002).

Experimental

The title compound, (I), was crystallized from an aqueous solution of DL-phenylalanine and nitric acid by slow evaporation. The solution was prepared from equal volumes (10 ml) of 1 molar concentrations of phenylalanine and nitric acid. The crystals were grown within one week.

Crystal data

$C_9H_{12}NO_2^+\cdot NO_3^-$
$M_r = 228.21$
Monoclinic, $P2_1/c$
$a = 12.005$ (7) Å
$b = 5.758$ (2) Å
$c = 16.250$ (9) Å
$\beta = 107.48$ (6)°
$V = 1071.4$ (9) Å^3
$Z = 4$
$D_x = 1.415$ Mg m^{-3}
$D_m = 1.413$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 8.1$–13.9°
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.33 × 0.13 × 0.10 mm

Data collection

Enraf–Nonis CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.754$, $T_{max} = 0.990$
1968 measured reflections
1874 independent reflections
791 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 24.9°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 6$
$l = -19 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.141$
$S = 0.96$
1874 reflections
145 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—O1	1.234 (4)	O1*A*—C1	1.184 (4)
N11—O2	1.254 (4)	O1*B*—C1	1.308 (4)
N11—O3	1.256 (4)		
O1*A*—C1—C2—N1	−34.0 (5)	C2—C3—C4—C9	−101.3 (5)
O1*B*—C1—C2—N1	145.6 (3)	C2—C3—C4—C5	81.2 (4)
N1—C2—C3—C4	−174.7 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1B—H1···O3	0.82	1.89	2.666 (4)	157
N1—H1A···O1A^{i}	0.89	1.99	2.841 (4)	160
N1—H1B···O3^{ii}	0.89	2.07	2.934 (4)	163
N1—H1C···O2^{iii}	0.89	2.05	2.898 (4)	159

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

All H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with U_{iso} equal to $1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl and NH_3 H 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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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