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Ammonium L-alanyl-L-phenylalaninate

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Key indicators

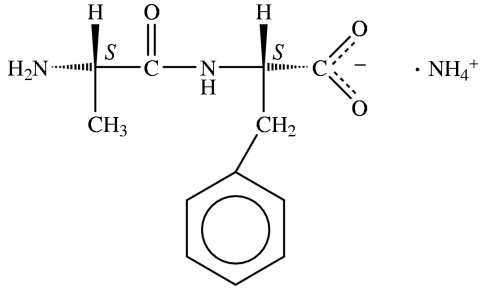
Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.082
Data-to-parameter ratio = 6.9

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

The title compound, $NH_4^+ \cdot C_{12}H_{15}N_2O_3^-$, was crystallized by slow evaporation of a liquid ammonia solution of L-alanyl-L-phenylalanine. The crystal-packing arrangement and the hydrogen-bonding pattern are very similar to those observed for ammonium L-isoleucyl-L-isoleucinate [Görbitz (2004). *Acta Cryst.* B**60**, 569–577], the other known ammonium salt of an amino acid or a peptide.

Comment

The crystal structures of a number of dipeptides with two hydrophobic residues have been presented as parts of a systematic survey focused on this group of compounds [see Görbitz (2004), and references therein]. L-Alanyl-L-phenylalanine (AF) has not yet been investigated due to the difficulties encountered in growing single crystals of suitable quality. One of the crystallization experiments led to formation of crystals of the ammonium salt of AF, hereafter (I), the structure of which is presented in this paper.



(I)

The molecular structure of (I) is shown in Fig. 1. After ammonium L-isoleucyl-L-isoleucinate, (II) (Görbitz, 2004), this is the second structure of an ammonium salt of a peptide (or amino acid), and it is the third, after (II) and (*R*)-phenylglycyl-(*R*)-phenylglycine [in the (*S*)-1-phenylethylamine salt (Akazome *et al.*, 1997)], in which a peptide is present as an anion. Just as for (II), the peptide bond >N—H forms an intramolecular hydrogen bond to the uncharged main-chain amino group, rendered possible by a highly unusual value, −7.9 (3)°, for the ψ_1 torsion angle (N1—C1—C3—N2, Table 1). In the structure of (II), this hydrogen bond is bifurcated with an O atom of the C-terminal carboxylate group as the second acceptor. The latter intramolecular contact is missing in (I), since a rotation about the N2—C4 bond compared to (II) places the carboxylate group out of the plane of the peptide bond (Fig. 1). The associated φ_2 torsion

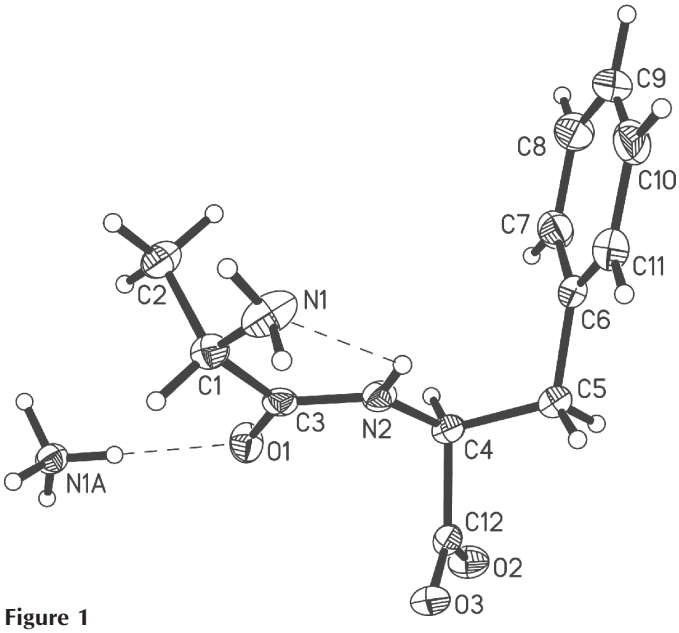


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as spheres of arbitrary size and hydrogen bonds are indicated by dashed lines.

angles are −67.3 (3)° for (I) (C3—N2—C4—C12), and −137.1 (4) and −138.9 (4)° for the two peptides in the asymmetric unit of (II).

The unit cells of (I) (Fig. 2) and (II) both contain two peptide anions, related by twofold screw symmetry in (I) (monoclinic, $P2_1$) and pseudo-twofold screw symmetry in (II) (triclinic, $P\overline{1}$), and generate very similar crystal-packing arrangements by three-dimensional translation. The hydrogen-bonding motif shown in Fig. 3, which involves three strong interactions between the ammonium ions and the peptide carboxylate groups, occurs in both structures. Equivalent patterns have been found in a number of ammonium–carboxylate salts, but also for amino acids and peptides in the zwitterionic state, with the N-terminal $-NH_3^+$ groups playing the role of the ammonium ions in the structures of (I) and (II).

The only significant difference between (I) and (II) concerns the very long interaction between atoms H2 and O2 in Table 2. In (II), the amino group is rotated so that the corresponding H atom is accepted instead by the peptide bond carbonyl group.

Experimental

Crystals of the title salt were obtained by dissolving a few mg of the peptide in about 1 ml of NH_3(l). Dry ice was used as a cooling agent, which meant that the procedures had to be carried out quite rapidly to avoid formation of NH_3(s) (freezing point 195.5 K, dry ice is 194.7 K). Care was taken to prevent exposure of the sample to humidity. The solution was placed in a specially constructed bomb container with an adjustable vent and left for slow evaporation in a cold room at 250 K. Evaporation to dryness was completed in less than 24 h.

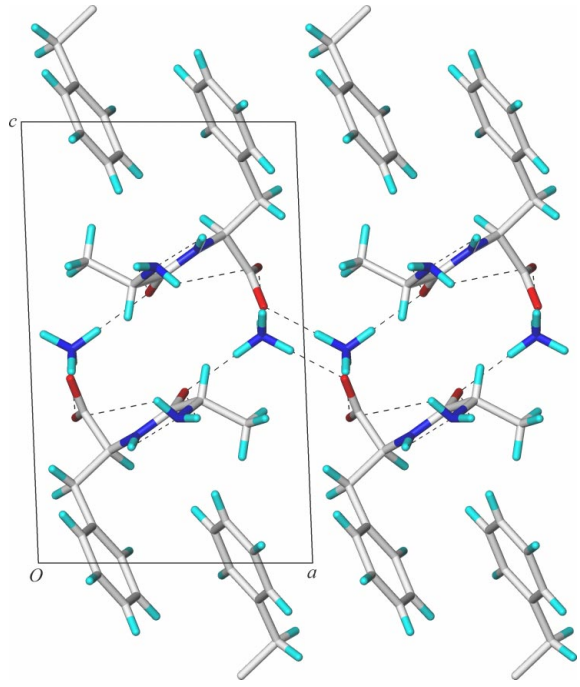


Figure 2
The molecular packing and unit cell, viewed along the *b* axis. Hydrogen bonds are indicated by dashed lines. To illustrate the stacking of the aromatic groups, the benzyl side chains of some neighbouring L-phenylalanine residues have been included.

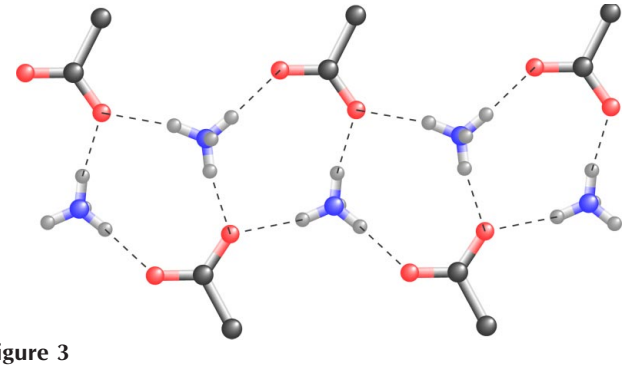


Figure 3
Detail of the hydrogen-bonding pattern involving the C-terminal peptide carboxylate groups and the ammonium ions.

Crystal data

$NH_4^+\cdot C_{12}H_{15}N_2O_3^-$
M_r = 253.30
Monoclinic, $P2_1$
a = 8.0494 (12) Å
b = 6.4253 (9) Å
c = 12.950 (2) Å
β = 92.248 (4)°
V = 669.27 (17) Å^3
Z = 2
D_x = 1.257 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1233 reflections
θ = 2.5–25.1°
μ = 0.09 mm^{-1}
T = 105 (2) K
Block, colourless
0.37 × 0.25 × 0.19 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.842, T_{max} = 0.983
2193 measured reflections
1297 independent reflections
1128 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 25.1°
$h = -9 \rightarrow 9$
$k = -7 \rightarrow 6$
$l = -6 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.082$
$S = 1.03$
1297 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C1—C3—N2	−7.9 (3)	N2—C4—C5—C6	−57.8 (3)
C1—C3—N2—C4	−173.5 (2)	C4—C5—C6—C7	−62.9 (3)
C3—N2—C4—C12	−67.3 (3)	C4—C5—C6—C11	118.2 (3)
N2—C4—C12—O2	152.1 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.92 (4)	2.31 (4)	3.007 (3)	133 (3)
N1—H2···O2^{i}	0.85 (4)	2.59 (4)	3.185 (3)	129 (3)
N2—H4···N1	0.78 (3)	2.27 (3)	2.648 (3)	111 (2)
C1—H11···O3^{ii}	0.95 (3)	2.62 (3)	3.435 (3)	144 (2)
N1A—H1A···O2^{ii}	0.92 (2)	1.84 (2)	2.761 (3)	176 (3)
N1A—H2A···O3^{iii}	0.90 (2)	1.88 (2)	2.766 (3)	168 (3)
N1A—H3A···O1	0.92 (2)	1.93 (2)	2.851 (3)	178 (3)
N1A—H4A···O3^{iv}	0.94 (2)	1.86 (2)	2.794 (3)	172 (3)

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

Positional parameters were refined for H atoms involved in hydrogen bonds. Other H atoms were positioned with idealized geometry and fixed C—H distances. U_{iso} values were set at $1.5U_{eq}$ of the carrier atom for the ammonium ion as well as for the methyl side chain and the amino group of AF, and $1.2U_{eq}$ for other H atoms. In the absence of significant anomalous scattering effects, 463 Friedel pairs were merged. The absolute configuration was known for the purchased material.

Data collection: *SMART-Plus* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Akazome, M., Matsuno, H. & Ogura, K. (1997). *Tetrahedron Asymmetry*, **8**, 2331–2336.
Bruker (1998). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS, Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT-Plus*. Version 6.22. Bruker AXS Inc., Madison, Wisconsin, USA.
Görbitz, C. H. (2004). *Acta Cryst.* B**60**, 569–577.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.