

L-Phenylalanine–4-nitrophenol (1/1)

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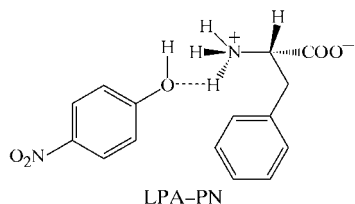
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In the 1:1 adduct formed between L-phenylalanine and 4-nitrophenol [alternative IUPAC name: (2*S*)-2-ammonio-3-phenylpropanoate–4-nitrophenol (1/1)], C₉H₁₁NO₂·C₆H₅NO₃, the L-phenylalanine molecule is in the zwitterionic state. The overall structure is stabilized *via* strong hydrogen bonding between polar zones and van der Waals interactions between non-polar zones, which alternate with the polar zones.

Comment

Compounds containing amino acids and other molecules or ions have attracted a lot of attention because of their potential applications in domains such as pharmaceutical drugs, non-linear optics and biochemistry. Much information has thus been gathered on these materials regarding properties such as aggregation patterns, conformational effects caused by the presence of other molecules or ions, non-linear optical behaviour, ferroelastic/electric properties and phase diagrams. Furthermore, molecules containing π -electron bonds, unbalanced by the presence of polar groups and capable of accepting or donating electrons, are highly polarizable (Pecaut & Bagieu-Beucher, 1993); nitrophenols can also act as π acceptors with other aromatic molecules, as well as acidic



ligands, forming co-compounds/salts through strong hydrogen bonding (In *et al.*, 1997). The synthesis of the title compound has been undertaken in order to obtain a material with strong second harmonic generation properties. However, the non-linear optical properties of L-phenylalanine–4-nitrophenol (LPA-PN) (Fig. 1) were found to be rather weak in comparison to urea.

The LPA molecule is in the neutral zwitterionic state with a protonated amino group positively charged and a negatively charged carboxylate group. The conformation of this amino acid is described by the torsion angles $\chi^1 = 67.5(2)^\circ$ and $\chi^{21} = 95.9(2)^\circ$ (IUPAC–IUB Commission on Biochemical Nomenclature, 1970); the χ^1 value corresponds to a sterically less favoured G⁺ conformation already found in L-phenylalaninium L-phenylalanine perchlorate (Srinivasan & Rajaram, 1997) and the χ^{21} angle is indicative of a folded conformation.

The PN molecule shows typical bond lengths and angles (Coppens & Schmidt, 1965). The whole molecule is nearly planar, with the expected small deviations of the nitro and hydroxy O atoms. The latter deviate towards the same side of the ring plane; one of O atoms of the nitro group lies slightly above the ring plane, whereas the other is positioned below the ring. Asymmetry between the two C–C–O angles due to repulsion between the H atom and the C atom carrying the hydroxy group (Hirshfeld, 1964) is also present.

The LPA molecules are bonded to each other *via* the strong N1–H1B...O1ⁱⁱ hydrogen bond [symmetry code: (ii) $x + 1, y, z$; Table 1], forming C(5) chains (Grell *et al.*, 1999) running along the *a* axis (Fig. 2). These chains are interlinked through additional hydrogen bonds giving rise to hydrophilic sheets parallel to the (001) planes; these sheets are formed by the [100] chains of the LPA molecules and the hydroxy groups of the PN molecules. In each of these sheets, N1–H1B...O1ⁱⁱ, O3–H3...O2ⁱⁱ and N1–H1C...O3 hydrogen bonds generate an $R_3^3(8)$ ring, N1–H1A...O1ⁱ, O3–H3...O2ⁱⁱ and N1–H1C...O3 hydrogen bonds [symmetry code: (i) $-x, y - \frac{1}{2}, -z + 1$] generate an $R_5^5(16)$ ring, and N1–H1B...O1ⁱⁱ and N1–H1A...O1ⁱ hydrogen bonds give rise to an $R_4^3(14)$ ring.

In the hydrogen-bonding scheme, atom N1 acts as the centre of a set of trifurcated donor bonds, atom O1 is the acceptor of two (bifurcated) bonds, whereas atom O3 acts simultaneously as the acceptor of one bond and the donor of another. The aromatic rings of both the LPA and the NP molecules border the hydrophilic layers, forming hydrophobic coatings on both sides of the layers. The slabs, made of a

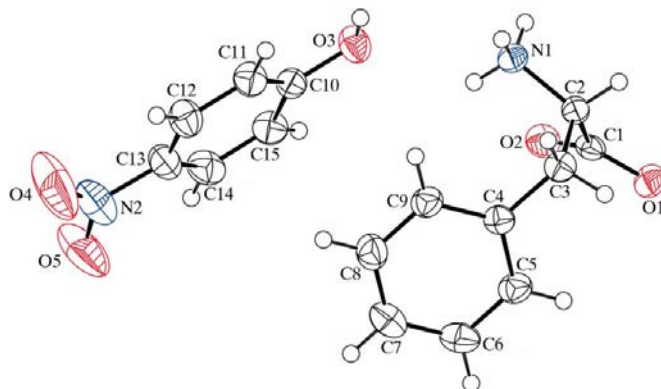


Figure 1

An ORTEP (Johnson, 1976) plot of the title adduct. Displacement ellipsoids are drawn at the 50% probability level.

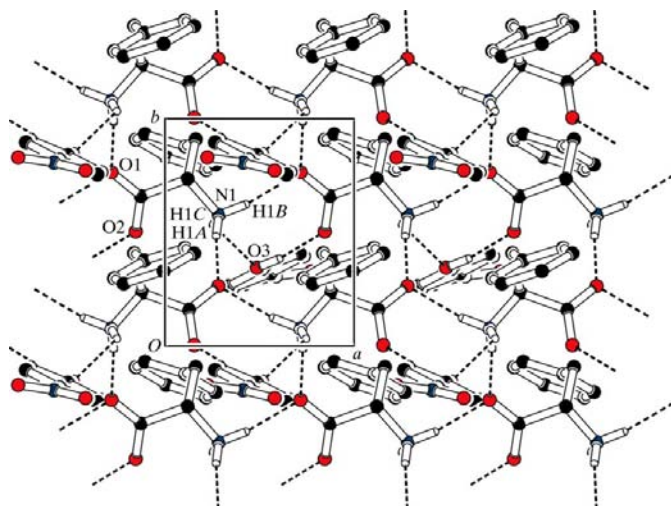


Figure 2
The packing, viewed along the *c* axis, showing the hydrogen-bonding network. H atoms not involved in hydrogen bonds have been omitted for clarity.

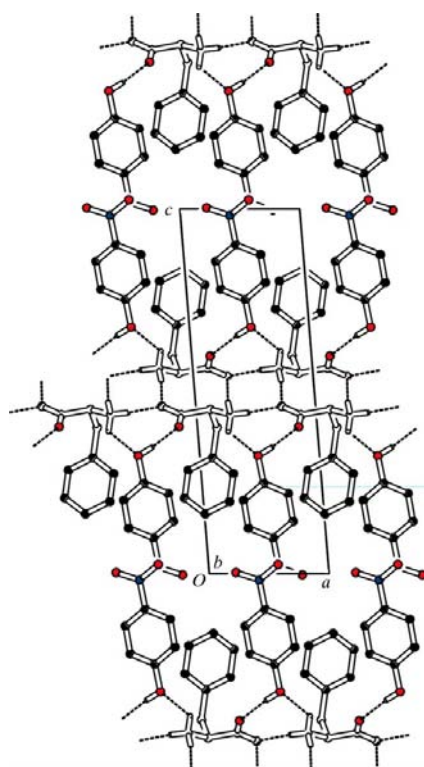


Figure 3
A view along the *b* axis of the alternating hydrophilic and hydrophobic slabs. H atoms not involved in intermolecular hydrogen bonds are not shown.

central hydrophilic layer and two bordering hydrophobic aromatic ring layers, are repeated along the [001] direction and bond to each other through van der Waals interactions, leading to alternating hydrophilic and hydrophobic zones (Fig. 3).

Experimental

Analytical grade L-phenylalanine (Aldrich) and 4-nitrophenol (Aldrich) were dissolved separately in water and methanol, respectively. The solutions were then mixed in a 1:1 molar ratio and stirred at 323 K for several hours; the resulting solution was allowed to cool to room temperature and crystals were obtained after two weeks by slow evaporation. A suitable crystal was selected and checked by photographic methods before data collection.

Crystal data

$C_9H_{11}NO_2 \cdot C_6H_5NO_3$
 $M_r = 304.30$
 Monoclinic, $P2_1$
 $a = 5.8327(2) \text{ \AA}$
 $b = 7.0099(9) \text{ \AA}$
 $c = 17.8751(4) \text{ \AA}$
 $\beta = 94.59(10)^\circ$
 $V = 728.51(14) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.387 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation
 $\mu = 0.89 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Rod, clear colourless
 $0.34 \times 0.17 \times 0.17 \text{ mm}$

Data collection

Enraf-Nonius CAD-4
 diffractometer
 Profile data from ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.72$, $T_{\max} = 0.86$
 2983 measured reflections

2894 independent reflections
 2770 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 72.4^\circ$
 3 standard reflections
 frequency: 180 min
 intensity decay: 4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.140$
 $S = 1.17$
 2894 reflections
 202 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0909P)^2 + 0.1548P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.018 (2)
 Absolute structure: Flack (1983),
 1320 Friedel pairs
 Flack parameter: $-0.2(2)$

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

<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>
N1—H1A···O1 ⁱ	0.89	2.00	2.887 (2)	172
N1—H1B···O1 ⁱⁱ	0.89	1.96	2.838 (2)	170
N1—H1C···O3	0.89	2.29	2.919 (3)	128
O3—H3···O2 ⁱⁱ	0.82	1.87	2.678 (3)	171

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

All H atoms were placed at geometrically idealized positions and refined as riding [C—H = 0.97, 0.98 and 0.93 \AA for secondary, tertiary and aromatic H atoms, respectively; O—H = 0.82 \AA , N—H = 0.89 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O}, \text{N})$]. Examination of the crystal structure with *PLATON* (Spek, 2003) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3062). Services for accessing these data are described at the back of the journal.

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