DL-Phenylalanine DL-phenylalaninium picrate

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In the title compound, $C_9H_{11}NO_2 \cdot C_9H_{12}NO_2^+ \cdot C_6H_2N_3O_7^-$, the phenylalanine cation forms a strong O—H···O hydrogen bond with a phenylalanine zwitterion and is involved in a $DL1$ head-to-tail sequence. Each of the phenylalanine residues adopts a folded conformation. In the crystal structure, the hydrophobic double layers are aggregated about the $y = 0$ plane and sandwiched between hydrophilic layers about the $y = \frac{1}{2}$ plane.

Comment

Phenylalanine is an essential aromatic amino acid. In the study of the hydrogen-bonding and aggregation patterns of phenylalanine in the presence of inorganic acids, a number of crystal structures have been reported, *viz*. bis-DL-phenylalaninium sulfate monohydrate (Srinivasan *et al.*, 2001), DL-phenylalaninium dihydrogen phosphate (Ravikumar *et al.*, 2001) and DL-phenylalaninium nitrate (Sridhar *et al.*, 2002). In this paper, in a study of the structure of phenylalanine in the presence of an organic acid, the crystal structure of DL-phenylalanine DL-phenylalaninium picrate, (I), is described.

(I)
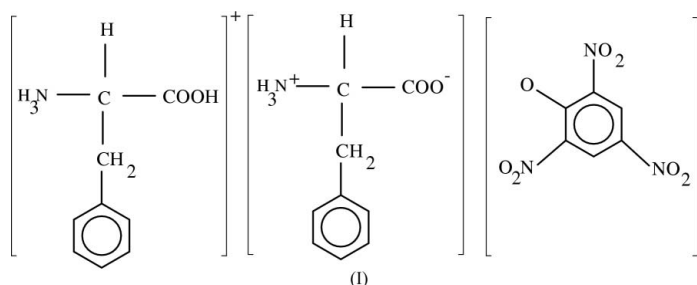
The asymmetric unit of (I) (Fig. 1) comprises a zwitterionic phenylalanine, a phenylalaninium cation and a picrate anion. The bond distances and angles (Table 1) confirm the protonation of one of the phenylalanine residues.

In the zwitterionic phenylalanine residue, the backbone conformation angle ψ^1 is in the *cis* form and ψ^2 is in the *trans* form. The branched side-chain conformation angle χ^1 is indicative of a *gauche* I form, and the angles χ^{21} and χ^{22} correspond to a folded conformation. These values are expected to lie in the range $90 \pm 30°$ (Cotrait *et al.*, 1984). For the protonated phenylalaninium residue, the conformation angles are as described above for the neutral molecule (Table 1). The picrate anion plays a vital role in the hydrogen bonding, as it links both residues *via* N—H···O bonds. The picrate O atoms (O1, O2, O3, O4 and O7) participate in hydrogen bonds. One of the three nitro groups of the picrate anion is twisted from the plane of the ring (Soriano-Garcia *et al.*, 1978).
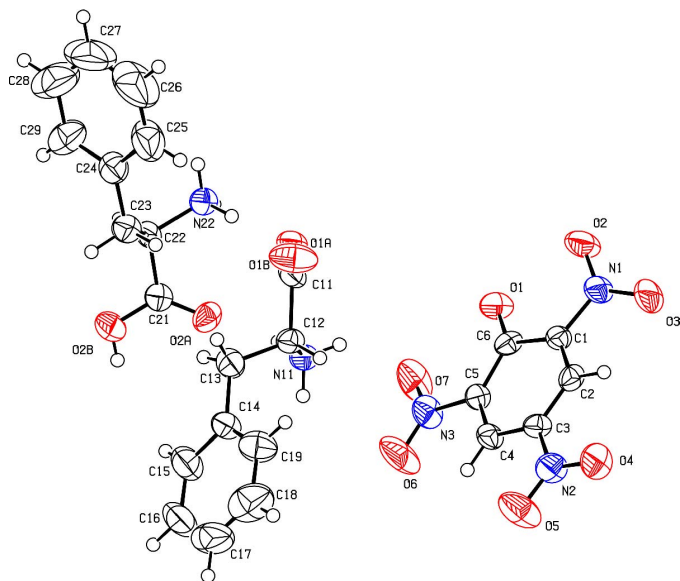
Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. Molecules are orientated to indicate their relative orientations in the unit cell.
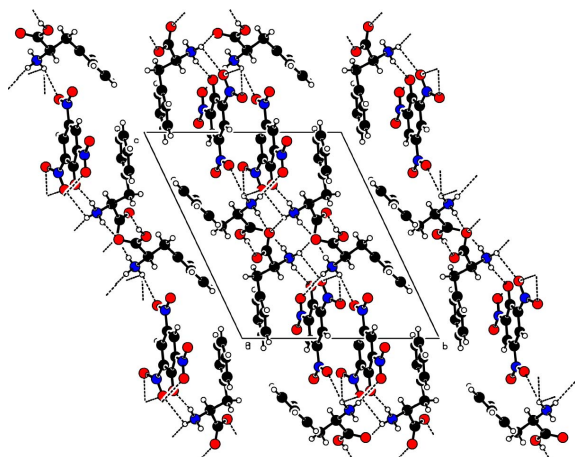

Figure 2
A packing diagram of the molecule of (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

The phenylalaninium residue forms a strong $O-H\cdots O$ hydrogen bond [2.473 (5) Å] with a zwitterionic phenylalanine residue. An inversion-related *DL*1 head-to-tail sequence (*DL* refers to the inversion-related N and O atoms, and 1 refers to the *cis* O and N atoms) is also observed [$N11-H11B-O1A^i$; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. The phenylalaninium residue has a two-centred, a chelated three-centred and a four-centred hydrogen bond. Because of the four-centred hydrogen bond and the chelation, the $N-H\cdots O$ bond angles are very low. Table 2 gives details of the hydrogen bonding. The amino group of the phenylalaninium residue connects two different picrate anions *via* $N-H\cdots O$ hydrogen bonds [$N22-H22A\cdots O2^i$ and $N22-H22B\cdots O1^{iii}$], resulting in an infinite chain along the **a** direction [symmetry code: (iii): $-x, 1 - y, 1 - z$].

The phenylalanine residue of (I) is an example of a class I hydrogen-bonding pattern, by having three two-centred hydrogen bonds (Jeffrey & Saenger, 1991). In the crystal strucutre of (I) (Fig. 2), the hydrophobic double layers along the $y = 0$ plane are sandwiched between hydrophilic layers along the $y = \frac{1}{2}$ plane.

Experimental

The title compound was crystallized by the slow evaporation at room temperature of a mixture containing equimolar quantities of DL-phenylalanine and picric acid.

Crystal data

$C_9H_{11}NO_2 \cdot C_9H_{12}NO_2^+ \cdot C_6H_2N_3O_7^-$	$D_m = 1.380$ Mg m^{-3}
$M_r = 559.49$	D_m measured by flotation in carbon
Triclinic, $P\bar{1}$	tetrachloride and xylene
$a = 7.333$ (3) Å	Mo $K\alpha$ radiation
$b = 13.737$ (3) Å	Cell parameters from 25
$c = 15.381$ (6) Å	reflections
$\alpha = 113.04$ (2)°	$\theta = 8.4$–13.9°
$\beta = 94.93$ (4)°	$\mu = 0.11$ mm^{-1}
$\gamma = 105.23$ (3)°	$T = 293$ (2) K
$V = 1344.2$ (9) Å^3	Block, yellow
$Z = 2$	$0.3 \times 0.2 \times 0.12$ mm
$D_x = 1.382$ Mg m^{-3}	

Data collection

Enraf-Nonius MACH3	$R_{int} = 0.048$
diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = -1 \rightarrow 8$
Absorption correction: ψ scan	$k = -16 \rightarrow 16$
(North *et al.*, 1968)	$l = -18 \rightarrow 18$
$T_{min} = 0.974$, $T_{max} = 0.987$	3 standard reflections
6021 measured reflections	frequency: 60 min
4724 independent reflections	intensity decay: none
1945 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$+ 0.223P]$
$wR(F^2) = 0.188$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} < 0.001$
4724 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
362 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	Extinction correction: none

Table 1
Selected geometric parameters (Å, °).

C11—O1A	1.227 (5)	C21—O2A	1.211 (5)
C11—O1B	1.269 (6)	C21—O2B	1.298 (5)
O1A—C11—O1B	126.0 (4)	O2A—C21—O2B	125.3 (4)
O1A—C11—C12	120.9 (5)	O2A—C21—C22	122.8 (4)
O1B—C11—C12	113.1 (4)	O2B—C21—C22	111.9 (4)
O1A—C11—C12—N11	15.2 (6)	C22—C23—C24—C29	69.7 (6)
O1B—C11—C12—N11	−166.0 (4)	C22—C23—C24—C25	−111.1 (6)
N11—C12—C13—C14	80.3 (5)	C4—C3—N2—O5	−4.3 (6)
C12—C13—C14—C19	59.9 (6)	C2—C3—N2—O4	−4.4 (6)
C12—C13—C14—C15	−124.4 (5)	C6—C5—N3—O7	4.6 (6)
O2A—C21—C22—N22	11.3 (6)	C4—C5—N3—O6	4.4 (6)
O2B—C21—C22—N22	−169.1 (3)	C6—C1—N1—O2	25.9 (6)
N22—C22—C23—C24	59.8 (5)	C2—C1—N1—O3	23.1 (6)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$N11-H11A\cdots O1$	0.89	2.01	2.875 (4)	165
$N11-H11B\cdots O1A^{\mathrm{i}}$	0.89	2.07	2.923 (4)	159
$N11-H11C\cdots O2A$	0.89	2.01	2.888 (4)	168
$N22-H22A\cdots O2^{\mathrm{i}}$	0.89	2.60	3.037 (4)	111
$N22-H22A\cdots O3^{\mathrm{i}}$	0.89	2.48	3.266 (5)	148
$N22-H22A\cdots O4^{\mathrm{ii}}$	0.89	2.57	3.061 (4)	116
$N22-H22C\cdots O1A$	0.89	2.00	2.883 (4)	174
$N22-H22B\cdots O1^{\mathrm{iii}}$	0.89	1.94	2.778 (5)	156
$N22-H22B\cdots O7^{\mathrm{iii}}$	0.89	2.40	3.036 (5)	129
$O2B-H2B\cdots O1B^{\mathrm{iv}}$	0.82	1.67	2.473 (5)	167

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y, z+1$; (iii) $-x, -y+1, -z+1$; (iv) $x-1, y, z$.

All H atoms were included in the refinement in the riding-model approximation, with C—H = 0.93 (phenyl), 0.97 (methylene) and 0.98 Å (methine), N—H = 0.89 Å and O—H = 0.82 Å, and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $1.5U_{\mathrm{eq}}(\mathrm{O,N})$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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