

L-Phenylalanine L-phenylalaninium malonate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(C-C)$ = 0.006 Å

R factor = 0.035

wR factor = 0.101

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 asymmetric unit of the title compound, $C_9H_{11}NO_2 \cdot C_9H_{12}NO_2^+ \cdot C_3H_3O_4^-$, consists of two phenylalanine molecules, one as a zwitterion (P) and the other as a cation (P^+), in addition to a malonate anion (Mal^-). The phenylalaninium and phenylalanine molecules are linked by a very short *syn-syn* carboxyl-carboxylate ($-COO^- \cdots HOOC-$) hydrogen bond [$O \cdots O = 2.429(4)$ Å]. The Mal^- anion is stabilized by a strong intramolecular $O-H \cdots O$ hydrogen bond. The aggregation of P and P^+ is mediated through Mal^- , leading to an infinite double chain along the *c* axis.

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Comment

L-Phenylalanine, an essential amino acid, forms many proton transfer complexes with organic and inorganic acids. Interestingly, the crystal structure of L-phenylalanine itself has not yet been reported, but that of D-phenylalanine has been published, with a high *R* factor of 0.15 (Weissbuch *et al.*, 1990). Precise X-ray crystal structure determinations of complexes of amino acids with carboxylic acids are expected to provide information regarding preferences of specific aggregation patterns, stoichiometry and ionization states of the constituent molecules. In a few instances, such complexes are also found to exhibit non-linear optical (NLO) properties. The present study reports the crystal structure of L-phenylalaninium malonate L-phenylalanine, (I). Recently, the crystal structures of L-phenylalaninium maleate (Alagar *et al.*, 2001), DL-phenylalaninium maleate (Alagar, Subha Nandhini *et al.*, 2003) and L-phenylalanine fumaric acid (Alagar, Krishnakumar *et al.*, 2003) have been reported.

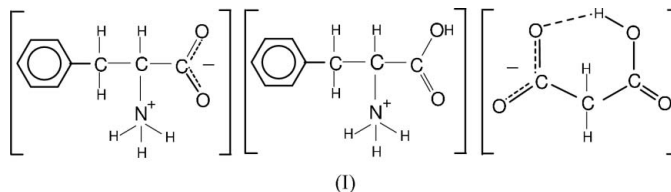


Fig. 1 shows the molecular structure with the atom-numbering scheme. The asymmetric unit consists of two phenylalanine molecules, one as a zwitterion (P) and the other as a cation (P^+), in addition to a malonate anion (Mal^-). The phenylalaninium and phenylalanine molecules are linked by a very short *syn-syn* carboxyl-carboxylate ($-COO^- \cdots HOOC-$) Speakman-salt-type hydrogen bond [$O \cdots O = 2.429(4)$ Å]. Such strong interactions (with a normal range of 2.50–2.60 Å and a minimum of 2.40 Å) have already been thoroughly investigated (Speakman, 1972). The preferential formation of a PP^+ aggregate, as observed in the case of L-phenylalaninium formate L-phenylalanine (henceforth PHEFOR) (Görbitz &

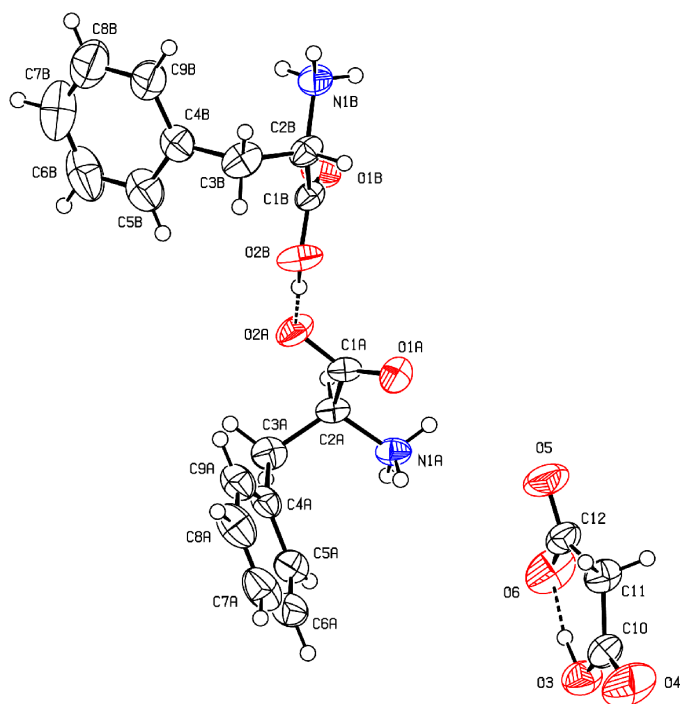


Figure 1
The molecular structure of (I), with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

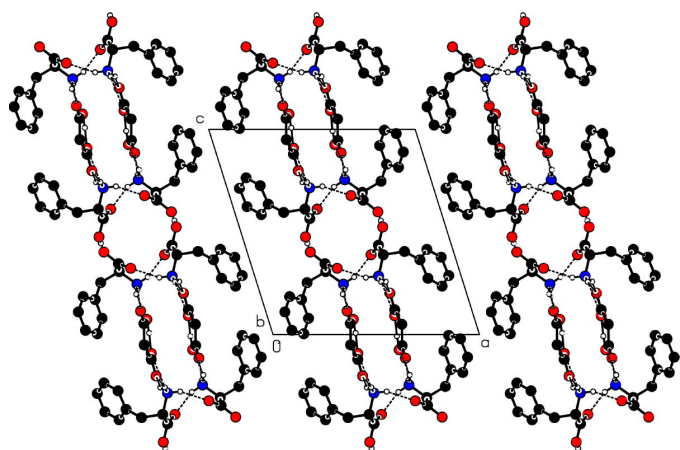


Figure 2
Packing diagram of the molecules of (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds. C-bound H atoms have been omitted.

Etter, 1992), may be attributed to the specific stability associated with the nearly symmetric short hydrogen bonds between chemically identical groups. The geometry of the carboxylate group of P is unusual, with unequal C1A—O1A and C1A—O2A bonds [1.217 (4) and 1.285 (3) Å, respectively], presumably as a result of the participation of O2A in the formation of the PP⁺ aggregate. The side-chain conformations of P and P⁺ are found to be *gauche*⁺, as observed in PHEFOR (Table 1). The Mal[−] anion is essentially planar, except for the methylene H atoms, and is stabilized by a strong intramolecular O—H...O hydrogen bond. The O3...O6 distance, 2.413 (4) Å, agrees well with the values expected for

a symmetrical hydrogen bond (Gilli *et al.*, 1994). However, as evidenced in Table 2, the intramolecular hydrogen bond is asymmetric. Similar instances involving Mal[−] have been observed in several other crystal structures (Briggman & Oskarsson, 1978; Djinović *et al.*, 1990; Kalsbeek, 1992; Barnes & Weakley, 2000; Saraswathi & Vijayan, 2002*a,b*).

Fig. 2 shows the packing of molecules, viewed along the *b* axis. The further aggregation of P and P⁺ is mediated through Mal[−], leading to an infinite double chain along the *c* axis. There are no direct hydrogen-bonded head-to-tail P—P or P⁺—P⁺ interactions. However, the amino group of P forms a hydrogen bond with the carboxylic acid group of P⁺ and *vice versa*. The double chain on either side is flanked by the hydrophobic side chains of P and P⁺, both occurring alternately along the *a* and *c* axes. Thus, the double chain is characterized by thick layers of alternating hydrophilic and hydrophobic zones along the *a* axis. The distance between the centroids of P and P⁺ [8.943 (4) Å] and the angle between their planes [70.2 (1)°] leads to edge-to-face phenyl–phenyl interactions among P—P and P⁺—P⁺, a phenomenon observed in PHEFOR. The aggregation pattern, stoichiometry and ionization states of individual molecules show striking similarities with other phenylalanine–carboxylic acid complexes.

Experimental

Colourless single crystals of (I) were grown, as transparent needles, from a saturated aqueous solution containing L-phenylalanine and malonic acid in a 1:1 stoichiometric ratio.

Crystal data

C₉H₁₁NO₂·C₉H₁₂NO₂⁺·C₃H₃O₄[−]
M_r = 434.44
 Monoclinic, *P*2₁
a = 14.031 (3) Å
b = 5.5082 (10) Å
c = 14.601 (3) Å
 β = 107.412 (3)°
V = 1076.7 (4) Å³
Z = 2
D_x = 1.340 Mg m^{−3}
D_m = 1.35 Mg m^{−3}

D_m measured by flotation in a mixture of xylene and bromoform
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 7.4–16.3°
 μ = 0.10 mm^{−1}
T = 293 (2) K
 Block cut from a needle, colourless
 0.30 × 0.22 × 0.15 mm

Data collection

Nonius MACH3 four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 T_{\min} = 0.89, T_{\max} = 0.98
 2761 measured reflections
 2032 independent reflections
 1921 reflections with $I > 2\sigma(I)$

R_{int} = 0.049
 θ_{max} = 25.0°
 h = −1 → 16
 k = −1 → 5
 l = −17 → 16
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.035
 $wR(F^2)$ = 0.101
 S = 1.06
 2032 reflections
 296 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.0894P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1A—C1A	1.217 (4)	O3—H3	1.05 (4)
O2A—C1A	1.285 (3)	O4—C10	1.204 (5)
N1A—C2A	1.480 (4)	O5—C12	1.213 (4)
O1B—C1B	1.226 (4)	O6—C12	1.291 (5)
O2B—C1B	1.271 (4)	C10—C11	1.496 (5)
O2B—H2B	0.91 (8)	C11—C12	1.501 (5)
N1B—C2B	1.484 (4)	C11—H1	1.01 (6)
O3—C10	1.284 (5)	C11—H2	0.95 (5)
O1A—C1A—C2A—N1A	−2.7 (4)	O1B—C1B—C2B—N1B	2.4 (4)
O2A—C1A—C2A—N1A	177.6 (2)	O2B—C1B—C2B—N1B	−177.4 (3)
N1A—C2A—C3A—C4A	66.9 (4)	N1B—C2B—C3B—C4B	61.7 (4)
C2A—C3A—C4A—C5A	−90.0 (4)	C2B—C3B—C4B—C5B	85.8 (4)
C2A—C3A—C4A—C9A	89.3 (4)	C2B—C3B—C4B—C9B	−94.5 (4)

Table 2

Hydrogen-bond 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>
N1A—H5...O4 ⁱ	0.89	1.90	2.699 (4)	148
N1A—H6...O3 ⁱⁱ	0.89	2.06	2.889 (4)	154
N1A—H7...O1B ⁱⁱⁱ	0.89	1.90	2.757 (3)	160
N1B—H16...O5 ^{iv}	0.89	2.12	3.005 (4)	174
N1B—H17...O5	0.89	2.35	3.167 (5)	152
N1B—H18...O1A ^v	0.89	2.05	2.864 (3)	152
O2B—H2B...O2A ^{vi}	0.91 (8)	1.53 (8)	2.429 (4)	175 (6)
O3—H3...O6	1.04 (4)	1.41 (4)	2.413 (4)	160 (4)

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

The H atoms attached to O2B, O3 and C11 were located in a difference map and refined freely; the O—H and C—H distances are listed in Table 1. All other H atoms were positioned geometrically and were allowed to ride on their parent atoms, with C—H = 0.93–0.98 Å, N—H = 0.89 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{N})$. The absolute configuration of (I) was not established by the analysis but is known from the configuration of the starting reagents. In the absence

of significant anomalous dispersion effects, Friedel pairs were averaged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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