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DL-Phenylalaninium maleate at 123 K

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Key indicators

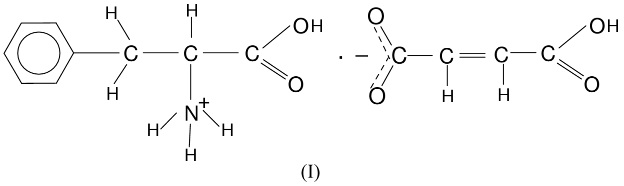
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.146
Data-to-parameter ratio = 14.8

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

In the title compound, $C_9H_{12}NO_2^+\cdot C_4H_3O_4^-$, the amino acid molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecules exits in the mono-ionized state. In the semi-maleate anion, the intramolecular O—H···O hydrogen bond is asymmetric. The phenylalaninium cations and the semi-maleate anions form hydrogen-bonded double layers, linked together by N—H···O and O—H···O hydrogen bonds, extending along [101].

Comment

Phenylalanine, an essential amino acid commonly found in proteins, has a variety of important physiological roles to play in animals. Interestingly, the crystal structures of the L- and racemic forms of phenylalanine remain unknown. However, the crystal structure of its D-form has been reported with a high R factor of 15% (Weissbuch *et al.*, 1990). Though phenylalanine is known to form innumerable complexes with inorganic acids, crystallographic data for their complexation with organic acids remain scarce. The present study, which reports the crystal structure of DL-phenylalaninium maleate, is part of a series of X-ray investigations being carried out in our laboratory on amino acid–carboxylic acid complexes. Recently, the crystal structures of glycinium maleate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2001), L-alaninium maleate (Alagar, Subha Nandhini, Krishnakumar & Natarajan, 2001), β-alaninium maleate (Rajagopal, Krishnakumar & Natarajan, 2001), DL-valinium maleate (Alagar, Krishnakumar, Mostad & Natarajan, 2001), L-phenylalaninium maleate (Alagar, Krishnakumar & Natarajan, 2001), sarcosinium maleate (Rajagopal, Nandhini, Krishnakumar, Mostad & Natarajan, 2002) and DL-methioninium maleate (Alagar, Nandhini, Krishnakumar & Natarajan, 2002) have been reported from our laboratory.



(I)

Fig. 1 shows the molecular structure of the title compound, (I), with the atom-numbering scheme. The amino acid molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The conformation of the phenylalaninium cation in the present structure differs considerably from that observed in L-

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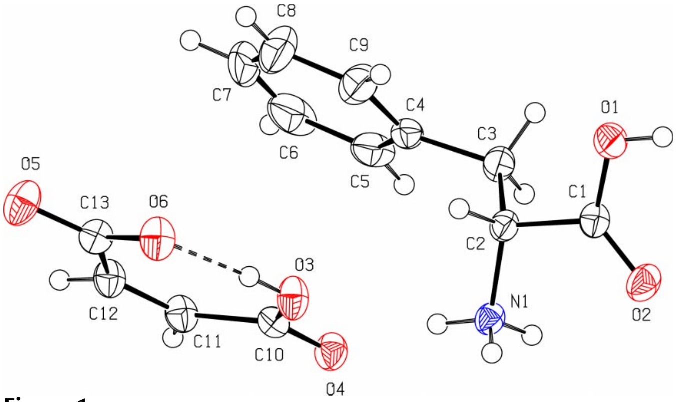

Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

phenylalaninium maleate. The torsion angles χ^{21} and χ^{22} [−122.0 (2) and 62.1 (2)°, respectively] indicate a distorted, folded conformation in the present case. These values are significantly different from those observed in L-phenylalaninium maleate [91.5 (3) and −88.8 (2)°, respectively]. The maleic acid molecule exists in the mono-ionized state (*i.e.* as a semi-maleate anion). In the semi-maleate anion, the intramolecular hydrogen bond is asymmetric, as observed in the crystal structures of maleic acid itself (James & Williams, 1974), glycinium maleate, L-alaninium maleate, DL-valinium maleate and DL-methioninium maleate. However, in the crystal structures of maleic acid with DL- and L-arginine (Ravishankar *et al.*, 1998), L-histidine and L-lysine (Pratap *et al.*, 2000) and L-phenylalaninium maleate, this intramolecular hydrogen bond is symmetric.

Fig. 2 shows the packing of the molecules of (I), viewed down the *b* axis. The phenylalaninium cations and the semi-maleate anions form hydrogen-bonded double layers linked toegether by N—H···O and O—H···O hydrogen bonds and extend along [101]. These double layers are flanked, on either side, by the hydrophobic side chains of phenylalanine, leading to alternating hydrophilic and hyrophobic zones, and have no classical hydrogen-bonded interactions between them. A weak head-to-tail hydrogen bond between the glide-related phenylalaninium ions is present. The aggregation pattern observed in (I) has striking similarities to those observed in L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992), L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), L-phenylalaninium maleate and other amino acid–maleic acid complexes, *viz.* glycinium maleate, sarcosinium maleate and DL-valinium maleate. Thus, it seems that the mode of assembly is determined chiefly by the semi-maleate anions, irrespective of the chemical nature of the amino acids.

Experimental

Colourless single crystals of (I) were grown as transparent plates from a saturated aqueous solution containing DL-phenylalanine and maleic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_9H_{12}NO_2^+\cdot C_4H_3O_4^-$
$M_r = 281.26$
Monoclinic, $P2_1/n$
$a = 12.308$ (3) Å
$b = 5.9942$ (12) Å
$c = 18.061$ (4) Å
$\beta = 99.15$ (3)°
$V = 1315.5$ (5) Å^3
$Z = 4$
$D_x = 1.420$ Mg m^{-3}
$D_m = 1.42$ Mg m^{-3}
D_m measured by flotation in a mixture of xylene and bromoform
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
$\theta = 1.9$–26.4°
$\mu = 0.11$ mm^{-1}
$T = 123$ (2) K
Plate, colourless
0.3 × 0.3 × 0.1 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.97$, $T_{\max} = 0.99$
13 028 measured reflections
2704 independent reflections
2250 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\max} = 26.4$°
$h = -15 \rightarrow 15$
$k = -7 \rightarrow 7$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.146$
$S = 1.13$
2704 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.6066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.313 (2)	C4—C5	1.381 (3)
O2—C1	1.209 (2)	C4—C9	1.383 (3)
O3—C10	1.303 (2)	C5—C6	1.391 (3)
O4—C10	1.229 (2)	C6—C7	1.390 (5)
O5—C13	1.246 (2)	C7—C8	1.378 (5)
O6—C13	1.276 (2)	C8—C9	1.380 (3)
N1—C2	1.485 (2)	C10—C11	1.497 (2)
C1—C2	1.524 (2)	C11—C12	1.333 (3)
C2—C3	1.535 (3)	C12—C13	1.501 (3)
C3—C4	1.513 (2)		
O2—C1—O1	126.02 (17)	C8—C7—C6	119.6 (2)
O2—C1—C2	122.41 (16)	C7—C8—C9	120.5 (3)
O1—C1—C2	111.57 (15)	C8—C9—C4	120.5 (3)
N1—C2—C1	107.48 (14)	O4—C10—O3	120.46 (16)
N1—C2—C3	111.26 (15)	O4—C10—C11	118.87 (16)
C1—C2—C3	110.82 (15)	O3—C10—C11	120.67 (16)
C4—C3—C2	115.14 (15)	C12—C11—C10	130.92 (17)
C5—C4—C9	119.13 (19)	C11—C12—C13	130.59 (17)
C5—C4—C3	120.77 (18)	O5—C13—O6	124.02 (17)
C9—C4—C3	119.97 (18)	O5—C13—C12	115.88 (16)
C4—C5—C6	120.8 (2)	O6—C13—C12	120.09 (16)
C7—C6—C5	119.4 (3)		
O2—C1—C2—N1	4.1 (2)	C5—C6—C7—C8	0.0 (4)
O1—C1—C2—N1	−176.15 (15)	C6—C7—C8—C9	0.6 (4)
O2—C1—C2—C3	−117.6 (2)	C7—C8—C9—C4	0.3 (4)
O1—C1—C2—C3	62.1 (2)	C5—C4—C9—C8	−1.7 (3)
N1—C2—C3—C4	85.72 (19)	C3—C4—C9—C8	174.2 (2)
C1—C2—C3—C4	−154.75 (16)	O4—C10—C11—C12	174.2 (2)
C2—C3—C4—C5	−122.01 (19)	O3—C10—C11—C12	−5.4 (3)
C2—C3—C4—C9	62.1 (2)	C10—C11—C12—C13	1.7 (4)
C9—C4—C5—C6	2.3 (3)	C11—C12—C13—O5	−174.5 (2)
C3—C4—C5—C6	−173.65 (19)	C11—C12—C13—O6	6.7 (3)
C4—C5—C6—C7	−1.4 (3)		

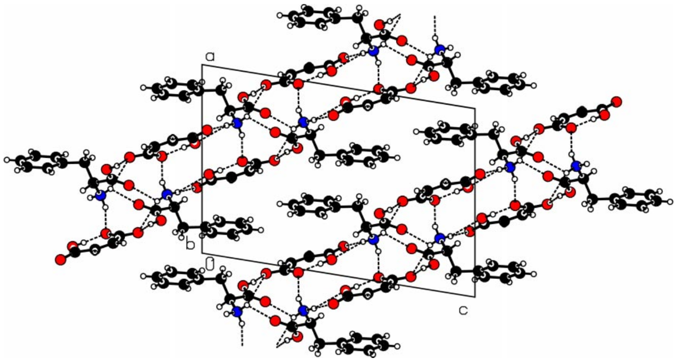

Figure 2
The packing of the molecules of (I), viewed down the *b* axis.

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O1-H1\cdots O5^{i}}$	0.82	1.78	2.5314 (19)	151
$\mathrm{O3-H3\cdots O6}$	0.82	1.65	2.468 (2)	176
$\mathrm{N1-H1}A\cdots\mathrm{O4^{ii}}$	0.89	1.98	2.861 (2)	170
$\mathrm{N1-H1}A\cdots\mathrm{O3^{ii}}$	0.89	2.40	3.047 (2)	130
$\mathrm{N1-H1}B\cdots\mathrm{O6^{iii}}$	0.89	1.98	2.823 (2)	159
$\mathrm{N1-H1}C\cdots\mathrm{O2^{iv}}$	0.89	2.26	2.839 (2)	123
$\mathrm{N1-H1}C\cdots\mathrm{O5^{v}}$	0.89	2.47	3.283 (2)	152

Symmetry codes: (i) $x-1, 1+y, z-1$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$; (v) $x-1, y, z-1$.

After checking for their presence in a difference map, all H atoms were positioned geometrically and were allowed to ride on their respective parent atoms with *SHELXL*97 (Sheldrick, 1997) defaults for bond lengths and isotropic displacement parameters. Rotating-group refinement was used for the OH groups.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); 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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