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L-Phenylalaninium maleate

M. Alagar,[a] R. V. Krishnakumar[b] and S. Natarajan[c]*

[a]Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi 626 123, India, [b]Department of Physics, Thiagarajar College, Madurai 625 009, India, and [c]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: xray@mrna.tn.nic.in

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In the title compound, $C_9H_{12}NO_2^+\cdot C_4H_3O_4^-$, the amino acid molecule exists in the cationic form and the maleic acid molecule in the mono-ionized state. In the semi-maleate anion, a nearly symmetric intramolecular O—H···O hydrogen bond is observed. The aggregation pattern observed in the title crystal has striking similarities with those observed in L-phenylalanine L-phenylalaninium formate and L-phenylalanine L-phenylalaninium perchlorate.

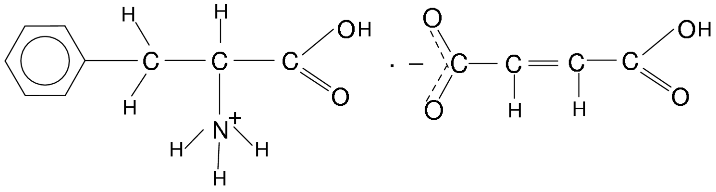
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.078
Data-to-parameter ratio = 7.2

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

Comment

Phenylalanine, an essential amino acid commonly found in proteins, plays a key role in the formation of a variety of physiologically important chemicals that transmit signals between nerve cells. Previous studies on phenylalanine report only the unit-cell dimensions (Khawas & Murthi, 1968; Khawas, 1970, 1971, 1985) and the crystal structure of the D-form with a high R factor of 15% (Weissbuch *et al.*, 1990). The crystal structure of L-phenylalanine, however, is yet to be reported. A number of complexes of L-phenylalanine with inorganic acids are already known. The present study, which reports the crystal structure of L-phenylalaninium maleate, (I), is part of a series of X-ray investigations being carried out in our laboratory on amino acid–carboxylic acid complexes. Recently, the crystal structure of glycinium maleate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2001), L-alaninium maleate (Alagar *et al.*, 2001) and β-alaninium maleate (Rajagopal, Krishnakumar & Natarajan, 2001) have been reported.



(I)

Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme adopted. The amino acid molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The phenylalaninium cation has the *gauche*$^-$ conformation with a χ^1 value of −59.3 (2)°. This is different from the values observed in L-

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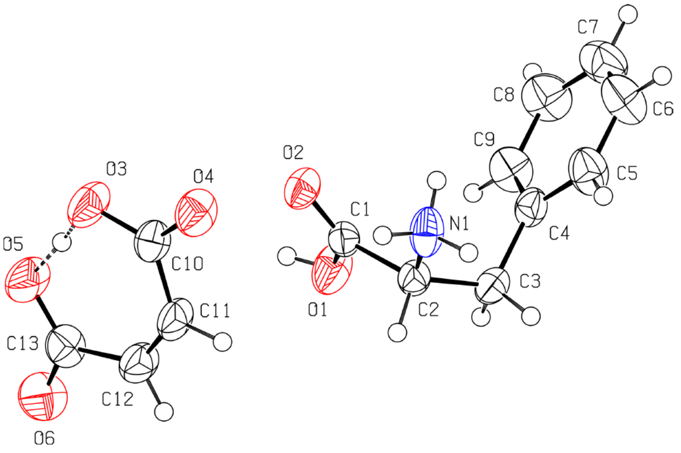

Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids.

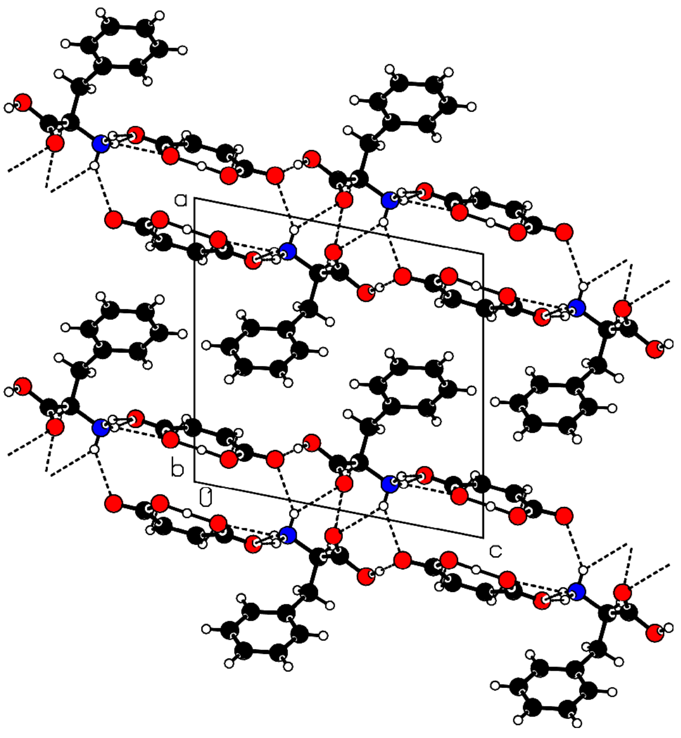

Figure 2
Packing of the molecules of (I) viewed down the *b* axis.

phenylalanine L-phenylalaninium formate with χ^1 = 72.3 (4) and 70.8 (4)°, respectively, for the zwitterion and the cation (Görbitz & Etter, 1992). The maleic acid molecule exists in the mono-ionized state (*i.e.* as a semi-maleate anion). In the semi-maleate anion, a nearly symmetric intramolecular hydrogen bond, with a proton shared between the O3 and O5 atoms, is observed as in the crystal structures of complexes of maleic acid with DL- and L-arginine (Ravishankar *et al.*, 1998) and L-histidine and L-lysine (Pratap *et al.*, 2000). However, in the crystal structures of maleic acid itself (James & Williams, 1974), glycinium maleate and L-alaninium maleate, this intramolecular hydrogen bond is asymmetric.

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 chains in which they alternate along the *c* axis and are held together by N—H···O hydrogen bonds. The double chain, on either side, is flanked by the hydrophobic side chains of phenylalanine leading to alternating hydrophilic and hydrophobic zones along the *a* axis. These double chains form an infinite two-dimensional network extending along the *b* axis, interconnected through O—H···O, N—H···O and C—H···O hydrogen bonds. The aggregation pattern observed in (I) has striking similarities with those observed in L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992) and L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997).

Experimental

Colorless single crystals of (I) were grown as transparent needles from a saturated aqueous solution containing L-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, $P2_1$
a = 11.0560 (9) Å
b = 5.3326 (4) Å
c = 11.4712 (7) Å
β = 101.07 (1)°
V = 663.73 (8) Å^3
Z = 2
D_x = 1.407 Mg m^{-3}
D_m = 1.41 Mg m^{-3}
D_m measured by flotation in a mixture of xylene and bromoform
Cu *Kα* radiation
Cell parameters from 25 reflections
θ = 28–42°
μ = 0.96 mm^{-1}
T = 293 (2) K
Needle, colorless
0.40 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.82, T_{max} = 0.91
1424 measured reflections
1353 independent reflections
1294 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 67.9°
$h = -13 \rightarrow 0$
$k = 0 \rightarrow 6$
$l = -13 \rightarrow 13$
2 standard reflections every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.078
S = 1.13
1353 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.0901P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.052 (3)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.307 (2)	C3—C4	1.508 (3)
O2—C1	1.203 (3)	C4—C9	1.379 (3)
O3—C10	1.270 (3)	C4—C5	1.384 (3)
O4—C10	1.244 (2)	C5—C6	1.378 (4)
O5—C13	1.278 (3)	C6—C7	1.366 (4)
O5—H3	1.28 (3)	C7—C8	1.373 (4)
O6—C13	1.230 (3)	C8—C9	1.381 (4)
N1—C2	1.486 (3)	C10—C11	1.476 (3)
C1—C2	1.511 (3)	C11—C12	1.331 (3)
C2—C3	1.528 (3)	C12—C13	1.481 (3)
O2—C1—O1	124.68 (19)	C6—C7—C8	119.7 (2)
O2—C1—C2	122.17 (17)	C7—C8—C9	119.8 (2)
O1—C1—C2	113.08 (18)	C4—C9—C8	121.2 (2)
N1—C2—C1	107.14 (17)	O4—C10—O3	120.9 (2)
N1—C2—C3	111.81 (16)	O4—C10—C11	118.3 (2)
C1—C2—C3	115.91 (17)	O3—C10—C11	120.76 (18)
C4—C3—C2	115.43 (19)	C12—C11—C10	130.3 (2)
C9—C4—C5	118.1 (2)	C11—C12—C13	130.7 (2)
C9—C4—C3	121.64 (19)	O6—C13—O5	121.5 (2)
C5—C4—C3	120.3 (2)	O6—C13—C12	118.9 (2)
C6—C5—C4	120.7 (2)	O5—C13—C12	119.6 (2)
C7—C6—C5	120.5 (2)		
O2—C1—C2—N1	−9.4 (2)	O1—C1—C2—C3	47.7 (2)
O1—C1—C2—N1	173.33 (17)	N1—C2—C3—C4	−59.3 (2)
O2—C1—C2—C3	−135.0 (2)	C1—C2—C3—C4	63.9 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O5	1.13 (3)	1.28 (3)	2.412 (2)	175 (4)
O1—H1···O4^{i}	0.82	1.73	2.547 (2)	170
N1—H1A···O5^{ii}	0.89	2.29	2.999 (2)	137
N1—H1A···O6^{ii}	0.89	2.20	3.068 (3)	164
N1—H1B···O2^{iii}	0.89	2.45	3.077 (2)	128
N1—H1B···O4^{iv}	0.89	2.25	3.011 (2)	144
N1—H1C···O6^{v}	0.89	2.10	2.947 (3)	159
C2—H2···O2^{vi}	0.98	2.49	3.324 (3)	142
C2—H2···O2^{iii}	0.98	2.48	3.073 (2)	118
C11—H11···O3^{vi}	0.93	2.60	3.239 (3)	127
C12—H12···O5^{vi}	0.93	2.53	3.303 (3)	140

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

The absolute configuration of L-phenylalaninium maleate was not established by the analysis but is known from the configuration of the starting reagents. The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms with *HFIX* instructions using *SHELXL*97 (Sheldrick, 1997) defaults. The H atom shared between atoms O3 and O5 of the semimaleate anion was, however, refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; 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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References

Alagar, M., Krishnakumar, R. V., Subha Nandhini, M. & Natarajan, S. (2001). *Acta Cryst.* E**57**, o855–o857.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Görbitz, C. H. & Etter, M. C. (1992). *Acta Cryst.* C**48**, 1317–1320.

James, M. N. G & Williams, G. J. B. (1974). *Acta Cryst.* B**30**, 1249–1257.

Khawas, B. & Murthi, G. S. R. K. (1968). *Indian J. Phys.* **42**, 175–180.

Khawas, B. (1970). *Acta Cryst.* B**26**, 1919–1922.

Khawas, B. (1971). *Acta Cryst.* B**27**, 1517–1520.

Khawas, B. (1985). Indian *J. Phys. A*, **59**, 219–226.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pratap, J. V., Ravishankar, R. & Vijayan, M. (2000). *Acta Cryst.* B**56**, 690–696.

Rajagopal, K., Krishnakumar, R. V., Mostad, A. & Natarajan. S. (2001) *Acta Cryst.* E**57**, o751–o753.

Rajagopal, K. Krishnakumar, R. V. & Natarajan, S. (2001). *Acta Cryst.* E**57**, o922–o924.

Ravishankar, R., Chandra, N. R. & Vijayan, M. (1998). *J. Biomol. Struct. Dyn.* **15**, 1093–1100.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON for Windows*. Utrecht University, The Netherlands.

Srinivasan, N. & Rajaram, R. K. (1997). *Acta Cryst.* C**53**, 1711–1713.

Weissbuch, I., Frolow, F., Addadi, L., Lahav, M. & Leiserowitz, L. (1990). *J. Am. Chem. Soc.* **112**, 7718–7724.