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DL-Phenylalaninium dihydrogen phosphate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 7.1

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

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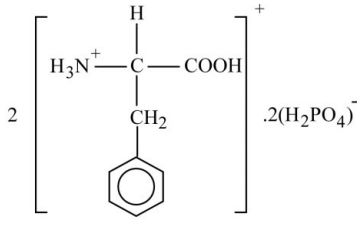
In the title compound, $C_9H_{12}NO_2^+\cdot H_2PO_4^-$, the racemate has crystallizes in a non-centrosymmetric space group, *Pc*. However, both the phenylalaninium and dihydrogen phosphate residues are related by a pseudo-inversion center at about (0.5, 0.25, 0.25). Each phosphate anion forms a strong O—H···O hydrogen bond with a phenylalaninium residue. The aggregation of the hydrophilic zone is in a layer parallel to (010) at x = 0, and the hydrophobic zone is sandwiched between two such layers at x = 0 and x = 1.

Comment

The crystal structures of L-phenylalanine hydrochloride (Gurskaya & Vainshtein, 1963; Al-Karaghouli & Koetzle, 1975), L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992), bis(L-phenylalanine) sulfate monohydrate (Nagashima *et al.*, 1992), L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), bis(DL-phenylalaninium)sulfate monohydrate (Srinivasan *et al.*, 2001*b*) and L-phenylalanine–nitric acid (2/1) (Srinivasan *et al.*, 2001*c*) have been reported. In the present study, the conformation and hydrogen bonding of DL-phenylalanine in the presence of *ortho*phosphoric acid was undertaken.



(I)

The title compound, (I), crystallizes in an unusual, but not uncommon, non-centrosymmetric space group, *Pc*. However, racemates with more than one molecule in the asymmetric unit are found to grow in non-centrosymmetric, non-polar space groups (Dalhus & Görbitz, 2000). The asymmetric unit contains two crystallographically independent phenylalaninium residues (*A* and *B*) and dihydrogen phosphate anions (1 and 2). The two phenylalaninium and phosphate residues are related by a pseudo-inversion center at about (0.5, 0.25, 0.25). The deviation from the pseudo-inversion center is less for the phosphate anions and the backbone of the amino-acid, but more for the branched side chain. An attempt to look for higher symmetry using *LEPAGE* (Spek, 1999) yielded a *C*-centred orthorhombic lattice, possibly in the space group *Cmm*2, with a = 9.051, b = 26.327 and c = 9.956 Å, with a

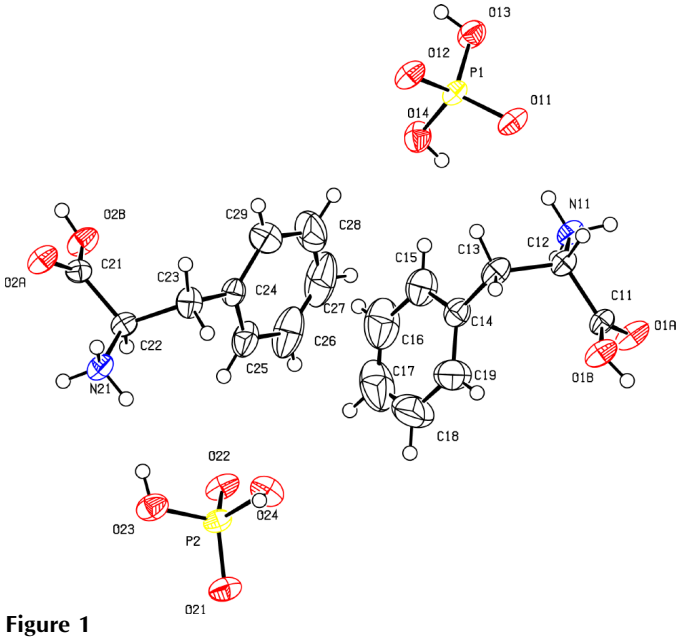


Figure 1
The molecular structures of the two independent molecules showing the atomic numbering scheme and 50% probability displacement ellipsoids. (Johnson, 1976)

transformation $a' = -c$; $b' = -(2a + c)$ and $c' = b$. However R_{int} was 0.61 and hence no attempt was made to solve the structure in the orthorhombic system.

The conformation angles ψ^1 for residues *A* and *B* are 1.3 (4) and 21.0 (4)°, respectively, (see Table 1). The branched-side-chain conformation angle χ^1 is in *gauche* I form [62.5 (4)°] for residue *A*, while for residue *B*, it is in nearly *trans* form [145.7 (3)°]. The torsion angles χ^{21} and χ^{22} for residue *A* [90.4 (4) and −94.3 (4)°] indicate a folded conformation, while those for residue *B* [129.3 (4)° and −55.7 (4)°] indicate a distorted folded conformation. The difference in the conformation angle for the two residues and the unusual less favoured χ^1 conformation for residue *B* may be due to the large deviation from the pseudo-inversion center.

The phosphate anions have similar geometry. However the distances of the H atom from the O atoms in each ion [H1*B*—O12 1.27 (7) and H2*B*—O22 1.28 (6) Å] are longer than the expected O—H distance, and the P—O distances [P1—O12 1.518 (2) and P2—O22 1.523 (3) Å] are in between expected single- and double-bonded P—O distances [1.55 and 1.49 Å; Blessing *et al.*, 1988].

Both phosphate anions play a vital role in forming hydrogen bonds with both phenylalaninium residues and stabilizing the structure (Table 2). Each phosphate anion forms a strong hydrogen bond with a phenylalaninium residue (O1*B*—H1*B*···O12 and O2*B*—H2*B*···O22). The O—H and H···O distances [1.22 (7) and 1.27 (7) Å for *A*, 1.21 (6) and 1.28 (6) Å for *B*] are nearly the same. Precise neutron diffraction measurements at various temperatures have revealed two inversion-related maleate residues connected by a short hydrogen bond with disordered H atoms about a pseudo-centrosymmetric site in potassium hydrogen dichloromaleate (Olovsson *et al.*, 2001). The C—O distances are

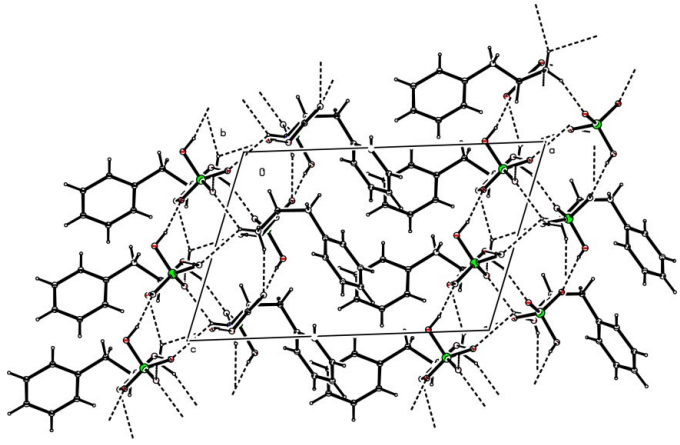


Figure 2
Packing diagram of the molecule, viewed down the *b* axis.

also very similar to those in the title compound. Hence, in the title compound, these hydrogen bonds may be termed symmetric hydrogen bonds or asymmetric hydrogen bonds with flip-flop disorder (Jeffrey & Saenger, 1991). For both phosphate anions, a strong O—H···O intermolecular hydrogen bond connects two symmetry-related phosphate anions. Besides these, the O atoms (O13 and O23) of the phosphate anions form strong hydrogen bonds with the carboxyl-O atoms O1*A* and O2*A* of the two phenylalaninium residues. A bifurcated hydrogen bond is observed in the phenylalaninium residue *A* [amino-N atom with atoms O21 and O23 of phosphate anion (II)], while a similar bifurcated hydrogen bond occurs in phenylalaninium residue *B* [amino-N atom with O atom of carboxyl group (zigzag *Z*2 glide-related head-to-tail sequence] and atom O13 of phosphate anion (I)]. In the phenylalaninium residue *A*, a head-to-tail *Z*2 sequence is engaged, since N11—H11*B*···O1*B* connects two glide-related amino acids (Vijayan, 1988). The packing arrangement leads to the formation of a hydrophilic zone along $x = 0$. The aggregation of the hydrophilic zone is in a layer parallel to (010) and the hydrophobic zone at $x = \frac{1}{2}$ is sandwiched between two such layers at $x = 0$ and $x = 1$ (Fig. 2), as in bis(D-phenylglycinium) sulfate monohydrate (Srinivasan *et al.*, 2001*a*) and L-phenylalanine–nitric acid (2/1) (Srinivasan *et al.*, 2001*c*).

Experimental

The title compound was crystallized from an aqueous solution of DL-phenylalanine and *ortho*phosphoric acid (1:1) by slow evaporation.

Crystal data

$C_9H_{12}NO_2^+\cdot H_2PO_4^-$
$M_r = 263.18$
Monoclinic, *Pc*
$a = 13.899$ (7) Å
$b = 9.956$ (8) Å
$c = 9.051$ (2) Å
$\beta = 108.726$ (8)°
$V = 1186.1$ (12) Å^3
$Z = 4$
$D_x = 1.474$ Mg m^{-3}
$D_m = 1.469$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.3$–13.9°
$\mu = 0.25$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.60 × 0.33 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.918, T_{max} = 0.967
2235 measured reflections
2235 independent reflections
2078 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.074
S = 1.07
2235 reflections
317 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.1839P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0238 (18)
Absolute structure: [Flack, 1983]
Flack parameter = −0.03 (10)

Table 1
Selected geometric parameters (Å, °).

P1—O11	1.483 (3)	P2—O24	1.556 (3)
P1—O12	1.518 (2)	P2—O23	1.572 (3)
P1—O13	1.552 (3)	O1*A*—C11	1.224 (4)
P1—O14	1.562 (3)	O1*B*—C11	1.293 (4)
P2—O21	1.488 (3)	O2*A*—C21	1.226 (4)
P2—O22	1.523 (2)	O2*B*—C21	1.287 (4)
O1*A*—C11—C12—N11	1.3 (4)	O2*A*—C21—C22—N21	21.0 (4)
N11—C12—C13—C14	62.5 (4)	N21—C22—C23—C24	145.7 (3)
C12—C13—C14—C19	90.4 (4)	C22—C23—C24—C29	129.3 (3)
C12—C13—C14—C15	−94.3 (4)	C22—C23—C24—C25	−55.7 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13···O1*A*^{i}	0.82	1.80	2.615 (4)	178
O14—H14···O12^{ii}	0.82	1.94	2.684 (3)	150
O23—H23···O2*A*^{iii}	0.82	1.86	2.684 (4)	178
O24—H24···O22^{iv}	0.82	1.87	2.668 (4)	164
O1*B*—H1*B*···O12^{iii}	1.22 (7)	1.27 (7)	2.473 (4)	170 (6)
N11—H11*A*···O11	0.89	1.82	2.709 (4)	173
N11—H11*B*···O1*B*^{v}	0.89	2.10	2.944 (4)	157
N11—H11*C*···O21^{vi}	0.89	2.13	2.806 (4)	132
N11—H11*C*···O23^{vii}	0.89	2.50	3.142 (4)	129
O2*B*—H2*B*···O22^{i}	1.21 (6)	1.28 (6)	2.497 (4)	177 (6)
N21—H21*A*···O21	0.89	1.86	2.708 (4)	159
N21—H21*B*···O11^{viii}	0.89	1.92	2.771 (4)	160
N21—H21*C*···O2*B*^{ix}	0.89	2.38	3.167 (4)	147
N21—H21*C*···O13^{x}	0.89	2.47	2.934 (4)	113

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

Atoms H1*B* and H2*B* of the carboxyl group of both phenylalaninium residues (*A* and *B*) were located and refined isotropically (since these suggest a strong nearly symmetric hydrogen bond), while all other H atoms of both phenylalaninium residues and phosphate anions were fixed by *HFIX* and allowed to ride on the atoms to which they are attached.

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, 1997); 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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