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Structures of β-Alanine, DL-Alanine and Sarcosine Monophosphates

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Abstract. β-Alanine phosphate, $C_3H_7NO_2.H_3PO_4$, M_r = 187·09, monoclinic, $P2_1/n$, a = 16·115 (20), b = 5·829 (2), c = 8·019 (5) Å, β = 93·30 (6)°, V = 752 (2) Å^3, Z = 4, D_x = 1·652 Mg m^{-3}, λ(Ag $K\alpha$) = 0·5608 Å, μ = 0·192 mm^{-1}, $F(000)$ = 392, T = 295 K, final R = 0·038 for 1351 unique reflexions. Bis(DL-alanine) phosphate, $2C_3H_7NO_2.H_3PO_4$, M_r = 276·18, monoclinic, $C2/c$, a = 14·442 (7), b = 10·352 (6), c = 9·062 (4) Å, β = 119·08 (4)°, V = 1184 (2) Å^3, Z = 4, D_x = 1·549 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 0·275 mm^{-1}, $F(000)$ = 584, T = 295 K, final R = 0·032 for 1238 unique reflexions. Sarcosine phosphate, $C_3H_7NO_2.H_3PO_4$, M_r = 187·09, orthorhombic, $P2_12_12_1$, a = 13·180 (8), b = 9·275 (3), c = 6·245 (2) Å, V = 763 (1) Å^3, Z = 4, D_x = 1·628 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 0·357 mm^{-1}, $F(000)$ = 392, T = 295 K, final R = 0·023 for 1150 unique reflexions. The three $C_3H_7NO_2$ isomers have different behaviors towards monophosphoric acid. The β-alanine and sarcosine monophosphates correspond to a 1/1 stoichiometry while the stoichiometry is 1/2 for DL-alanine. In the case of this last compound the carboxylic group is deprotonated and the phosphoric anion is a triacidic one. A common feature for the three salts is the existence of chains of phosphoric groups linked by hydrogen bonds. In all cases the H atoms have been located and refined. A complete scheme for the hydrogen-bond network is reported for each compound.

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Introduction. The present study is part of a systematic investigation of the interaction of various phosphoric acids with amines, amino acids and amino alcohols.

In the field of amino acid phosphates, glycine monophosphates, glycine *cyclo*-triphosphate and glycine *cyclo*-tetraphosphate have been recently reported by the authors (Averbuch-Pouchot, Durif & Guitel, 1988).

Experimental.

I. *β-Alanine*.H_3PO_4: $C_3H_8NO_2^+.H_2PO_4^-$

Single crystals were prepared by slow evaporation, at room temperature, of a water solution of β-alanine and H_3PO_4 in a stoichiometric ratio. Crystals appear as stout monoclinic prisms. Crystal size: 0·24 × 0·24 × 0·32 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h0l$ ($h+l=2n$); $0k0$ ($k=2n$). 16 reflexions ($10<\theta<12·5°$) for refining unit-cell dimensions. $\omega/2\theta$ scan. 3079 reflexions collected. 2907 independent reflexions, R_{int} = 0·016. $2<\theta<20°$, $\pm h,k,l$, h_{max} = 24, k_{max} = 8, l_{max} = 11. Scan width: 1·20°, scan speed variable, between 0·03 and 0·06° s^{-1}, total background measuring time between 11 and 23 s. Two intensity (040 and $0\bar{4}0$) and orientation (10,0,0 and $\bar{1}0$,0,0) reference reflexions (no variation). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN*77; Main, Hull, Lessinger, Germain, Declercq & Woolfson,

1977). H atoms from difference-Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Final refinement cycles with 1351 reflexions corresponding to $I > 4\sigma_I$. Final $R = 0.039$ ($wR = 0.039$). $S = 0.710$. Max. $\Delta/\sigma = 0.09$ for B_{iso} of H(1C1). Max. peak height in the final difference-Fourier synthesis 0·463 e Å^{-3}. No extinction correction. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: Microvax-II.*

II. 2DL-*Alanine*.H_3PO_4: $2C_3H_7NO_2.H_3PO_4$

Crystals were prepared by slow evaporation, at room temperature, of a water solution of DL-alanine and H_3PO_4 in a stoichiometric ratio. After a week, colorless monoclinic prisms of 2DL-alanine.H_3PO_4 appear. Prism fragment: 0·26 × 0·26 × 0·26 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: hkl ($h+k = 2n$); $h0l$ ($l = 2n$). 25 reflexions ($11{\cdot}5 < \theta < 14{\cdot}5°$) for refining the unit-cell dimensions. ω scan, scan width: 1·20°, scan speed variable, between 0·02 and 0·06° s^{-1}, total background measuring time between 27 and 10 s. 1976 reflexions measured ($2 < \theta < 30°$), $\pm h,k,l$; 1855 unique reflexions, $R_{int} = 0.01$; $h_{max} = 17$, $k_{max} = 14$, $l_{max} = 12$. Two intensity ($\bar{3}\bar{3}\bar{3}$ and $\bar{3}3\bar{3}$) and two orientation (333 and $7\bar{1}\bar{6}$) reference reflexions: no significant variation. Lorentz and polarization corrections, no absorption correction. Structure determination strategy identical to that used for the first compound. Final refinement with 1238 independent reflexions ($I > 9\sigma_I$). Final $R = 0.032$ ($wR = 0.033$), $S = 0.361$, max. $\Delta/\sigma = 0.22$. Max. peak height in the final difference-Fourier synthesis 0·17 e Å^{-3}. No extinction correction. Computer used: Microvax-II.

III. *Sarcosine*.H_3PO_4: $C_3H_8NO_2^+.H_2PO_4^-$

Crystals were prepared by slow evaporation, at room temperature, of a water solution of sarcosine and H_3PO_4 in a stoichiometric ratio. After some days, one obtains colorless stout prisms. Prism fragment: 0·27 × 0·32 × 0·32 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h00$ ($h = 2n$); $0k0$ ($k = 2n$); $00l$ ($l = 2n$). 21 reflexions ($11 < \theta < 15°$) for refining the unit-cell dimensions. ω scan. Scan width: 1·20°, scan speed variable, between 0·02 and 0·04° s^{-1}, total background measuring time between 30 and 15 s. 2552 reflexions measured ($2 < \theta < 30°$), $\pm h,k,l$; 1296 independent reflexions, $R_{int} = 0.02$; $h_{max} = 18$, $k_{max} = 13$, $l_{max} = 8$. Two intensity ($1\bar{2}3$ and 060) and one orientation (403) reference reflexions: no significant variation. Lorentz and polarization corrections, no absorption corrections. Structure determination strategy identical to that used for the first compound. Final refinement with 1150 independent reflexions ($I > 4\sigma_I$), final R 0·023 ($wR = 0.026$), $S = 0.365$, max. $\Delta/\sigma = 0.21$. Max. peak height in the final difference-Fourier synthesis 0·21 e Å^{-3}. No extinction correction. Computer used: Microvax-II.

* Lists of structure factors, anisotropic thermal parameters and bond lengths involving H atoms for all 3 compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51161 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates for β-alanine*.H_3PO_4

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i\mathbf{a}_j\beta_{ij}$.

	x	y	z	B_{eq}(Å^2)
P	0·08103 (4)	0·7469 (1)	0·42418 (8)	1·865 (8)
O(1)	0·1051 (1)	0·6176 (4)	0·5908 (3)	3·01 (4)
O(2)	0·1273 (1)	0·6453 (3)	0·2853 (3)	2·77 (4)
O(3)	0·1129 (1)	0·9968 (3)	0·4580 (3)	2·86 (4)
O(4)	−0·0125 (1)	0·7482 (4)	0·3935 (2)	2·31 (3)
O(5)	0·2961 (1)	0·7991 (4)	0·4514 (3)	3·90 (5)
O(6)	0·0688 (1)	0·3137 (4)	0·0837 (3)	3·97 (5)
N	0·2453 (1)	0·8067 (4)	0·0723 (3)	2·17 (4)
C(1)	0·3035 (2)	0·3576 (5)	0·5860 (4)	2·69 (5)
C(2)	0·1182 (2)	−0·0088 (5)	0·9455 (4)	2·79 (5)
C(3)	0·3646 (2)	0·7167 (5)	0·4711 (3)	2·52 (5)
H(1)	0·417 (2)	0·020 (6)	0·900 (4)	1·4 (7)*
H(2)	0·087 (2)	0·060 (7)	0·499 (4)	2·5 (9)*
H(3)	0·419 (2)	0·919 (6)	0·364 (4)	1·6 (7)*
H(1N)	0·289 (2)	0·267 (7)	0·354 (4)	1·7 (7)*
H(2N)	0·221 (2)	0·191 (6)	0·440 (4)	1·1 (7)*
H(3N)	0·273 (2)	0·922 (6)	0·111 (4)	1·4 (7)*
H(1C1)	0·316 (2)	0·215 (6)	0·632 (4)	1·3 (7)*
H(2C1)	0·269 (2)	0·443 (6)	0·654 (4)	1·8 (8)*
H(1C2)	0·090 (2)	0·024 (6)	0·845 (4)	1·4 (7)*
H(2C2)	0·083 (2)	0·910 (6)	0·009 (4)	1·5 (7)*

* Refined isotropically.

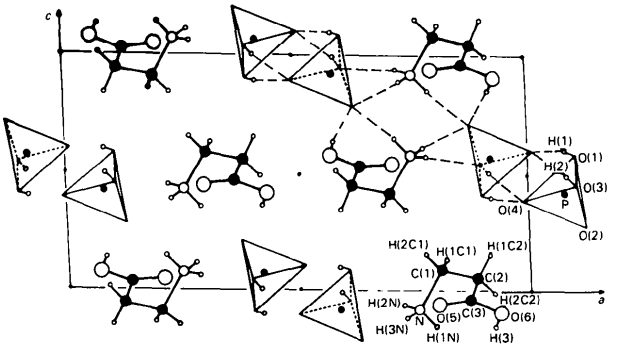

Fig. 1. Projection along the b axis of the atomic arrangement of β-alanine.H_3PO_4.

Discussion.

I. *β-Alanine*.H_3PO_4

Table 1 reports the final atomic coordinates for this salt, while Fig. 1 gives a projection of its atomic arrangement along the b axis.

The structure can be described as chains of $H_2PO_4^-$ groups parallel to the b axis surrounded by six

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in β-alanine.*H_3PO_4

The PO_4 tetrahedron

P	O(1)	O(2)	O(3)	O(4)
O(1)	1·563 (3)	2·501 (4)	2·460 (4)	2·514 (3)
O(2)	109·6 (2)	1·498 (2)	2·492 (4)	2·532 (3)
O(3)	103·8 (2)	109·0 (1)	1·563 (3)	2·516 (3)
O(4)	109·7 (1)	114·5 (1)	109·8 (1)	1·512 (2)

The β-alanine group

N–C(1)	1·484 (5)	N–C(1)–C(2)	111·4 (3)
C(1)–C(2)	1·516 (5)	C(1)–C(2)–C(3)	113·1 (3)
C(2)–C(3)	1·493 (5)	C(2)–C(3)–O(5)	123·7 (3)
O(5)–C(3)	1·205 (4)	C(2)–C(3)–O(6)	113·3 (3)
O(6)–C(3)	1·312 (4)	O(5)–C(3)–O(6)	123·3 (3)

Hydrogen bonds

	O(N)–H	H···O	O(N)···O	O(N)–H···O
O(1)–H(1)···O(4)	0·67 (5)	1·94 (5)	2·610 (3)	174 (5)
O(3)–H(2)···O(4)	0·66 (5)	1·89 (5)	2·543 (3)	177 (6)
O(6)–H(3)···O(2)	0·76 (5)	1·91 (5)	2·657 (4)	169 (5)
N–H(1N)···O(2)	0·86 (4)	1·94 (5)	2·792 (4)	171 (4)
N–H(2N)···O(3)	0·88 (4)	2·08 (4)	2·933 (4)	162 (4)
N–H(3N)···O(2)	0·86 (5)	2·19 (5)	3·024 (4)	164 (4)

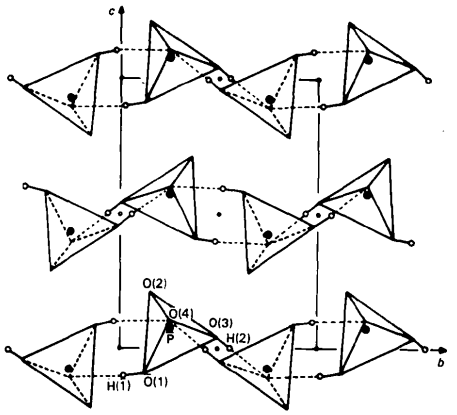

Fig. 2. Projection along the *a* axis of the chain of the $H_2PO_4^-$ groups.

$[NH_3–(CH_2)_2–COOH]^+$ groups. The distances P–P are rather short (4·117 and 4·168 Å) and the H_2PO_4 groups are linked by double hydrogen bonds to form a chain, illustrated by Fig. 2. Table 2 reports the main interatomic distances and bond angles in these groups. As expected, the two P–OH distances are significantly longer [P–O(1) 1·563 and P–O(3) 1·563 Å] than the other P–O distances (1·498 and 1·512 Å).

The carboxylic group of the β-alanine is not ionized and its H atom is involved in a hydrogen bond with an O atom of the $H_2PO_4^-$ group (Table 2). The amino group is protonated by a phosphate H atom.

The three H atoms of the NH_3 group are connected to O atoms of two different phosphoric anions and each of these entities is connected to two different organic groups. There is no direct hydrogen bonding between the organic groups.

Table 3. *Final atomic coordinates for* 2DL-*alanine.*H_3PO_4

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i\mathbf{a}_j\beta_{ij}$

	x	*y*	*z*	B_{eq}(Å²)
P	0	0·41984 (5)	¾	2·001 (9)
O(1)	0·9074 (1)	0·3417 (1)	0·6202 (2)	4·38 (3)
O(2)	0·4624 (1)	0·9949 (2)	0·3447 (2)	5·90 (3)
O(3)	0·69201 (8)	0·3803 (1)	0·6997 (1)	2·71 (2)
O(4)	0·63850 (9)	0·3881 (1)	0·4234 (1)	3·06 (2)
N	0·7675 (1)	0·6178 (1)	0·7565 (1)	2·37 (2)
C(1)	0·6761 (1)	0·4367 (1)	0·5708 (2)	2·01 (2)
C(2)	0·5987 (2)	0·6589 (2)	0·5017 (2)	4·06 (5)
C(3)	0·6993 (1)	0·5806 (1)	0·5782 (1)	2·11 (2)
H(1)	0·893 (2)	0·756 (3)	0·097 (3)	5·5 (8)*
H(2)	0·494 (4)	0·002 (5)	0·442 (5)	3 (1)*
H(1N)	0·716 (1)	0·796 (2)	0·228 (2)	1·9 (4)*
H(2N)	0·728 (2)	0·602 (2)	0·814 (3)	3·0 (5)*
H(3N)	0·668 (2)	0·923 (2)	0·195 (3)	2·5 (5)*
H(C3)	0·736 (2)	0·595 (2)	0·516 (2)	2·1 (5)*
H(1C2)	0·443 (2)	0·632 (2)	0·939 (3)	2·8 (5)*
H(2C2)	0·943 (2)	0·874 (3)	0·591 (4)	5·4 (8)*
H(3C2)	0·109 (2)	0·755 (2)	0·004 (3)	3·2 (6)*

* Refined isotropically.

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *in* 2DL-*alanine.*H_3PO_4

The DL-alanine group

C(1)–O(3)	1·223 (2)	O(3)–C(1)–O(4)	126·7 (1)
C(1)–O(4)	1·275 (2)		
O(3)–O(4)	2·234 (2)		
C(1)–C(3)	1·521 (2)	C(1)–C(3)–N	108·6 (1)
C(3)–N	1·477 (2)	C(1)–C(3)–C(2)	111·4 (1)
C(3)–C(2)	1·507 (2)	C(2)–C(3)–N	110·1 (1)

The PO_4 tetrahedron

P	O(1)	O(1)	O(2)	O(2)
O(1)	1·515 (1)	115·46 (8)	107·31 (8)	109·19 (8)
O(1)	2·563 (2)	1·515 (1)	109·19 (8)	107·31 (8)
O(2)	2·432 (2)	2·461 (2)	1·504 (2)	108·20 (10)
O(2)	2·461 (2)	2·432 (2)	2·437 (3)	1·504 (2)

Hydrogen bonds

	O(N)–H	H–O	O(N)···O	O(N)–H···O
O(1)–H(1)···O(4)	1·03 (3)	1·42 (3)	2·449 (2)	170 (4)
O(2)–H(2)···O(2)	0·98 (4)	1·72 (4)	2·479 (2)	168 (6)
N–H(1N)···O(3)	0·92 (2)	1·85 (2)	2·767 (2)	177 (2)
N–H(2N)···O(4)	0·95 (3)	1·98 (3)	2·916 (2)	166 (2)
N–H(3N)···O(2)	0·91 (2)	1·89 (2)	2·781 (2)	163 (2)

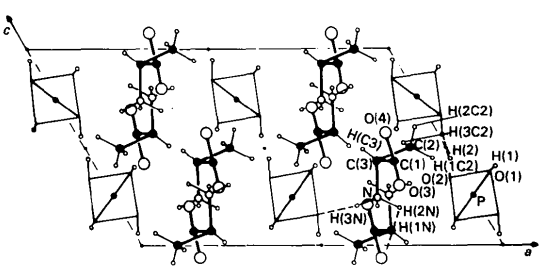

Fig. 3. Projection along the *b* axis of the atomic arrangement of 2DL-alanine.H_3PO_4.

II. 2DL-*Alanine*.H_3PO_4

Fig. 3 gives a projection of the structure along the *b* axis.

Table 3 reports the final atomic coordinates and Table 4 the main interatomic distances and bond angles.

For this compound, the phosphoric group is a triacidic one: H_3PO_4. The P atom is on a binary axis and one H-atom site [H(2)] is statistical. As expected, the two different P–OH distances (1·515 and 1·504 Å) are approximately of the same order. These phosphoric groups are linked by hydrogen bonds by means of the H(2) atom to form chains parallel to the *c* axis.

Besides this hydrogen bond, each phosphate group is also involved in two other donor hydrogen bonds with O(4) atoms of two different organic groups.

The amino group is protonated by the carboxylic H atom, the neutrality of the molecule being thus preserved. The ammonium group is connected to one O atom of a phosphate group and with the O(3) and O(4) atoms of two different alanine groups.

III. *Sarcosine*.H_3PO_4

Table 5 reports the final atomic coordinates for this compound and Table 6 the main interatomic distances and angles. Fig. 4 is a projection of its atomic arrangement along the *c* axis.

In this structure one can observe a layer arrangement: planes of $H_2PO_4^-$ groups linked by hydrogen bonds [O(1)–H(1)···O(2)] to form chains alternating with planes of organic groups. The phosphate group is involved in another donor hydrogen bond with the O(6) atom of the carboxylic function.

As usual, the P–OH distances [P–O(1) 1·558 and P–O(4) 1·569 Å] are longer than the other P–O distances (1·503 and 1·488 Å).

The amino group is protonated by an H atom of the phosphoric group. The two H atoms of the NH_2 group are connected to O(3) of two different H_2PO_4 anions.

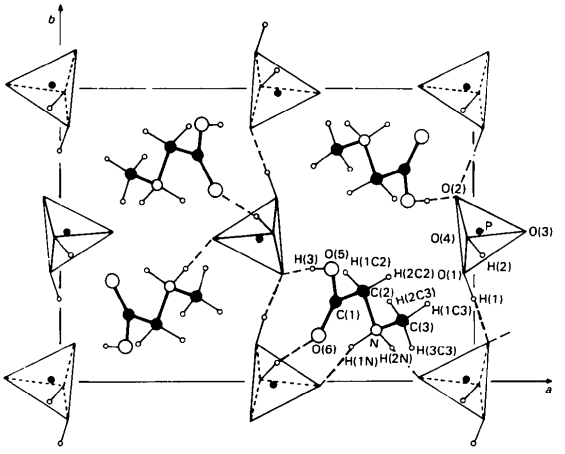

Fig. 4. Projection along the *c* axis of the atomic arrangement of sarcosine.H_3PO_4.

Table 5. *Final atomic coordinates for sarcosine*.H_3PO_4

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

	x	*y*	*z*	B_{eq}(Å²)
P	0·98216 (3)	0·00581 (5)	0·22676 (7)	1·906 (6)
O(1)	0·0249 (1)	−0·1282 (2)	0·3470 (3)	3·54 (3)
O(2)	0·0391 (1)	0·1337 (1)	0·3128 (3)	2·90 (3)
O(3)	0·86954 (9)	0·0123 (2)	0·2390 (2)	2·46 (2)
O(4)	0·0155 (1)	−0·0078 (2)	−0·0135 (2)	3·54 (3)
O(5)	0·8416 (1)	0·6179 (2)	0·8689 (3)	3·05 (3)
O(6)	0·1246 (1)	0·3422 (2)	0·7388 (3)	3·61 (3)
C(1)	0·3342 (1)	0·7734 (2)	0·2603 (3)	2·11 (3)
C(2)	0·7331 (2)	0·3062 (2)	0·0534 (3)	2·26 (3)
C(3)	0·6698 (2)	0·7922 (2)	0·2516 (4)	2·83 (4)
N	0·7648 (1)	0·1740 (2)	0·9386 (3)	1·97 (3)
H(1)	−0·001 (3)	0·283 (3)	0·212 (5)	4·3 (8)*
H(2)	0·026 (2)	0·432 (3)	0·579 (5)	3·5 (8)*
H(3)	0·112 (2)	0·120 (3)	0·529 (5)	4·3 (8)*
H(1C2)	0·810 (2)	0·626 (3)	0·458 (5)	2·7 (7)*
H(2C2)	0·297 (2)	0·143 (3)	0·886 (4)	2·0 (6)*
H(1C3)	0·887 (2)	0·264 (3)	0·784 (5)	2·6 (6)*
H(2C3)	0·798 (2)	0·271 (3)	0·655 (5)	1·7 (6)*
H(3C3)	0·650 (2)	0·886 (3)	0·177 (5)	2·4 (6)*
H(1N)	0·206 (2)	0·381 (3)	0·110 (5)	2·6 (7)*
H(2N)	0·697 (2)	0·885 (3)	0·530 (4)	1·3 (5)*

* Refined isotropically.

Table 6. *Main interatomic distances* (Å) *and bond angles* (°) *in sarcosine*.H_3PO_4

The PO_4 tetrahedron

P	O(1)	O(2)	O(3)	O(4)
O(1)	1·558 (2)	2·446 (2)	2·519 (2)	2·516 (2)
O(2)	106·08 (8)	1·503 (1)	2·545 (2)	2·444 (2)
O(3)	111·61 (8)	116·62 (8)	1·488 (1)	2·495 (2)
O(4)	107·18 (9)	105·41 (9)	109·40 (8)	1·569 (1)

P–O(1)–H(1)	113 (2)	P–O(4)–H(2)	109 (2)

The sarcosine group

C(1)–O(5)	1·295 (2)	O(5)–C(1)–O(6)	125·9 (2)
C(1)–O(6)	1·209 (2)	O(5)–C(1)–C(2)	111·8 (2)
C(1)–C(2)	1·495 (3)	O(6)–C(1)–C(2)	122·3 (2)
C(2)–N	1·481 (2)	C(1)–C(2)–N	112·0 (2)
C(3)–N	1·485 (3)	C(2)–N–C(3)	111·7 (2)

Hydrogen bonds

	O(N)–H	H···O	O(N)···O	O(N)–H···O
O(1)–H(1)···O(2)	0·95 (3)	1·61 (3)	2·566 (2)	180 (5)
O(4)–H(2)···O(6)	0·88 (3)	1·84 (3)	2·707 (2)	168 (3)
O(5)–H(3)···O(2)	0·88 (3)	1·66 (3)	2·539 (2)	171 (3)
N–H(1N)···O(3)	0·97 (3)	1·84 (3)	2·770 (2)	160 (3)
N–H(2N)···O(3)	0·94 (3)	1·84 (3)	2·770 (2)	172 (2)

The carboxylic group is not deprotonated and its H atom is involved in a hydrogen bond with the O(2) atom of the $H_2PO_4^-$ group. It should be noticed that there is no bonding between the organic groups.

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Structures of Pivaloyl-L-prolyl-*N*-methyl-D-phenylalaninamide and Pivaloyl-L-prolyl-*N*-methyl-D-valinamide*

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Abstract. $C_{20}H_{29}N_3O_3$ (Piv-L-Pro-D-Phe-NHMe, 1; Piv, pivaloyl and NHMe, methylamino): $M_r = 359{\cdot}4$, monoclinic, $P2_1$, $a = 11{\cdot}615$ (3), $b = 14{\cdot}701$ (3), $c = 5{\cdot}912$ (3) Å, $\beta = 98{\cdot}04$ (10)°, $V = 999{\cdot}6$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}194$, $D_m = 1{\cdot}19$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}756$ cm^{-1}, $F(000) = 388$, $T = 297$ K. $C_{16}H_{29}N_3O_3$ (Piv-L-Pro-D-Val-NHMe, 2): $M_r = 311{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 17{\cdot}868$ (3), $b = 16{\cdot}062$ (3), $c = 6{\cdot}183$ (3) Å, $V = 1774{\cdot}5$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}166$, $D_m = 1{\cdot}16$ g cm^{-3}, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}756$ cm^{-1}, $F(000) = 680$, $T = 297$ K. Final R values: 0·047 for 1613 observed [$I \geq 3\sigma(I)$] reflections of (1) and 0·079 for 1102 observed [$I \geq 3\sigma(I)$] reflections of (2). The backbone conformation and crystal packing motif of the two compounds are similar and typical of Piv-L-Pro-D-Xxx-NH*R* terminally-blocked heterochiral dipeptides. In particular, the structure is folded at the L-Pro-D-Xxx sequence to form a type-II β-bend stabilized by a 4→1 intramolecular N—H···O=C H-bond between the methylamide N—H and pivaloyl C=O groups.

Introduction. Among the variety of chain reversals found in crystallized peptides and proteins two of them, denoted type-I and type-II β-bends, are characterized by a 4→1 intramolecular N—H···O=C H-bond and an all-*trans* peptide bond conformation. These two types of β-bends differ by the values of the φ, ψ torsion angles associated with the corner residues and are typically adopted by homochiral L–L and heterochiral L–D sequences, respectively (Venkatachalam, 1968; Toniolo, 1980; Rose, Gierasch & Smith, 1985).

The tendency of Pro-Xxx sequences to facilitate either type-I or type-II β-bend formation has stimulated several studies by spectroscopic and X-ray diffraction methods (Aubry, Cung & Marraud, 1985). As part of our continuing investigation of the various types of intramolecularly H-bonded conformations formed by Pro-containing short peptides (Venkataram Prasad, Balaram & Balaram, 1982; Benedetti, Bavoso, Di Blasio, Pavone, Pedone, Toniolo & Bonora, 1983) we have determined the molecular and crystal structures of Piv-L-Pro-D-Phe-NHMe (1) and Piv-L-Pro-D-Val-NHMe (2).

Experimental. Colourless crystals of Piv-L-Pro-D-Phe-NHMe (1) (Aubry *et al.*, 1985) were obtained from an ethyl acetate/petroleum ether solution by slow evaporation. X-ray diffraction data were collected on a Philips PW 1100 four-circle diffractometer from a crystal of approximate dimensions 0·6 × 0·4 × 0·4 mm. Accurate unit-cell parameters and crystal orientation matrices (together with their e.s.d.'s) were obtained from least-squares refinement of the 2θ, ω, χ and φ values of 25 carefully centred reflections with $7 < \theta < 14°$. The h, k, l ranges measured were −13 to 13, 0 to 17, and 0 to 7, respectively. The $\theta/2\theta$ scan mode (scan width 1·5°, scan speed 0·03° s^{-1}, total background time 20 s) and Mo $K\alpha$ radiation monochromatized by a graphite crystal ($\lambda = 0{\cdot}71069$ Å) were used. During data collection three standard reflections (222, $\bar{3}31$ and 132) were measured every 180 min to check the stability of

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