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Structure of 4-Amino-4-phosphonobutyric Acid

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Abstract. $C_4H_{10}NO_5P$, $M_r = 183{\cdot}1$, monoclinic, $P2_1/c$, $a = 5{\cdot}470$ (3), $b = 9{\cdot}677$ (4), $c = 14{\cdot}466$ (3) Å, $\beta = 100{\cdot}20$ (3)°, $V = 753{\cdot}6$ Å^3, $Z = 4$, $D_m = 1{\cdot}61$ (1), $D_x = 1{\cdot}614$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}35$ mm^{-1}, $F(000) = 384$, $T = 290$ K, $R = 0{\cdot}038$ for 1223 observed reflexions. The molecule exists as a zwitterion; the amino group is protonated and the carboxyl group is un-ionized, the phosphonic acid group being ionized. The molecule is in an extended conformation, with the N–C–C–C and C–C–C–C torsion angles 173·6 (4) and 178·3 (4)°, respectively. There is extensive intermolecular hydrogen bonding, but no intramolecular hydrogen bonding.

Introduction. In a view of the biological activity of the aminophosphonates we have studied the synthesis of the analogues of glutamic acid. It is well known that substituting the γ-carboxylic acid group of glutamic acid by the phosphonic or phosphinic acid function is an effective method of producing mimetics. These possess antibiotic properties (Kondo, Shomura, Ogawa, Tsuruoka, Watanabe, Totzukawa, Suzuki, Moriyama, Yoshida, Inouye & Niida, 1973) and antiviral (Fukuyasu, Oya, Kawakami, Kikuchi, Shomura, Tsuruoka, Watanabe, Kazuho, Inouye & Sekizawa, 1978), neuroactive (De Tinguy-Moreaud, Bioulac & Neuzil, 1981) and herbicidal activities (Rupp, Finke, Beringer & Lagenlueddeke, 1977). Except for a single report (Lejczak, Starzemska & Mastalerz, 1981) that the α-aminophosphonic acid structurally related to glutamate is a weak inhibitor of glutamine synthetase, nothing has been reported as yet about the biological activity of the α-phosphono analogues of glutamic acid.

The present structural investigation was undertaken as part of our study on the conformation and hydrogen bonding of this new aminophosphonic acid.

Experimental. Synthesis described by Kowalik, Kupczyk-Subotkowska & Mastalerz (1981). Clear, colourless crystals from water at room temperature, dimensions 0·28 × 0·47 × 0·45 mm; D_m by flotation in bromoform/benzene; monoclinic $P2_1/c$ from Weissenberg photographs; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $15 \le 2\theta(\text{Mo}) \le 24°$ measured on diffractometer; 1299 independent reflexions; $2\theta_{max} = 50{\cdot}0°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1}, depending on intensity; two standards (237, 24$\bar{6}$) measured every 50 reflexions, variation in intensities ±3·5%; data corrected for Lorentz and polarization, not for absorption; 1223 with $I > 4{\cdot}0\sigma(I)$ used for structure determination; index range h 0 to 6, k 0 to 10, l ±15; calculations performed with Syntex (1976) *XTL/XTLE* system; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); direct methods, Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$; difference synthesis revealed H atoms; non-H atoms refined with anisotropic and H atoms with isotropic temperature factors; max. Δ/σ in final LS cycle 0·01; max. electron density in final difference map 0·22 e Å^{-3}, max. negative electron

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density -0.20 e Å^{-3}; $R = 0.038$, $wR = 0.048$, $S = 6.4$. Final positional parameters are given in Table 1.*

Discussion. Interatomic distances and selected torsion angles are in Table 2 [the atom-labelling scheme in this paper is that recommended by the IUPAC–IUB Commission on Biochemical Nomenclature (1970)]. As can be seen in Fig. 1 the phosphonic acid group is ionized, the proton being transferred to the amino group. The γ-carboxyl group is in the un-ionized form.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond angles and details of the hydrogen bonding have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43291 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{1}{3}\sum_i B_{ii}$.

	x	y	z	B_{eq}
P	0·1864 (1)	0·5221 (1)	0·1419 (1)	1·39 (4)
O(1)	−0·0825 (3)	0·5562 (2)	0·1077 (1)	1·9 (1)
O(2)	0·2419 (4)	0·4400 (2)	0·2316 (1)	2·0 (1)
O(3)	0·3074 (4)	0·4476 (2)	0·0660 (1)	2·2 (1)
O$^{\varepsilon}$(4)	0·4724 (4)	0·8822 (2)	−0·0892 (2)	2·9 (2)
O$^{\varepsilon}$(5)	0·0735 (4)	0·9382 (3)	−0·1319 (2)	3·1 (2)
N	0·5973 (4)	0·6653 (2)	0·2289 (2)	1·7 (2)
C$^{\alpha}$(1)	0·3521 (5)	0·6878 (3)	0·1648 (2)	1·6 (2)
C$^{\beta}$(2)	0·4070 (6)	0·7633 (3)	0·0780 (2)	2·2 (2)
C$^{\gamma}$(3)	0·1844 (6)	0·8106 (3)	0·0083 (2)	2·7 (2)
C$^{\varepsilon}$(4)	0·2619 (6)	0·8791 (3)	−0·0747 (2)	2·1 (2)

Table 2. *Bond distances* (Å) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

P–O(1)	1·503 (2)	C$^{\alpha}$(1)–N	1·505 (3)
P–O(2)	1·505 (2)	C$^{\beta}$(2)–C$^{\gamma}$(3)	1·508 (4)
P–O(3)	1·555 (2)	C$^{\gamma}$(3)–C$^{\delta}$(4)	1·497 (4)
P–C(1)	1·843 (3)	C$^{\delta}$(4)–O$^{\varepsilon}$(4)	1·207 (4)
C$^{\alpha}$(1)–C$^{\beta}$(2)	1·527 (4)	C$^{\delta}$(4)–O$^{\varepsilon}$(5)	1·331 (4)

O(1)–P–C(1)–N	160·6 (2)	P–C$^{\alpha}$(1)–C$^{\beta}$(2)–C$^{\gamma}$(3)	63·6 (4)
O(1)–P–C(1)–C(2)	−78·2 (2)	N–C$^{\alpha}$(1)–C$^{\beta}$(2)–C$^{\gamma}$(3)	−173·6 (4)
O(2)–P–C(1)–N	36·2 (3)	C$^{\alpha}$(1)–C$^{\beta}$(2)–C$^{\gamma}$(3)–C$^{\delta}$(4)	−178·3 (4)
O(2)–P–C(1)–C(2)	157·4 (2)	C$^{\beta}$(2)–C$^{\gamma}$(3)–C$^{\delta}$(4)–O(4)	7·9 (5)
O(3)–P–C(1)–N	−79·2 (3)	C$^{\beta}$(2)–C$^{\gamma}$(3)–C$^{\delta}$(4)–O(5)	−171·8 (4)
O(3)–P–C(1)–C(2)	42·0 (3)		

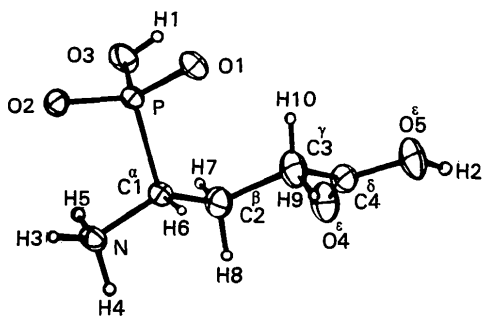

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme.

The γ-carboxyl group is planar. The C–O lengths corresponding to C=O and C–OH bonds are 1·207 (4) and 1·331 (4) Å. They are similar to those found in the α and β forms of L-glutamic acid (L-Glu) (Lehmann & Nunes, 1980; Lehmann, Koetzle & Hamilton, 1972) and DL-glutamic acid (DL-Glu) (Ciunik & Głowiak, 1983). The two O–C–C angles differ from each other, being 124·4 (3) and 113·0 (3)° (Marsh & Donohue, 1967). The angle O–C–O of 122·6 (3)° compares well with those found in amino acids.

The maximum deviation from the least-squares plane through the carboxyl group, O$^{\varepsilon}$(4), O$^{\varepsilon}$(5), C$^{\delta}$(4) and C$^{\gamma}$(3), is 0·002 (3) Å. The distance of N from this plane is −0·551 (2) Å.

The bond lengths and angles in the aminomethylphosphonic acid part of the molecule are in good agreement with those found in aminomethylphosphonic acid, β-AMP (Darriet, Darriet, Cassaigne & Neuzil, 1975) and in 2-amino-3-phosphonopropionic acid, β-PAsp (Sawka-Dobrowolska, Głowiak, Siatecki & Soroka, 1985, and references cited therein).

In the present structure, two of the three P–O bonds have rather short lengths of 1·503 (2) and 1·505 (2) Å while the third is 1·555 (2) Å. As in the case of β-AMP and β-PAsp the two shorter P–O bonds in the present crystal may have partial double-bond character, while the longer length corresponds to the P–OH bond.

The P–C(1) distance, 1·843 (3) Å, is slightly longer than the P–CH_2 distances in β-AMP [1·817 (3) Å] and β-PAsp [1·809 (4) Å], and similar to those found in α-(isopropylamino)salicylphosphonic acid [1·858 (3) Å] (Sawka-Dobrowolska, 1985) and 3-amino-3-phosphonopropionic acid, α-PAsp [1·846 (4) Å] (Kowalik, Sawka-Dobrowolska, Głowiak & Siatecki, 1986).

The P–C$^{\alpha}$(1)–C$^{\beta}$(2) bond angle of 115·5 (2)° is considerably greater than the tetrahedral value and is similar to that found in β-PAsp [116·4 (3)°]. The C$^{\alpha}$(1)–C$^{\beta}$(2)–C$^{\gamma}$(3) and C$^{\beta}$(2)–C$^{\gamma}$(3)–C$^{\delta}$(4) angles are 116·2 (3) and 111·1 (3)°, respectively. They are similar to those found in DL-Glu and L-Glu hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972) (C$^{\delta}$ *trans* to C$^{\alpha}$), whereas the corresponding angles for the β form of L-Glu are 117·8 (1) and 116·1 (1)° (C$^{\delta}$ *gauche* to C$^{\alpha}$).

The conformation of the molecule is described by the torsion angles χ^1, χ^2, χ^{31} and χ^{32} (see Table 2). The conformation about the C$^{\alpha}$–C$^{\beta}$ bond is *gauche–trans* [63·6 (4), −173·6 (4)°] and that about C$^{\beta}$–C$^{\gamma}$ is *trans* [−178·3 (4)°]. The torsion angles χ^{31} and χ^{32} about C$^{\gamma}$–C$^{\delta}$ of −171·8 (4) and 7·9 (5)° are near 180 and 0° as usually observed.

The conformation of the title compound is different from those of DL-Glu and the α and β forms of L-Glu.*

* A table comparing torsion angles for these compounds has been deposited.

There is extensive hydrogen bonding in the structure, with all potential donor and acceptor atoms participating.

The amino group interacts with three neighbouring molecules, O(4) of the carboxyl group and O(1) and O(2) of phosphonic acid groups. H(3) is donated to O(4) of a *c*-glide-related molecule, with N···O(4) and H(3)···O(4) distances and N—H(3)···O(4) angle of 2·869 (3), 1·99 (4) Å and 150 (3)°. H(4) is involved in a hydrogen bond with O(2) of a screw-related molecule. The N···O(2), H(4)···O(2) and N—H(4)···O(2) parameters in this case are 2·826 (3), 1·89 (4) Å and 172 (4)°. The third amino H atom, H(5), is donated to O(1) of the molecule one cell translation along **a**. The N—H(5)···O(1) [2·889 (3), 1·88 (4) Å and 163 (4)°] hydrogen bonds link molecules in a chain in the **a** direction.

The hydrogen-bonding scheme is completed with the formation of short hydrogen bonds from O(3) (phosphonic acid group) and O(5) (carboxyl group) to O(1) (related by a centre of symmetry) and O(2) (*c*-glide-related) of 2·595 (3) and 2·605 (3) Å. The H(1)···O(1) and H(2)···O(2) distances and O—H···O angles are 1·84 (4), 1·70 (4) Å and 169 (4), 171 (4)°, respectively.

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Structure of 2,5,5-Trimethyl-3-oxo-7-*t*-hydroxy-1-cycloheptanephosphonoacetic Acid *γ*-Lactone Diethyl Ester*

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Abstract. $C_{16}H_{27}O_6P$, $M_r = 346{\cdot}4$, triclinic, $P\bar{1}$, $a = 9{\cdot}812$ (5), $b = 9{\cdot}115$ (5), $c = 11{\cdot}857$ (4) Å, $\alpha = 116{\cdot}24$ (3), $\beta = 96{\cdot}45$ (4), $\gamma = 102{\cdot}57$ (4)°, $V = 901{\cdot}6$ (9) Å^3, $Z = 2$, $D_m = 1{\cdot}28$ (1), $D_x = 1{\cdot}276$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}18$ mm^{-1}, $F(000) = 372$, $T = 293$ K, $R = 0{\cdot}065$ for 1657 reflexions. The cycloheptane ring has a deformed boat conformation and is *cis*-fused with the *γ*-lactone at C(1)—C(7). The *γ*-lactone ring adopts an envelope

* Diethyl (5,5,8-trimethyl-2,7-dioxoperhydro-3-oxazulen-1-yl)-phosphonate.

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