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Acta Cryst. (1987). C**43**, 287–289

Structure of 5-Oxo-2-pyrrolidinylphosphonic acid

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(*Received* 22 *May* 1986; *accepted* 22 *July* 1986)

Abstract. $C_4H_8NO_4P$, $M_r = 165{\cdot}1$, orthorhombic, $Pbc2_1$ [non-standard setting of $Pca2_1$ (No. 29)], $a = 6{\cdot}990$ (3), $b = 7{\cdot}241$ (3), $c = 13{\cdot}075$ (5) Å, $V = 661{\cdot}8$ (6) Å^3, $Z = 4$, $D_m = 1{\cdot}66$ (1), $D_x = 1{\cdot}657$ Mg m^{-3}, $T = 291$ K, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}38$ mm^{-1}, $F(000) = 344$, $R = 0{\cdot}034$ for 748 reflexions. The pyrrolidone ring adopts a conformation intermediate between envelope and half-chair [$\Delta C_2 = 2{\cdot}2$ (8)°, $\Delta C_s = 2{\cdot}4$ (8)°; $Q = 0{\cdot}105$ (5) Å, $\varphi = 98$ (2)°]. The two O atoms of the un-ionized phosphonic acid group form strong intermolecular hydrogen bonds of 2·544 (3) Å (P—OH···O=P) and 2·469 (4) Å (P—OH···O=C).

Introduction. It is known that glutamic acid, or its γ-derivatives, cyclize to pyroglutamic acid, but the α-phosphonic acid analogue of glutamic acid, or its *C*-ester, are unable to cyclize. This paper presents the results of a study of the structure of an analogue of pyroglutamic acid.

Experimental. *C*-Methyl 4-amino-*P*,*P*-diethyl-4-phosphonobutyrate, obtained by the oxime method as described by Kowalik, Kupczyk-Subotkowska & Mastalerz (1981) was cyclized by heating at 423 K for 30 min and hydrolysed with 40% solution of hydrobromide in acetic acid at room temperature for 48 h (Oleksyszyn, Gruszecka, Kafarski & Mastalerz, 1982). The title compound was recrystallized from water, m.p. 511–514 K.

Clear, colourless crystals at room temperature, dimensions 0·25 × 0·30 × 0·33 mm, density by flotation in carbon tetrachloride/ethylene bromide, orthorhombic *Pbcm* or $Pbc2_1$ from Weissenberg photographs; $Pbc2_1$ confirmed by refinement; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, graphite monochromator; cell parameters by least squares from setting angles of 15 reflexions with $24 \le 2\theta(\text{Mo}) \le 32°$ measured on diffractometer, 774 independent reflexions; $2\theta_{max} = 55{\cdot}0°$; variable θ–2θ scans, scan rate 2·0–29·3° min^{-1} depending on intensity; two standards (235, 433) every 50 reflexions, variation in intensities ±3·0%; data corrected for Lorentz–polarization, not for absorption; 748 with $I > 3{\cdot}0\sigma(I)$ used for structure determination; index range h 0 to 9, k 0 to 8, l 0 to 16; calculations

0108-2701/87/020287-03$01.50

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performed with Syntex (1976) 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. positive electron density in final difference map 0·18, max. negative −0·17 e Å^{-3}; $R = 0{\cdot}034$, $wR = 0{\cdot}041$, $S = 3{\cdot}97$. Final positional parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, bond angles, details of hydrogen-bond geometries and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43276 (10 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 with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
P	0·3241 (1)	0·5132 (1)	0·0278	1·78 (4)
O(1)	0·5445 (3)	0·5069 (3)	0·0247 (4)	2·6 (2)
O(2)	0·2390 (4)	0·3993 (4)	−0·0607 (2)	2·8 (2)
O(3)	0·2605 (3)	0·7103 (3)	0·0295 (3)	2·7 (2)
O(4)	−0·1882 (4)	0·4729 (4)	0·2663 (2)	2·8 (2)
N	0·0422 (4)	0·3945 (5)	0·1529 (3)	2·3 (3)
C(1)	0·2508 (5)	0·3882 (6)	0·1402 (3)	2·3 (3)
C(2)	0·3240 (6)	0·4781 (8)	0·2404 (4)	4·0 (4)
C(3)	0·1526 (5)	0·4989 (5)	0·3101 (3)	2·2 (2)
C(4)	−0·0160 (5)	0 4564 (5)	0·2421 (3)	2·1 (2)

Table 2. *Bond distances* (Å) *and selected torsion angles* (°)

P–O(1)	1·542 (2)	C(1)–N	1·468 (4)
P–O(2)	1·541 (3)	C(2)–C(3)	1·513 (6)
P–O(3)	1·495 (2)	C(3)–C(4)	1·508 (5)
P–C(1)	1·800 (4)	C(4)–O(4)	1·250 (4)
C(1)–C(2)	1·550 (6)	C(4)–N	1·314 (5)

P–C(1)–N–C(4)	−125·4 (4)	H(O2)–O(2)–P–C(1)	160 (3)
P–C(1)–C(2)–C(3)	129·0 (4)	C(1)–C(2)–C(3)–C(4)	−10·6 (4)
O(1)–P–C(1)–N	177·1 (3)	C(2)–C(3)–C(4)–N	8·1 (4)
O(2)–P–C(1)–N	−66·2 (3)	C(3)–C(4)–N–C(1)	−2·0 (4)
O(3)–P–C(1)–N	57·4 (3)	C(4)–N–C(1)–C(2)	−4·8 (5)
H(O1)–O(1)–P–C(1)	50 (6)	N–C(1)–C(2)–C(3)	9·5 (4)

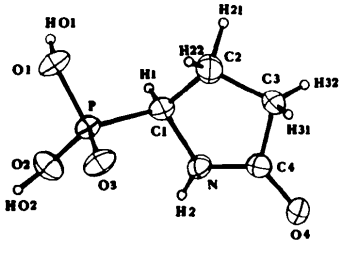

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme.

Discussion. The molecular structure and atom numbering are shown in Fig. 1. Bond distances are in Table 2. The phosphonic acid molecule is in the un-ionized form. Both O(1) and O(2) are protonated. The P–O(1) and P–O(2) bond lengths of 1·542 (2) and 1·541 (3) Å indicate single bonds and P–O(3) [1·495 Å] is a double bond. The P–C length of 1·800 (4) Å is essentially the same as the P–C bond length of 1·807 (4) Å in the biological compound 2-aminoethylphosphonic acid (*β*-ciliatine) (Okaya, 1966).

The O–P–O and O–P–C angles in the title compound range from 103·5 (2) to 114·0 (2)°. The smallest angle involves the protonated O(2) and C(1), while the largest angle involves the protonated O(2) and unsubstituted O(3).

The other bond lengths and angles are in good agreement with those found in other pyrrolidone derivatives (Dupont, Dideberg & Welter, 1975). The carbonyl C=O double bond has a 'normal' length of 1·205 Å and in this case our value is significantly greater [1·250 (4) Å]. The lengthening of the C=O bond may be attributed to hydrogen-bond formation (see below).

The torsion angles (Table 2) and asymmetry parameters of Duax, Weeks & Rohrer (1976), $\Delta C_s = 2{\cdot}4$ (8) and $\Delta C_2 = 2{\cdot}2$ (8)°, clearly show that in the pyrrolidone ring two pseudosymmetry elements occur, a mirror plane perpendicular to the N–C(4) bond and a twofold axis passing through N and the C(2)–C(3) bond. C(2) is 0·167 (6) Å out of the least-squares plane of C(3)–C(4)–N–C(1), on the same side as the phosphonic acid group [P deviates by 1·367 (1) Å], and C(2), C(3) are 0·126 (6) and −0·050 (4) Å out of the plane of C(4)–N–C(1).

The conformation of the ring is, therefore, intermediate between an envelope and a half-chair. The ring puckering parameters (Cremer & Pople, 1975) are $Q = 0{\cdot}105$ (5) Å and $\varphi = 98$ (2)°.

The molecules are held in the crystal by three hydrogen bonds. The protonated O(1) and O(2) form two strong hydrogen bonds to O(3) ($1-x$, $-\frac{1}{2}+y$, z) and to O(4) ($-x$, $1-y$, $-\frac{1}{2}+z$). The O···O and H···O distances are 2·544 (3), 2·469 (4), 1·74 (5), 1·63 (5) Å and O–H···O angles 163 (5) and 179 (5)°, respectively. The other hydrogen bond runs from the N atom to the phosphonic O(3) atom of the molecule at ($-x$, $-\frac{1}{2}+y$, z). The N···O(3), H···O distances and N–H···O angle are 2·976 (4), 2·21 (4) Å and 157 (4)°, respectively.

We acknowledge financial support from the Polish Academy of Sciences, and from a Government programme.

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Acta Cryst. (1987). C**43**, 289–291

Structure of 4-Amino-4-phosphonobutyric Acid

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(*Received* 9 *April* 1986; *accepted* 28 *July* 1986)

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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