| | | | |
|---|---|---|---|
| C(10)—C(5)—C(4) | 111.9 (2) | C(18)—C(13)—C(12) | 110.9 (1) |
| C(10)—C(5)—C(6) | 112.1 (2) | C(18)—C(13)—C(14) | 112.0 (1) |
| C(7)—C(6)—C(5) | 110.0 (2) | C(18)—C(13)—C(17) | 111.6 (2) |
| C(8)—C(7)—C(6) | 112.1 (2) | C(13)—C(14)—C(8) | 113.9 (1) |
| C(9)—C(8)—C(7) | 110.9 (2) | C(15)—C(14)—C(8) | 119.5 (2) |
| C(14)—C(8)—C(7) | 111.4 (1) | C(15)—C(14)—C(13) | 102.9 (1) |
| C(14)—C(8)—C(9) | 107.9 (1) | C(16)—C(15)—C(14) | 104.4 (2) |
| C(10)—C(9)—C(8) | 114.0 (2) | C(17)—C(16)—C(15) | 107.9 (2) |
| C(11)—C(9)—C(8) | 111.1 (1) | C(20)—C(17)—C(13) | 117.9 (2) |
| C(11)—C(9)—C(10) | 112.9 (1) | C(20)—C(17)—C(16) | 112.1 (2) |
| C(5)—C(10)—C(1) | 107.8 (2) | C(21)—C(20)—C(17) | 114.2 (2) |
| C(9)—C(10)—C(1) | 109.5 (2) | C(22)—C(20)—C(17) | 110.0 (2) |
| C(9)—C(10)—C(5) | 106.1 (1) | C(22)—C(20)—C(21) | 109.8 (2) |
| C(19)—C(10)—C(1) | 110.0 (2) | O(1)—C(12)—C(11) | 121.2 (2) |
| C(19)—C(10)—C(5) | 112.3 (2) | O(1)—C(12)—C(13) | 124.4 (2) |
| C(19)—C(10)—C(9) | 111.1 (2) | | |

| | |
|---|---|
| C(1)—C(2)—C(3)—C(4) | 53.3 (2) |
| C(2)—C(3)—C(4)—C(5) | −55.2 (2) |
| C(3)—C(4)—C(5)—C(10) | 57.3 (2) |
| C(4)—C(5)—C(10)—C(1) | −55.5 (3) |
| C(5)—C(10)—C(1)—C(2) | 55.5 (2) |
| C(10)—C(1)—C(2)—C(3) | −55.2 (1) |
| C(5)—C(6)—C(7)—C(8) | 55.0 (4) |
| C(6)—C(7)—C(8)—C(9) | −51.6 (8) |
| C(7)—C(8)—C(9)—C(10) | 54.0 (5) |
| C(8)—C(9)—C(10)—C(5) | −56.1 (2) |
| C(9)—C(10)—C(5)—C(6) | 58.6 (4) |
| C(10)—C(5)—C(6)—C(7) | −60.1 (4) |
| C(8)—C(14)—C(13)—C(12) | −62.4 (5) |
| C(14)—C(13)—C(12)—C(11) | 60.0 (4) |
| C(13)—C(12)—C(11)—C(9) | −58.4 (2) |
| C(12)—C(11)—C(9)—C(8) | 53.4 (3) |
| C(11)—C(9)—C(8)—C(14) | −55.0 (4) |
| C(9)—C(8)—C(14)—C(13) | 62.2 (3) |
| C(13)—C(14)—C(15)—C(16) | −35.2 (11) |
| C(14)—C(15)—C(16)—C(17) | 12.3 (34) |
| C(15)—C(16)—C(17)—C(13) | 15.7 (35) |
| C(16)—C(17)—C(13)—C(14) | −36.7 (8) |
| C(17)—C(13)—C(14)—C(15) | 45.4 (8) |

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Refinement was performed by *SHELX*76 (Sheldrick, 1976) using full-matrix least squares, with anisotropic thermal factors for all the non-H atoms, isotropic for H atoms. The H atoms were placed in calculated positions on the corresponding C atoms (C—H = 1.08 Å) and were not refined. Calculations were carried out on a VAX 3300. Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975). Molecular illustrations were drawn with *FRODO* (Jones, 1978).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71222 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1047]

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# 2-Amino-2-carboxyethylphosphinic Acid Monohydrate

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## Abstract

2-Amino-2-carboxyethylphosphinic acid exists as a zwitterion (2-ammonio-2-carboxyethylphosphinate) with anionic phosphinic, cationic alkylammonium and neutral carboxyl groups. The P—C—C—C and P—C—C—N conformations are *gauche* and *trans*, respectively. In contrast to 2-amino-2-carboxyethylphosphonic acid, intramolecular hydrogen bonding from ammonium to phosphinic moieties does not occur. Each phosphinic O atom accepts two intermolecular hydrogen bonds, as does the water molecule; every ammonium, carboxyl and water H atom participates.

## Comment

2-Amino-2-carboxyethylphosphinic acid [(1), 2-amino-3-(hydroxyphosphinyl)propionic acid, phosphinoalanine] has been isolated from fermentation broths of *Streptomyces hygroscopicus* (Seto, Imai, Tsuruoka, Ogawa, Satoh, Sasaki & Otake, 1983). As part of our continued interest in the biosynthesis and energetics of carbon-phosphorus bond formation (Seidel, Freeman, Seto & Knowles, 1988; Schwalbe & Freeman, 1990; Seidel, Freeman, Schwalbe & Knowles, 1990; Pollack, Freeman, Pompliano & Knowles, 1992) we have determined the crystal structure of (1), which was a key intermediate in the synthesis of the natural products phosphinopyruvate and carboxyphosphinopyruvate (Pollack *et al.*, 1992). The structurally related phosphonate analogues are antagonists of the NMDA receptor (Whitten, Harrison, Weintraub & McDonald, 1992).

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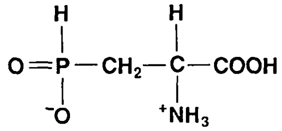
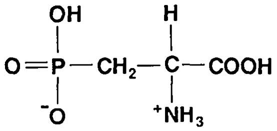


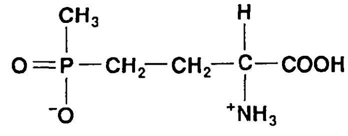
$\mathrm{O{=}P(H)(O^-){-}CH_2{-}CH(NH_3^+){-}COOH}$

(1)



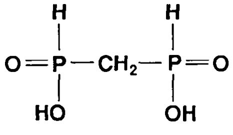
$\mathrm{O{=}P(OH)(O^-){-}CH_2{-}CH(NH_3^+){-}COOH}$

(2)



$\mathrm{O{=}P(CH_3)(O^-){-}CH_2{-}CH_2{-}CH(NH_3^+){-}COOH}$

(3)



$\mathrm{O{=}P(H)(HO){-}CH_2{-}P(H)(OH){=}O}$

(4)

In the zwitterionic molecule the phosphinic group is anionic, the amine group exists as the protonated cation and the carboxyl group is undissociated. The analogous phosphonate (2), phosphonoalanine, exhibits a similar pattern of ionization (Sawka-Dobrowolska, Głowiak, Siatecki & Soroka, 1985), as does the herbicide phosphinothricin, (3), in a racemic form (Paulus & Grabley, 1982*a*). However, against the trend, the pure L-enantiomer of (3) (Paulus & Grabley, 1982*b*) has neutral phosphinic acid and anionic carboxylate groups. Among the limited data on phosphorus oxo acids with a P—H bond is the structure of methylenebis(phosphinic acid), (4) (King, Roundhill & Fronczek, 1986). The length of the P—H bond is 1.33 (2) Å in (1) compared with 1.30 (2) and 1.28 (1) Å in the two halves of (4). The P—O distances in (1) of 1.501 (1) and 1.515 (1) Å are typical for this class of compound, and the O2—P1—O3 angle at 116.7 (1)° is the largest bond angle at phosphorus, as usual. Whatever the steric requirements of the P—*R* group [(1), (4) *R* = H, (2) *R* = OH and racemic (3) *R* = $CH_3$], the contact distance between the anionic O atoms attached to phosphorus stays within the narrow range of 2.566-2.571 Å.

The torsion angles $\varphi$, $\varphi'$, $\psi_1$, $\psi_2$ defined by Sawka-Dobrowolska *et al.* (1985) that determine both the carbon chain conformation and the relationship between amino and carboxyl groups take the following values in (1): $\varphi$ = P1—C4—C5—C6 = 78.8 (2)°, $\varphi'$ = P1—C4—C5—N9 = −159.1 (1)°, $\psi_1$ = O7—C6—C5—N9 = −8.5 (2)° and $\psi_2$ = O8—C6—C5—N9 = 170.8 (1)°. Corresponding values in (2) are 60.1 (4), −62.1 (4), 17.8 (5) and −162.8 (4)°. The antiperiplanar $\varphi'$ implies a straight P—C—C—N chain in (1) and does not allow the intramolecular N—H···O—P hydrogen bond found in (2). Only intermolecular hydrogen bonds form, in which the strongly negative phosphinic and water O atoms each accept two hydrogen bonds and all polar H atoms participate. A carboxylic acid dimer does not form and, unlike (2), neither carboxyl O atom accepts any hydrogen bonds.

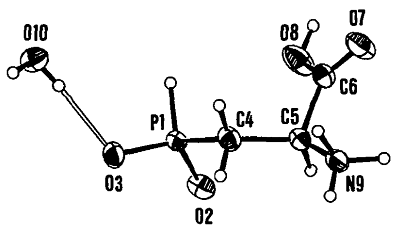


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of 2-amino-2-carboxyethylphosphinic acid monohydrate showing the labelling scheme for non-H atoms. Thermal ellipsoids are drawn at the 50% probability level.

## Experimental

*Crystal data*

$C_3H_8NO_4P.H_2O$
$M_r$ = 171.1
Monoclinic
$P2_1/n$
$a$ = 6.669 (2) Å
$b$ = 14.842 (1) Å
$c$ = 7.700 (1) Å
$\beta$ = 96.58 (1)°
$V$ = 757.1 (2) Å$^3$
$Z$ = 4

$D_x$ = 1.501 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å
Cell parameters from 25 reflections
$\theta$ = 10.2-14.2°
$\mu$ = 0.324 mm$^{-1}$
$T$ = 293 K
Tabular
0.60 × 0.25 × 0.12 mm
Colourless

*Data collection*

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
3625 measured reflections
1651 independent reflections
1532 observed reflections [$F > 3\sigma(F)$]
$R_{\rm int}$ = 0.012

$\theta_{\rm max}$ = 27.0°
$h = 0 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity variation: 3.5%

*Refinement*

Refinement on $F$
Final $R$ = 0.030
$wR$ = 0.047
$S$ = 0.44
1532 reflections
132 parameters
All H-atom parameters refined
Calculated weights
$w = 6.3776/[\sigma^2(F) + 0.000064F^2]$

$(\Delta/\sigma)_{\rm max}$ = 0.038
$\Delta\rho_{\rm max}$ = 0.37 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.26 e Å$^{-3}$
Extinction correction: *SHELX*76
Extinction coefficient: 0.0004
Atomic scattering factors from *SHELX*76

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATRED* (Brookhaven National Laboratory & University of Birmingham, 1986). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELX*76. Molecular graphics: *CHEM-X* (Chemical Design Ltd, 1991). Software used to prepare material for publication: *CALC* (Gould & Taylor, 1983).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| P1 | 0.53981 (6) | 0.17359 (3) | 0.46447 (5) | 0.0230 (2) |
| O2 | 0.5371 (2) | 0.1058 (1) | 0.3195 (1) | 0.0311 (6) |
| O3 | 0.3418 (2) | 0.2200 (1) | 0.4860 (2) | 0.0320 (6) |
| C4 | 0.6229 (3) | 0.1193 (1) | 0.6704 (2) | 0.0261 (8) |
| C5 | 0.7956 (2) | 0.0515 (1) | 0.6675 (2) | 0.0240 (8) |
| C6 | 1.0012 (2) | 0.0967 (1) | 0.6716 (2) | 0.0264 (8) |
| O7 | 1.1326 (2) | 0.0893 (1) | 0.7914 (2) | 0.0426 (8) |
| O8 | 1.0124 (2) | 0.1422 (1) | 0.5284 (2) | 0.0445 (8) |
| N9 | 0.7994 (2) | −0.0114 (1) | 0.8177 (2) | 0.0267 (7) |
| O10 | 0.3335 (2) | 0.3935 (1) | 0.6046 (2) | 0.0310 (7) |

Table 2. *Geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| P1—O2 | 1.501 (1) | C5—C6 | 1.524 (2) |
| P1—O3 | 1.515 (1) | C5—N9 | 1.484 (2) |
| P1—C4 | 1.808 (2) | C6—O7 | 1.202 (2) |
| C4—C5 | 1.531 (2) | C6—O8 | 1.303 (2) |
| O2—P1—O3 | 116.7 (1) | C4—C5—N9 | 110.3 (1) |
| O2—P1—C4 | 109.3 (1) | C6—C5—N9 | 109.0 (1) |
| O3—P1—C4 | 106.8 (1) | C5—C6—O7 | 123.4 (2) |
| P1—C4—C5 | 115.8 (1) | C5—C6—O8 | 110.4 (1) |
| C4—C5—C6 | 112.7 (1) | O7—C6—O8 | 126.1 (2) |
| O2—P1—C4—C5 | 40.1 (1) | C4—C5—C6—O7 | 114.4 (2) |
| O3—P1—C4—C5 | 167.2 (1) | C4—C5—C6—O8 | −66.3 (2) |
| P1—C4—C5—C6 | 78.8 (2) | N9—C5—C6—O7 | −8.5 (2) |
| P1—C4—C5—N9 | −159.1 (1) | N9—C5—C6—O8 | 170.8 (1) |

Table 3. *Hydrogen-bonding geometry* (Å, °)

| $D$ | H | $A$ | $D\cdots A$ | $\mathrm{H}\cdots A$ | $D$—$\mathrm{H}\cdots A$ |
|---|---|---|---|---|---|
| O8 | H15 | O3$^{\rm i}$ | 2.536 (2) | 1.69 (3) | 172 (3) |
| N9 | H16 | O10$^{\rm ii}$ | 2.807 (2) | 1.72 (2) | 167 (2) |
| N9 | H17 | O2$^{\rm iii}$ | 2.752 (2) | 2.02 (2) | 156 (2) |
| N9 | H18 | O10$^{\rm iv}$ | 2.830 (2) | 1.82 (2) | 163 (2) |
| O10 | H19 | O3 | 2.735 (2) | 1.98 (3) | 172 (3) |
| O10 | H20 | O2$^{\rm v}$ | 2.719 (2) | 1.70 (4) | 173 (3) |

Symmetry code: (i) $1+x, y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1-x, -y, 1-z$; (iv) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

2-Amino-2-carboxyethylphosphinic acid (1) was prepared by the method of Dingwall, Ehrenfreund & Hall (1989) and crystals were obtained by recrystallization from water/methanol. All non-H atoms were found by direct methods, and all H atoms were located in difference electron density maps. In the final full-matrix least-squares refinement coordinates of all atoms were adjusted along with anisotropic thermal parameters for non-H atoms and isotropic temperature factors for H atoms.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71251 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1053]

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# Functionalized Hydrocarbons with Condensed Ring Skeletons. XIV. A Dioxotricyclo[8.4.0.0$^{2,7}$]tetradec-6-ene

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## Abstract

The structure of methyl 1,2-*trans*-1,10-*cis*-8,14-dioxotricyclo[8.4.0.0$^{2,7}$]tetradec-6-ene-1-carboxylate consists of three angularly fused six-membered rings, *A*, *B* and *C*. The tricyclic compound has a *cis A*/*B* ring junction and an *anti* arrangement between the C(9) proton and the C(10) methoxycarbonyl substituent. Rings *A* and *B* adopt chair

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