

formation {O(carbonyl) is acceptor of a short hydrogen bond [2.425 (3) Å] from O(1) of the phosphonic acid group of the molecule at $x-1, y, z$ } (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980).

The phenyl ring is also planar to within experimental accuracy. The maximum deviation from the best plane through the ring atoms is 0.019 (8) Å. The mean C—C bond length is 1.383 Å as in benzene and C—C—C angles are close to 120°. The angle between the phenyl-ring plane and the plane defined by atoms C(11), C(3) and C(1) is 17.2 (5)°.

The conformation of the molecule is described by the torsion angles $\varphi, \chi^1, \chi^{21}, \chi^{22}, \chi^{31}$ and χ^{32} (Table 2). The molecule assumes a *trans-gauche* conformation with φ and χ^1 , the torsion angles about C α —C β , 177.1 (4) and 57.2 (5)°. This conformation about C(1)—C(3) is similar to that found in PheP. The torsion angles χ^{21} [−163.6 (5)°] and χ^{22} [18.3 (6)°] differ from those in PheP, where these angles are 83.6 (5) and −99.2 (5)°, respectively.

The crystal structure contains a network of hydrogen bonds which plays an important role in stabilization. Details of these are given in Table 3 and Fig. 2.

This work was supported by the Polish Ministry of Science and Higher Education (Project RP. II. 10).

References

- CROMER, D. T. & LARSON, A. C. (1974). *J. Chem. Phys.* **60**, 176–184.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HARKEMA, S., BRAKE, J. H. M. & MEUTSTEGE, H. J. G. (1979). *Acta Cryst.* **B35**, 2087–2093.
 HUISZON, C. & TIEMESSEN, G. W. M. (1976). *Acta Cryst.* **B32**, 1604–1606.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 JEFFREY, G. A., RUBLE, J. R., MCMULLAN, R. K., DEFREES, D. J., BINKLEY, J. S. & POPLE, J. A. (1980). *Acta Cryst.* **B36**, 2292–2299.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KASHINO, S. & HAISA, M. (1977). *Acta Cryst.* **B33**, 855–860.
 KOWALIK, J., SAWKA-DOBROWOLSKA, W. & GŁOWIAK, T. (1984). *J. Chem. Soc. Chem. Commun.* pp. 446–447.
 SAWKA-DOBROWOLSKA, W. (1985). *Acta Cryst.* **C41**, 84–86.
 SAWKA-DOBROWOLSKA, W., GŁOWIAK, T., KOWALIK, J. & MASTALERZ, P. (1985). *Acta Cryst.* **C41**, 1773–1776.
 SAWKA-DOBROWOLSKA, W. & GRUSZECKA-KOWALIK, E. (1987). *Acta Cryst.* **C43**, 289–291.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18. London: The Chemical Society.
 SUZUKI, T., IGARASHI, K., HASE, K. & TUZIMURA, K. (1973). *Agric. Biol. Chem.* **37**, 411–416.
 Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California, USA.

Acta Cryst. (1987). **C43**, 1944–1946

Structure of 2-Aminoethyl(phenyl)phosphinic Acid Dihydrate

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(Received 14 October 1986; accepted 13 May 1987).

Abstract. C₈H₁₂NO₂P.2H₂O, $M_r = 221.2$, monoclinic, $P2_1/c$, $a = 12.059$ (3), $b = 8.990$ (3), $c = 11.698$ (3) Å, $\beta = 113.88$ (3)°, $V = 1159.6$ Å³, $Z = 4$, $D_m = 1.27$ (1), $D_x = 1.27$ Mg m^{−3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.23$ mm^{−1}, $F(000) = 472$, $T = 293$ K, $R = 0.040$ for 1677 reflexions. The title compound exists as a zwitterion, NH₃⁺—(CH₂)₂—PO₂[−]Ph, and adopts a *trans* conformation with the P—C—C—N torsion angle 166.6 (3)°. The coordination around P is distorted tetrahedral with normal P—O and P—C bond lengths. There are seven independent hydrogen bonds in the structure, three of type N—H...O with lengths 2.778 (3), 2.807 (4) and 2.753 (4) Å and four of type O—H...O with lengths 2.758 (3), 2.757 (3), 2.736 (3) and 2.759 (3) Å.

Introduction. Aminophosphonic acids, broadly defined as analogues of amino acids in which a COOH group is replaced with PO₃H₂ or related functions [P(CH₃)₂O₂H, P(Ph)O₂H *etc.*], are now receiving considerable attention because of their occurrence in nature and because several synthetic and natural phosphonic and phosphinic analogues of amino acids have interesting biological properties.

Extensive studies by numerous workers (Hilderbrand, Curley-Joseph, Lubansky & Henderson, 1982) have established the presence of 2-aminoethylphosphonic acid in bacteria, unicellular plants, protozoa, molluscs and human tissues.

This paper reports the structure of the title compound, a derivative of (2-aminoethyl)phosphonic acid,

β -ciliatine (Okaya, 1966), as part of a study on the conformation and hydrogen bonding of aminophosphonic and aminophosphinic acids.

Experimental. Clear, colourless crystals from water, dimensions $0.2 \times 0.25 \times 0.3$ mm; density by flotation in benzene/1,1,2,2-tetrachloroethane; 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 $20 \leq 2\theta(\text{Mo}) \leq 27^\circ$ measured on diffractometer; 2053 independent reflexions; $2\theta_{\text{max}} = 51^\circ$, variable θ - 2θ scan rate 2.0 - $29.3^\circ \text{ min}^{-1}$ depending on intensity; two standards (224, 326) every 50 reflexions, variation in intensities $\pm 2\%$; correction for Lorentz and polarization factors, not for absorption; 1677 with $I > 3.0\sigma(I)$ used for structure determination; index range $h 0$ to 14 , $k 0$ to 10 , $l -13$ to 12 ; 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 refinement minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, difference synthesis revealed H atoms; non-H atoms refined anisotropically and H atoms bonded to O(water) and N refined with isotropic temperature factors; nine H atoms with fixed coordinates and thermal parameters ($B = 6.0 \text{ \AA}^2$); max. shift in final LS cycle 0.008σ ; minimum and maximum electron density in final $\Delta\rho$ map: -0.10 and 0.11 e \AA^{-3} ; $R = 0.040$, $wR = 0.047$, $S = 3.93$.

Final positional parameters are given in Table 1.*

Discussion. The molecular structure and atom numbering are shown in Fig. 1. Bond distances and selected and torsion angles are in Table 2. No significant deviations from normal values of lengths and angles occur.

As can be seen in Fig. 1, the title compound exists as a zwitterion with the amino N atom protonated and the phosphinic-acid group ionized. As is also apparent in Fig. 1 the molecule adopts a *trans* [$166.6(3)^\circ$] conformation around the central C(1)-C(2) bond: this is similar to (2-aminoethyl)phosphonic acid, β -ciliatine (Okaya, 1966), which also adopts a *trans* conformation.

The two O atoms of the phosphinic acid group are in resonance with each other, as indicated by the lengths of the bonds P-O(1) and P-O(2), $1.505(2)$ and

$1.515(2) \text{ \AA}$, respectively. The P-O lengths agree within the limits of error with similar bonds in aminomethyl(methyl)phosphinic acid (Głowiak & Sawka-Dobrowolska, 1977) and in aminophosphonic acids. The P-C(1) and P-C(11) distances [$1.811(3)$ and $1.797(3) \text{ \AA}$] are typical of values reported for such bonds.

The coordination around the P atom departs significantly from regular tetrahedral, the angles varying from $105.8(1)$ [C(1)-P-C(11)] to $115.9(1)^\circ$ [O(1)-P-O(2)]; they agree well with the values found in aminomethyl(methyl)phosphinic acid and in β -ciliatine.

Table 1. Positional parameters and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses

	$B_{\text{eq}} = \frac{1}{3} \sum_i B_{ii}$			$B_{\text{eq}}(\text{\AA}^2)$
	<i>x</i>	<i>y</i>	<i>z</i>	
P	0.1883 (1)	0.1949 (1)	0.0730 (1)	2.32 (4)
O(1)	0.1481 (2)	0.1336 (2)	0.1698 (2)	3.5 (2)
O(2)	0.1471 (2)	0.3518 (2)	0.0289 (2)	2.9 (1)
O(3w)	0.0948 (2)	0.6101 (3)	0.1242 (2)	3.7 (2)
O(4w)	0.1979 (3)	0.5457 (3)	-0.1264 (3)	4.3 (2)
N	0.0904 (2)	-0.1799 (3)	-0.1464 (2)	3.1 (2)
C(1)	0.1276 (2)	0.0771 (3)	-0.0641 (2)	2.7 (2)
C(2)	0.1654 (3)	-0.0855 (3)	-0.0387 (3)	3.0 (2)
C(11)	0.3503 (2)	0.1839 (3)	0.1272 (3)	3.1 (2)
C(12)	0.4078 (3)	0.2409 (5)	0.0557 (4)	6.7 (4)
C(13)	0.5311 (4)	0.2369 (6)	0.0953 (5)	9.0 (5)
C(14)	0.6002 (3)	0.1768 (6)	0.2069 (5)	7.8 (5)
C(15)	0.5467 (4)	0.1125 (7)	0.2769 (4)	7.7 (5)
C(16)	0.4223 (3)	0.1173 (5)	0.2375 (3)	5.8 (4)

Table 2. Bond distances (\AA) and selected bond angles and torsion angles ($^\circ$)

P-O(1)	1.505 (2)	C(11)-C(12)	1.382 (5)
P-O(2)	1.515 (2)	C(11)-C(16)	1.367 (5)
P-C(11)	1.797 (3)	C(12)-C(13)	1.368 (6)
P-C(1)	1.811 (3)	C(13)-C(14)	1.345 (8)
C(1)-C(2)	1.523 (4)	C(14)-C(15)	1.359 (7)
C(2)-N	1.484 (4)	C(15)-C(16)	1.379 (6)
O(1)-P-O(2)	115.9 (1)	O(2)-P-C(11)	106.5 (1)
O(1)-P-C(1)	108.4 (1)	O(2)-P-C(1)	109.3 (1)
O(1)-P-C(11)	110.4 (1)	C(1)-P-C(11)	105.8 (1)
O(1)-P-C(1)-C(2)	-57.6 (2)	P-C(1)-C(2)-N	166.6 (3)
O(2)-P-C(1)-C(2)	177.1 (2)	C(1)-P-C(11)-C(12)	66.2 (4)
C(11)-P-C(1)-C(2)	60.8 (2)	C(1)-P-C(11)-C(16)	-112.3 (4)

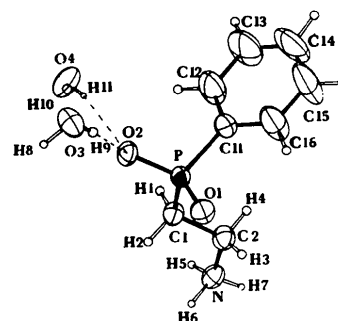


Fig. 1. ORTEP projection (Johnson, 1976) of the molecule with the atom-numbering scheme and thermal ellipsoids at the 50% probability level.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44052 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

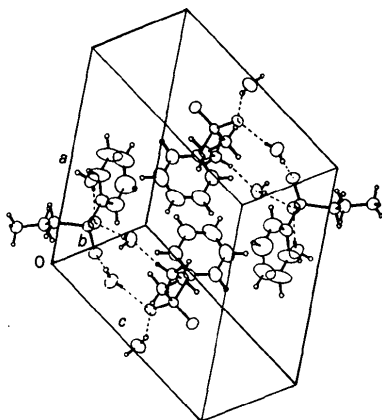


Fig. 2. View of the unit-cell contents. H bonds are indicated by dashed lines.

The crystal structure is stabilized by hydrogen bonds involving the amino and phosphinic-acid groups and the water molecules (Fig. 2). Table 3 gives the hydrogen-bond distances and angles. The two water molecules O(3) and O(4) are involved in O—H...O(P) bonds and the protonated amino group forms three N—H...O hydrogen bonds. Each water molecule acts as donor in two hydrogen bonds and as acceptor in one.

The phenyl moiety is nearly planar; the maximum deviation from the best plane through the ring atoms is 0.030 (6) Å.

Table 3. Hydrogen-bond distances (Å) and angles (°)

D—H...A	D—H	H...A	D—H...A	∠D—H...A
N—H(5)...O(3 ⁱ)	0.91 (3)	1.88 (3)	2.778 (3)	167 (3)
N—H(6)...O(1W ⁱⁱ)	1.01 (4)	1.80 (4)	2.807 (4)	175 (3)
N—H(7)...O(4w ⁱⁱⁱ)	0.85 (3)	1.91 (3)	2.753 (4)	170 (3)
O(3w)—H(8)...O(2 ^{iv})	0.90 (4)	1.86 (4)	2.758 (3)	174 (3)
O(3w)—H(9)...O(2)	0.77 (4)	2.04 (4)	2.757 (3)	156 (4)
O(4w)—H(10)...O(1 ⁱ)	0.85 (4)	1.91 (4)	2.736 (3)	164 (4)
O(4w)—H(11)...O(2)	0.64 (3)	2.13 (3)	2.759 (3)	167 (4)

Symmetry code: (i) $x, 0.5 - y, -0.5 + z$; (ii) $-x, -y, -z$; (iii) $x, -1 + y, z$; (iv) $-x, 1 - y, -z$.

This work was supported by the Polish Ministry of Science and Higher Education (Project RP.II.10).

References

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- GŁOWIAK, T. & SAWKA-DOBROWOLSKA, W. (1977). *Acta Cryst.* B33, 1522–1525.
- HILDERBRAND, R., CURLEY-JOSEPH, J., LUBANSKY, H. J. & HENDERSON, T. O. (1982). *Top. Phosphorus Chem.* pp. 297–338.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- OKAYA, Y. (1966). *Acta Cryst.* 20, 712–715.
- Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California, USA.

Acta Cryst. (1987). C43, 1946–1949

Structure of (R,S)-Hesperetin Monohydrate

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(Received 17 March 1987; accepted 13 May 1987)

Abstract. 2,3-Dihydro-5,7-dihydroxy-2-(3-hydroxy-4-methoxyphenyl)-4H-1-benzopyran-4-one monohydrate, $C_{16}H_{14}O_6 \cdot H_2O$, $M_r = 320.29$, triclinic, $P\bar{1}$, $a = 9.073$ (4), $b = 12.162$ (5), $c = 6.856$ (3) Å, $\alpha = 95.49$ (8), $\beta = 81.32$ (9), $\gamma = 107.16$ (8)° (reduced cell $a = 6.856$, $b = 9.073$, $c = 12.162$ Å, $\alpha = 72.84$, $\beta = 84.51$, $\gamma = 81.32$ °), $V = 713.1$ Å³, $Z = 2$, $D_x = 1.491$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 8.97$ cm⁻¹, $F(000) = 336$, $T = 295$ K, $R = 0.065$ for 1050 observed reflections. The hydroxyl O(5) and keto O(4) atoms form a strong intramolecular hydrogen bond, making a six-membered ring. The pyrone ring adopts a slightly distorted sofa conformation and the phenyl ring is bonded equatorially to the pyrone ring. The two ring

systems in hesperetin are nearly parallel to each other, in contrast to the perpendicular arrangement in naringenin. Hydrogen bonds involving the water molecules form molecular double layers.

Introduction. Hesperetin is a naturally occurring flavanone which is unique in that it is, albeit faintly, sweet while most of the flavanoid compounds are known to be tasteless or bitter (Yamato, Hashigaki, Mito & Koyama, 1978). In an effort to provide detailed structural information for related compounds, we have determined the crystal structure of racemic hesperetin and will compare it with the structure of naringenin [2,3-dihydro-5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-1-