Structure of (1-Ureido-2-phenylethyl)phosphonic Acid

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Abstract. $C_9H_{13}N_2O_4P$, $M_r = 244 \cdot 2$, monoclinic, $P2_1$, $a = 7 \cdot 187$ (4), $b = 5 \cdot 216$ (3), $c = 15 \cdot 752$ (5) Å, $\beta = 91 \cdot 56$ (4)°, $V = 590 \cdot 3$ (5) Å^3, $Z = 2$, $D_m = 1 \cdot 37$ (1), $D_x = 1 \cdot 373$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 24$ mm^{-1}, $F(000) = 256$, $T = 293$ K, $R = 0 \cdot 041$ for 1250 nonzero independent amplitudes. The title compound was prepared by reaction of S-(+)-(1-amino-2-phenylethyl)phosphonic acid monohydrate with potassium cyanate. The molecule is in the un-ionized form, $Ph-CH_2-CH(NHCONH_2)-PO_3H_2$. The conformation about the $C\alpha-C\beta$ bond is *trans-gauche*, angles $\varphi[P-C-C-C(phenyl)]$ and $\chi^1[N-C-C-C(phenyl)]$ being $177 \cdot 1$ (4) and $57 \cdot 2$ (5)°, respectively. The crystal structure is stabilized by five intermolecular hydrogen bonds. Two O atoms of the phosphonic-acid group form two strong hydrogen bonds of $2 \cdot 425$ (3) [P—OH$\cdots$O(carbonyl)] and $2 \cdot 495$ (3) Å [P—OH$\cdots$O(phosphonate)].

Introduction. The title compound was obtained according to the preparation used for synthesis of hydantoins in which the substrates are acids (Suzuki, Igarashi, Hase & Tuzimura, 1973).

As a continuation of our research on the aminophosphonic acids (Kowalik, Sawka-Dobrowolska & Głowiak, 1984; Sawka-Dobrowolska, 1985; Sawka-Dobrowolska, Głowiak, Kowalik & Mastalerz, 1985; Sawka-Dobrowolska & Gruszecka-Kowalik, 1987, and references cited therein), the X-ray structure of the title compound is presented in this paper.

Experimental. A mixture of $0 \cdot 02$ mol S-(+)-(1-amino-2-phenylethyl)phosphonic acid monohydrate, $0 \cdot 02$ mol potassium hydroxide and $0 \cdot 02$ mol potassium cyanate in 30 ml of water was heated at 373 K for 30 min. Then 20 ml of concentrated hydrochloric acid was added and the solution was heated at 373 K for 30 min. After cooling the carbamide derivative crystallized from the reaction mixture. The crude product was then recrystallized from water. M.p., uncorrected 469 K, was determined on a Boetius apparatus. Colourless transparent crystals $0 \cdot 1 \times 0 \cdot 23 \times 0 \cdot 50$ mm. D_m by flotation in benzene/1,1,2,2-tetrachloroethane; monoclinic $P2_1$ 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 reflections with $20 \le 2\theta(\text{Mo}) \le 31°$ measured on diffractometer; 1469 independent reflexions; $2\theta_{max} = 55 \cdot 0°$; variable θ–2θ scans, scan rate $2 \cdot 0$–$29 \cdot 3°$ min^{-1} depending on intensity, two standards ($22\bar{2}$, 313) every 50 reflexions, variation in intensities $\pm 2 \cdot 0\%$; data corrected for Lorentz–polarization, but not for absorption and extinction, 1250 with $I > 3 \cdot 5\sigma(I)$ used for structure determination; index range h 0 to 9, k 0 to 6, l −20 to 19; calculations performed with the Syntex (1976) *XTL* system; scattering factors for neutral atoms, corrected for anomalous dispersion, from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods with a Syntex (1976) version of *MULTAN* (Germain, Main & Woolfson, 1971); full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F)$; H atoms located from difference synthesis; non-H atoms refined with anisotropic thermal parameters, H atoms bonded to O and N refined with isotropic temperature factors, remaining H atoms included with fixed coordinates and thermal parameters ($B = 11 \cdot 0$ Å^2 for phenyl and $B = 5 \cdot 0$ Å^2 for ethyl); max. shift in final LS cycle $0 \cdot 01\sigma$; max. and min. electron density in final difference map $0 \cdot 14$ and $-0 \cdot 13$ e Å^{-3}; $R = 0 \cdot 041$, $wR = 0 \cdot 036$, $S = 2 \cdot 958$.

The absolute configuration was assigned as S on the basis of the configuration of the starting material used in the synthesis. Final positional parameters are given in Table 1.*

Discussion. The molecular structure and atom numbering are shown in Fig. 1. Bond distances and selected angles and torsion angles are in Table 2.

The title compound occurs in the un-ionized form. Both O(1) and O(2) are protonated. The P—O(1) and P—O(2) bond lengths of $1 \cdot 537$ (3) and $1 \cdot 555$ (3) Å indicate single bonds and the P—O(3) length, $1 \cdot 494$ (3) Å, a double bond.

The coordination around P departs significantly from regular tetrahedral, the angles varying from $106 \cdot 2$ (2)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44051 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to 113·9 (1)°. The two protonated O atoms influence the bond angles at P. The smallest angle involves the protonated O(2) and C(1), while the two largest O—P—O angles of 113·9 (1) and 113·0 (1)° involve the unprotonated O(3) and protonated O(1) and O(2).

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

$$B_{eq} = \tfrac{1}{3}\Sigma_i B_{ii}.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
P	0·6014 (1)	0·3000 fixed	0·3814 (1)	2·60 (4)
O(1)	0·7689 (3)	0·4060 (5)	0·3339 (2)	3·5 (2)
O(2)	0·6785 (3)	0·0918 (5)	0·4437 (2)	3·2 (2)
O(3)	0·4908 (4)	0·5046 (5)	0·4232 (2)	3·6 (2)
O(4)	0·0889 (3)	0·2592 (6)	0·3448 (2)	5·0 (2)
N(1)	0·3246 (4)	−0·0267 (6)	0·3519 (2)	3·1 (2)
N(2)	0·0441 (4)	−0·1317 (7)	0·4063 (3)	5·0 (3)
C(1)	0·4526 (5)	0·1332 (7)	0·3048 (2)	2·9 (3)
C(2)	0·1497 (5)	0·0403 (8)	0·3663 (3)	3·4 (3)
C(3)	0·5647 (6)	−0·0308 (8)	0·2439 (2)	3·8 (3)
C(11)	0·4496 (7)	−0·1882 (11)	0·1800 (2)	5·3 (4)
C(12)	0·5430 (10)	−0·3895 (10)	0·1391 (3)	7·4 (6)
C(13)	0·4461 (13)	−0·5398 (12)	0·0805 (3)	11·1 (10)
C(14)	0·2617 (13)	−0·4944 (17)	0·0628 (4)	12·9 (11)
C(15)	0·1722 (11)	−0·2960 (17)	0·1001 (4)	12·2 (10)
C(16)	0·2675 (8)	−0·1384 (15)	0·1599 (3)	7·5 (6)

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

P—O(1)	1·537 (3)	C(1)—C(3)	1·530 (5)
P—O(2)	1·555 (3)	C(3)—C(11)	1·526 (6)
P—O(3)	1·494 (3)	C(11)—C(12)	1·412 (8)
P—C(1)	1·813 (4)	C(12)—C(13)	1·385 (9)
C(1)—N(1)	1·460 (5)	C(13)—C(14)	1·367 (13)
N(1)—C(2)	1·330 (4)	C(14)—C(15)	1·360 (12)
C(2)—N(2)	1·343 (5)	C(15)—C(16)	1·413 (10)
C(2)—O(4)	1·265 (5)	C(16)—C(11)	1·363 (8)

O(1)—P—O(2)	106·7 (1)	O(2)—P—O(3)	113·9 (1)
O(1)—P—O(3)	113·0 (1)	O(2)—P—C(1)	106·2 (2)
O(1)—P—C(1)	107·7 (2)	O(3)—P—C(1)	108·9 (2)

φ|P—C(1)—C(3)—C(11)|	177·1 (4)
χ¹|N(1)—C(1)—C(3)—C(11)|	57·2 (5)
φ¹|P—C(1)—N(1)—C(2)|	100·0 (4)
χ²|C(1)—C(3)—C(11)—C(12)|−163·6 (5)

χ²¹|C(1)—C(3)—C(11)—C(16)|	18·3 (6)
χ¹¹|C(1)—N(1)—C(2)—O(4)|	−5·6 (5)
χ¹²|C(1)—N(1)—C(2)—N(2)|	176·2 (5)

The P—C(1)—N(1) bond angle of 107·7 (2)° is smaller than the corresponding angle in (1-amino-2-phenylethyl)phosphonic acid monohydrate, PheP (Kowalik *et al.*, 1984) [110·0 (3)°]. The other angles about C(1) are about 1° greater than those found in PheP.

The carbamide moiety is nearly planar: the maximum deviation from the best plane through N(1), C(2), N(2) and O(4) is 0·010 (4) Å. H(3) and H(4) lie close to this plane, but H(5) deviates by 0·23 (4) Å. The C(1)—N(1) distance of 1·460 (5) Å corresponds well to the normal C—N single bond of 1·472 (5) Å (Sutton, 1965). The two C—N bonds involving the trigonally hybridized C(2) [N(1)—C(2) and C(2)—N(2)] are considerably shorter. The observed values of 1·330 (4) and 1·343 (5) Å are intermediate between a double bond and a single bond and compare well with the values for the analogous bonds in *N*-methylurea-oxalic acid (Harkema, Brake & Meutstege, 1979), phenylurea (Kashino & Haisa, 1977), 1,1'-azobis-carbamide (Cromer & Larson, 1974) and in mono-methylurea (Huiszoon & Tiemessen, 1976, and references cited therein).

The carbonyl C=O double bond, 1·265 (5) Å, is significantly longer than the normal length of 1·215 (5) Å (Sutton, 1965) and agrees to within experimental accuracy with the bond length expected when the O atom takes part in hydrogen-bond

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

$D–H\cdots A$	$D–H$	$H\cdots A$	$D–H\cdots A$	$\angle D–H\cdots A$
O(1)—H(1)···O(4¹)	1·08 (4)	1·36 (4)	2·425 (3)	171 (4)
O(2)—H(2)···O(3ⁱⁱ)	0·87 (4)	1·67 (4)	2·495 (3)	157 (4)
N(1)—H(3)···O(3ⁱⁱⁱ)	0·78 (4)	2·16 (4)	2·931 (4)	172 (3)
N(2)—H(4)···O(2ⁱᵛ)	0·86 (4)	2·09 (4)	2·949 (4)	173 (3)
N(2)—H(5)···O(4ⁱⁱⁱ)	1·03 (5)	2·43 (5)	3·340 (5)	148 (3)

Symmetry code: (i) $1 + x, y, z$; (ii) $1 - x, -0·5 + y, 1 - z$; (iii) $x, y - 1$ z; (iv) $x - 1, y, z$.
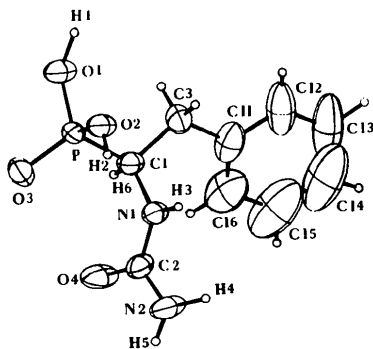

Fig. 1 An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.
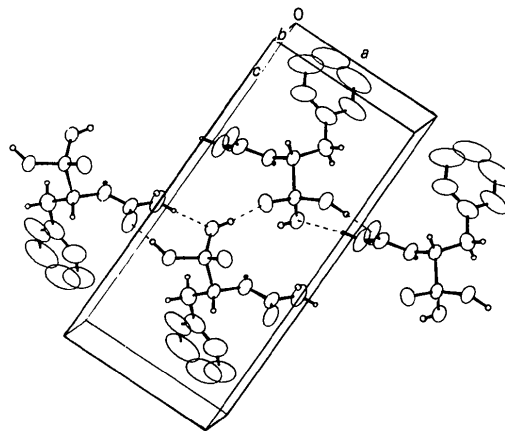

Fig. 2. View of the unit-cell contents. H bonds are indicated by dashed lines.

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 φ, χ^1, χ^{21}, χ^{22}, χ^{31} and χ^{32} (Table 2). The molecule assumes a *trans–gauche* conformation with φ and χ^1, the torsion angles about Cα—Cβ, 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.

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Structure of 2-Aminoethyl(phenyl)phosphinic Acid Dihydrate

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Abstract. $C_8H_{12}NO_2P.2H_2O$, $M_r = 221\cdot2$, monoclinic, $P2_1/c$, $a = 12\cdot059$ (3), $b = 8\cdot990$ (3), $c = 11\cdot698$ (3) Å, $\beta = 113\cdot88$ (3)°, $V = 1159\cdot6$ Å^3, $Z = 4$, $D_m = 1\cdot27$ (1), $D_x = 1\cdot27$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot23$ mm^{-1}, $F(000) = 472$, $T = 293$ K, $R = 0\cdot040$ for 1677 reflexions. The title compound exists as a zwitterion, NH_3^+–$(CH_2)_2$–PO_2^-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 PO_3H_2 or related functions [$P(CH_3)$-O_2H, $P(Ph)O_2H$ 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,