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Structure of Guanidinomethylphosphonic Acid Monohydrate, C$_2$H$_8$N$_3$O$_3$P.H$_2$O

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Abstract. $M_r = 171.1$, monoclinic, $C2/c$, $a = 13.222$ (4), $b = 7.502$ (3), $c = 13.936$ (5) Å, $\beta = 104.17$ (3)°, $V = 1340.3$ (9) Å^3, $Z = 8$, $D_m = 1.70$ (1), $D_x = 1.70$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.38$ mm^{-1}, $F(000) = 720$, final $R = 0.042$ for 1581 reflexions. The guanidinomethylphosphonic acid molecule exists as a zwitterion, (NH$_2$)$_2^+$C-NHCH$_2$PO$_3$H$^-$. The C–N–C–P torsion angle is -95.9 (3)°. The molecules are held together by a network of N–H$\cdots$O and O–H$\cdots$O hydrogen bonds.

Introduction. Guanidinophosphonic acids (1) were recently described (Rowley, Greenleaf & Kenyon, 1971; Moreaud, Lacoste & Neuzil, 1975). They have special biological interest as the phosphonic acid analogues of arginine (2) and creatine (3).

(1)

(2)

(3)
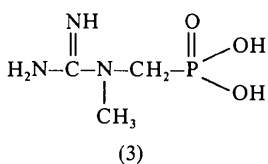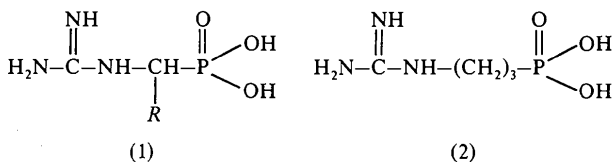
The synthesis of a series of guanidinophosphonic acids has been described both with free (Oleksyszyn, Tyka & Mastalerz, 1977) and substituted (Oleksyszyn & Tyka, 1978) guanidino groups. As a continuation of our research on the aminophosphonic acids, the X-ray structure of guanidinomethylphosphonic acid is presented in this paper.

Experimental. Clear, colourless crystals from water at room temperature, dimensions $0.2 \times 0.2 \times 0.3$ mm; density by flotation in carbon tetrachloride/ethylene bromide; monoclinic Cc or $C2/c$ from Weissenberg photographs, $C2/c$ 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; 1890 independent reflexions; $2\theta_{max} = 60°$; variable θ–2θ scans, scan rate 2.0–$29.3°$ min^{-1}, depending on intensity; two standards measured every 30 reflexions, no significant change; corrected for Lorentz and polarization, not for absorption; 1600 with $I > 1.96\sigma(I)$ used for structure determination; index range h 0 to 17, k 0 to 10, l −19 to 18; 19 reflexions showing a large $(F_o - F_c)/\sigma(F_o)$ ratio excluded in the final stages of refinement; calculations performed with Syntex (1976) *XTL* 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; 1581 observations, 132 variables; maximum parameter shift in final LS cycle 0·1 σ, maximum electron density in final difference map 0·3 e Å^{-3}; $R = 0·042$, $R_w = 0·053$, $S = 4·40$.

Discussion. Final positional parameters are given in Table 1.* The molecular structure and atom numbering are shown in Fig. 1. Fig. 2 shows a projection along **b**. Bond distances and angles and torsion angles are in Table 2. No significant deviations from normal values of lengths and angles occur.

The molecule occurs as a zwitterion with the guanidino group protonated by a phosphate proton so that it exists as a guanidinium residue. This group is attached to the PO$_3$H$^-$ group through a C—N bond of length 1·455 (3) Å, which is significantly shorter than the usual C—N single-bond length, but agrees well with similar bonds in various arginine derivatives (Aoki, Nagano & Iitaka, 1971; Salunke & Vijayan, 1982; Sudhakar & Vijayan, 1980).

The three C—N bonds in the guanidinium group are nearly equal with average length 1·331 (3) Å. The three N—C—N angles are close to 120°, average value 119·97° (e.s.d. *ca* 2°). The C—N lengths and N—C—N angles are in accord with those in the guanidino moieties of guanidinoacetic acid (Berthou, Laurent & Nakajima, 1976), β-guanidinopropionic acid (Steward, Warner & Clarke, 1974) and γ-guanidinobutyric acid hydrochloride (Maeda, Fujiwara & Tomita, 1972). The guanidino group is nearly planar. Deviations from the best plane through N(1), N(2), N(3) and C(2) are N(1) 0·006 (2), N(2) 0·007 (2), N(3) 0·007 (2) and C(2) −0·019 (2) Å. As in other analogous molecules C(1) is only slightly displaced [−0·184 (2) Å] from the plane of the guanidino group.

The bond lengths and angles in the aminomethyl-phosphonic part of the molecule are in good agreement with those found in aminomethylphosphonic acid, β-AMPh (Darriet, Darriet, Cassaigne & Neuzil, 1975) and in 2-aminoethylphosphonic acid (β-ciliatine) (Okaya, 1966). In the present structure, two of the three P—O bonds have rather short lengths of 1·498 (2) and 1·507 (2) Å while the third is 1·579 (2) Å. As in the case of AMPh and β-ciliatine 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.

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and hydrogen-bond parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38799 (16 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 isotropic temperature factors with e.s.d.'s in parentheses*

For non-hydrogen atoms $B_{eq} = \frac{1}{3}\sum_i B_{ii}$.

	x	y	z	$B_{eq}/B_{Iso}(\text{Å}^2)$
P	0·23721 (4)	0·21170 (7)	0·16300 (4)	1·38 (3)
O(1)	0·2219 (1)	0·2402 (2)	0·2708 (1)	2·0 (1)
O(2)	0·3454 (1)	0·2627 (2)	0·1581 (1)	2·3 (1)
O(3)	0·2032 (1)	0·0239 (2)	0·1328 (1)	2·0 (1)
O(4)$_w$	0	0·0337 (4)	0·25	3·3 (2)
O(5)$_w$	0·50	0·0276 (3)	0·25	2·2 (2)
N(1)	0·0397 (1)	0·3359 (3)	0·0891 (1)	1·9 (1)
N(2)	−0·1222 (2)	0·2054 (3)	0·0453 (2)	2·4 (1)
N(3)	−0·0142 (2)	0·1855 (3)	−0·0604 (1)	2·2 (1)
C(1)	0·1472 (2)	0·3667 (3)	0·0852 (2)	1·8 (1)
C(2)	−0·0299 (2)	0·2402 (3)	0·0254 (1)	1·6 (1)
H(1)	0·251 (3)	0·336 (5)	0·295 (2)	4·5 (8)
H(2)	0·155 (2)	0·355 (4)	0·017 (2)	3·2 (6)
H(3)	0·166 (2)	0·494 (4)	0·110 (2)	3·2 (6)
H(4)	0·015 (3)	0·377 (4)	0·144 (2)	3·5 (7)
H(5)	−0·171 (2)	0·131 (4)	0·001 (2)	2·8 (6)
H(6)	−0·127 (3)	0·192 (4)	0·103 (3)	4·4 (8)
H(7)	−0·064 (2)	0·118 (4)	−0·099 (2)	2·8 (6)
H(8)	0·047 (2)	0·201 (4)	−0·079 (2)	2·5 (6)
H(9)$_w$	−0·056 (4)	−0·052 (6)	0·247 (4)	9·2 (14)
H(10)$_w$	0·442 (3)	0·108 (4)	0·219 (2)	4·8 (8)

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

P—O(1)	1·579 (2)	O(1)—P—O(2)	110·8 (1)
P—O(2)	1·498 (2)	O(1)—P—O(3)	107·0 (1)
P—O(3)	1·507 (2)	O(2)—P—O(3)	116·7 (1)
N(1)—C(1)	1·455 (3)	O(1)—P—C(1)	105·3 (1)
N(1)—C(2)	1·323 (3)	O(2)—P—C(1)	107·6 (1)
N(2)—C(2)	1·341 (3)	O(3)—P—C(1)	108·9 (1)
N(3)—C(2)	1·328 (3)	P—C(1)—N(1)	112·3 (2)
P—C(1)	1·820 (2)	C(1)—N(1)—C(2)	125·9 (2)
		N(1)—C(2)—N(2)	119·1 (2)
		N(1)—C(2)—C(3)	122·3 (2)
		N(2)—C(2)—N(3)	118·5 (2)

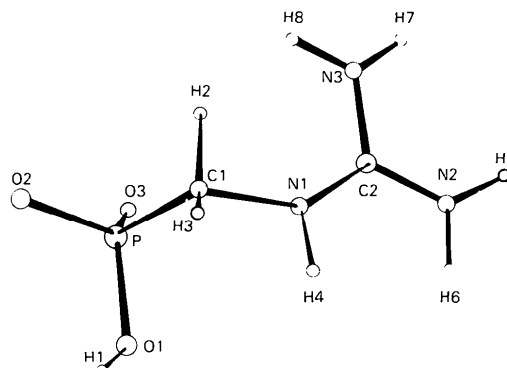|		
τ	N(1)—C(1)—P—O(1)	−58·4 (2)
	N(1)—C(1)—P—O(2)	−176·6 (2)
	N(1)—C(1)—P—O(3)	56·1 (2)
χ^1	C(2)—N(1)—C(1)—P	−95·9 (3)
χ^2	N(2)—C(2)—N(1)—C(1)	171·8 (2)
χ^{21}	N(3)—C(2)—N(1)—C(1)	−12·1 (3)
	H(8)—N(3)—C(2)—N(1)	5 (2)
	H(7)—N(3)—C(2)—N(1)	178 (3)
	H(5)—N(2)—C(2)—N(1)	−177 (2)
	H(6)—N(2)—C(2)—N(1)	−33 (3)
	H(1)—O(1)—P—C(1)	−75 (3)

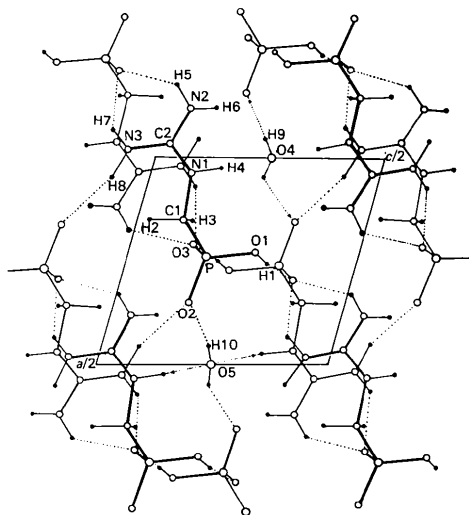
Fig. 1. View of the molecule along **b**.

Fig. 2. Projection of the crystal structure along **b**. Hydrogen bonds are shown by broken lines.

The state of ionization of the phosphate group and the protonation of the guanidino group indicate that the charge distribution of the present compound can be written as $(NH_2)_2^+CNHCH_2PO_3H^-$.

The conformation of the molecule is described by torsion angles χ^1, χ^2, χ^{21} and τ (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). The conformation of the guanidino group is defined by the torsion angles χ^2 and χ^{21} describing the conformation about C(2)–N(1). The values of χ^2 and χ^{21} are 171·8 (2) and −12·1 (3)° respectively (Table 2); χ^1 is −95·9 (3)° and τ [−58·4 (2)°] is similar to that observed in β-AMPh (Darriet et al., 1975).

The crystal structure contains a network of hydrogen bonds* which plays an important role in stabilization. The only H atom not participating in a hydrogen bond is H(6) of the guanidino group. The molecules are linked together through the hydrogen bonds O(1)–H(1)···

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* See deposition footnote.

$O(3)(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$, N(2)–H(5)···O(3)(−x, −y, −z), N(3)–H(7)···O(3)(−x, −y, −z) to form a chain, running along the diagonal of the *ac* plane. The donor···acceptor ($D···A$) lengths are 2·582 (2), 2·994 (3) and 2·915 (3) Å, respectively. Neighbouring chains are linked by N(1)–H(4)···O(5)$_w$(−1−x, −y, −z), N(3)–H(8)···O(2)($\frac{1}{2}-x$, $\frac{1}{2}-y$, −z), O(4)$_w$–H(9)$_w$···O(2)(−$\frac{1}{2}+x$, −$\frac{1}{2}+y$, z) and O(5)$_w$–H(10)$_w$···O(2) hydrogen bonds. Apart from the O(5)$_w$–H(10)$_w$···O(2) hydrogen bond the others are nonlinear, as shown by the D–H···A angles, which range from 145 (4) to 167 (4)°.

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Structure of Cataline, C21H25NO5, a Non-phenolic Aporphine Alkaloid

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Abstract. $M_r = 371·4$, orthorhombic, $P2_12_12_1$, $a = 7·3558$ (9), $b = 14·869$ (3), $c = 17·410$ (4) Å, $V = 1904·2$ (5) Å^3, $Z = 4$, $D_x = 1·295$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1·54178$ Å, $\mu = 0·8026$ mm^{-1}, $F(000) = 792$, room temperature; block-diagonal-matrix least-squares refinement based on 1822 Friedel pairs led to final R and R_w