

The Crystal Structure of Aminoguanidinium Dihydrogen Orthophosphate

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Crystals of $(\text{H}_2\text{N})_2\text{CNH}(\text{NH}_2) \cdot \text{H}_2\text{PO}_4$ have space group $P\bar{1}$ with $a = 7.13(1)$, $b = 6.81(1)$, $c = 7.46(1)$ Å, $\alpha = 99.5(1)$, $\beta = 86.6(1)$, $\gamma = 100.4(1)^\circ$. The structure has been determined from microdensitometer-scanned film data and refined to a final R of 0.074. The phosphate groups are linked by three, distinct, short hydrogen bonds (all near 2.50 Å) into infinite two-dimensional slabs parallel to (001) and these slabs are hydrogen-bonded together by aminoguanidinium ions which are almost parallel to (100). Only one of the H atoms in the asymmetric unit is not involved in hydrogen bonding.

Introduction

There has recently been some interest in simple guanidinium salts (*e.g.* Adams & Small, 1974, 1976) since these often contain multiple hydrogen bonds to O atoms, each O sometimes accepting four H atoms, although three is more common. This ability of the guanidinium ion to maximize the number of hydrogen bonds has also been utilized in the design of stable compounds containing H_2O_2 of crystallization (Adams, Pritchard & Thomas, 1976; Adams & Pritchard, 1976). The only aminoguanidinium compound studied structurally to date is the chloride (Bryden, 1957) and its hydrogen bonding has not been investigated. Since this ion contains seven H atoms per unit charge, all of which could form hydrogen bonds, it is potentially of use in crystal engineering schemes such as that mentioned above.

Experimental

The crystals were formed upon slow evaporation of a solution prepared by addition of aminoguanidinium hydrogen carbonate to orthophosphoric acid. Analysis (Table 1) confirmed that the colourless, almost equidimensional, parallelepipeds were $(\text{H}_2\text{N})_2\text{CNH}(\text{NH}_2) \cdot \text{H}_2\text{PO}_4$. Two different crystals (both about $0.5 \times 0.3 \times 0.5$ mm) were used to collect the data set $0kl-4kl$ and the cross-level $h0l$ data on a Stoe Weissenberg camera. The intensities were scanned by the SRC

Table 1. *Crystal data and analysis*

Space group $P\bar{1}$	$a = 7.13(1)$, $b = 6.81(1)$, $c = 7.46(1)$ Å,
	$\alpha = 99.5(1)$, $\beta = 86.6(1)$, $\gamma = 100.4(1)^\circ$
(Cu $K\alpha$, $\bar{\lambda} = 1.5418$ Å) $Z = 2$; $D_m = 1.59$. $D_c = 1.62$ g cm ⁻³	
Calculated for	
$(\text{H}_2\text{N})_2\text{CNH}(\text{NH}_2) \cdot \text{H}_2\text{PO}_4$	5.2% H, 7.0% C, 32.6% N
Found	5.2% H, 7.1% C, 32.9% N

Microdensitometer Service at the Atlas Computer Laboratory with an Optronics P1000 microdensitometer.

Determination and discussion of the structure

To the data set of 655 reflexions were added those planes which had been too weak to be measured by the film scanner. These unobserved reflexions were given intensities equal to three-quarters the weakest observed value. The data were corrected for Lorentz and polarization effects; a Wilson plot gave an overall isotropic temperature factor of 2.4 Å².

The structure was solved with *MULTAN* 76 [a suite of programs developed from, and enhancing, the phase-determining program of Germain, Main & Woolfson (1970)] with the 100 planes with $E \geq 1.52$. An E map computed with the phases from the set with the highest combined figure of merit gave a chemically reasonable set of peaks, although one of the N atoms was not located. One cycle of isotropic least-squares refinement, followed by a difference synthesis, enabled this N atom to be found. Refinement was continued, initially with isotropic, but later with anisotropic thermal parameters, and converged to $R = 0.084$. Atomic coordinates, temperature factors, bond lengths and angles, and least-squares planes are given in Tables 2–6.*

Centrosymmetric pairs of $\text{H}_2\text{PO}_4^{2-}$ ions are joined across the origin by a hydrogen bond between O(1) and O(1^{vii}) and each of these 'dimers' is joined to another dimer one **b** translation away by a hydrogen bond O(2)···O(2^{vi}) (Table 7). The chains so produced, which run parallel to **b**, are joined in turn by two,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32279 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

centrosymmetrically related, hydrogen bonds O(4)···O(3^v). These ions are arranged in two dimensional 'slabs' (Fig. 1) parallel to (001). The aminoguanidinium ions are almost exactly perpendicular to these slabs (Fig. 2) and are parallel to (100). Each aminoguanidinium group is involved in six hydrogen bonds, and is hydrogen-bonded to five different phosphate ions.

A difference synthesis computed at this stage did not show the H atoms; they were, therefore, added in calculated positions. Those of the cation were added at 1 Å from the N atoms such that $\angle C-N-H$ was 120°. This ion cannot be planar because of the close approach of H(5) and H(6) (Fig. 3) and since there is a hydrogen bond N(1)-H(5)···O(2^v) this NH₂ group was twisted until the hydrogen bond was more nearly linear and also the H(5) to H(6) distance exceeded the sum of the van der Waals radii. The H atoms of the

Table 2. Fractional atomic coordinates and their standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	0.2456 (4)	0.2991 (4)	0.0130 (3)
O(1)	0.1729 (11)	0.0707 (9)	-0.0194 (9)
O(2)	0.0878 (12)	0.4106 (12)	0.0955 (9)
O(3)	0.3331 (10)	0.3716 (10)	-0.1619 (8)
O(4)	0.4024 (1)	0.3352 (11)	0.1611 (9)
C(1)	0.2478 (17)	0.9580 (15)	0.4602 (11)
N(1)	0.1983 (17)	0.6533 (14)	0.5842 (11)
N(2)	0.2313 (15)	0.8640 (13)	0.6069 (10)
N(3)	0.2412 (15)	0.8459 (13)	0.2926 (10)
N(4)	0.2726 (17)	1.1566 (13)	0.4829 (11)
H(1)	0.033	0.014	-0.004
H(2)	0.018	0.482	0.019
H(3)	0.510	0.453	0.161
H(4)	0.270	0.560	0.495
H(5)	0.130	0.560	0.664
H(6)	0.240	0.932	0.736
H(7)	0.272	1.224	0.616
H(8)	0.272	1.204	0.376
H(9)	0.241	0.908	0.184
H(10)	0.241	0.688	0.280

NB Site occupancy of H(1) and H(2) is 0.5.

Table 3. Temperature factors ($U_{ij} \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	22 (3)	21 (1)	20 (1)	-6 (1)	-4 (1)	5 (1)
O(1)	23 (7)	17 (3)	36 (4)	-5 (3)	-4 (3)	2 (3)
O(2)	48 (7)	47 (5)	30 (4)	16 (5)	7 (4)	14 (4)
O(3)	25 (5)	34 (4)	17 (3)	-11 (4)	-2 (3)	9 (3)
O(4)	37 (6)	51 (5)	31 (4)	-26 (4)	-26 (4)	22 (3)
C(1)	34 (8)	34 (8)	18 (4)	-2 (6)	-4 (5)	6 (4)
N(1)	85 (10)	26 (5)	30 (5)	21 (6)	5 (5)	6 (4)
N(2)	49 (8)	35 (5)	17 (4)	3 (5)	3 (4)	10 (4)
N(3)	65 (9)	29 (5)	16 (4)	10 (5)	-1 (4)	-1 (3)
N(4)	69 (9)	26 (5)	24 (4)	3 (5)	-6 (5)	3 (4)

H₂PO₄²⁻ ion were placed differently. There is a hydrogen bond O(4)···O(3^v) and since P-O(4) is larger than P-O(3), the H atom was assumed to be bonded to O(4) and placed 1 Å from O(4) along the O(4)···

Table 4. Bond lengths

P(1)-O(1)	1.532 (7) Å	C(1)-N(2)	1.35 (1) Å
P(1)-O(2)	1.515 (9)	C(1)-N(3)	1.35 (1)
P(1)-O(3)	1.530 (7)	C(1)-N(4)	1.32 (1)
P(1)-O(4)	1.577 (8)	N(1)-N(2)	1.39 (1)

Table 5. Bond angles

O(1)-P(1)-O(2)	110.3 (5)°	O(3)-P(1)-O(4)	110.2 (4)°
O(1)-P(1)-O(3)	111.0 (4)	C(1)-N(2)-N(1)	119.7 (7)
O(1)-P(1)-O(4)	105.6 (4)	N(2)-C(1)-N(3)	119.1 (9)
O(2)-P(1)-O(3)	112.7 (5)	N(2)-C(1)-N(4)	119.3 (8)
O(2)-P(1)-O(4)	106.8 (4)	N(3)-C(1)-N(4)	121.5 (9)

Table 6. Least-squares planes and deviations of atoms from them (Å)

(a) Plane through the aminoguanidinium ion, defined by C(1), N(2), N(3), N(4)

$$7.1201x - 0.8881y + 0.2753z = 1.0451$$

C(1)	-0.005	N(4)	0.002
N(2)	0.002	N(1)	-0.052
N(3)	0.002		

(b) Plane through the phosphate ion, defined by C(1), N(1), N(2), N(3), N(4)

$$7.1246x - 0.9751y + 0.3305z = 0.9845$$

C(1)	-0.001	N(3)	0.006
N(1)	-0.016	N(4)	-0.011
N(2)	0.002		

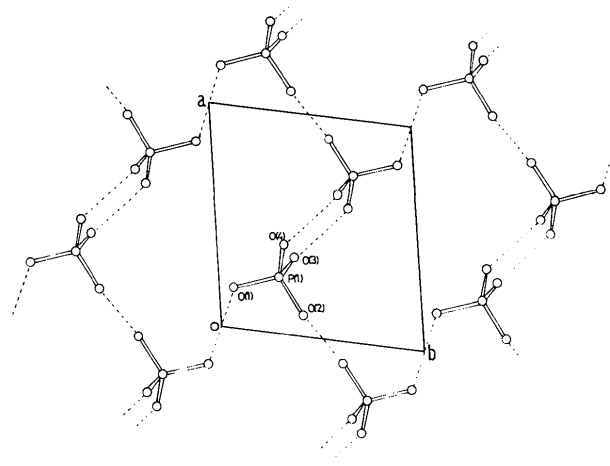


Fig. 1. Projection of the phosphate groups down the *c* axis, showing the hydrogen-bonding scheme.

Table 7. *Hydrogen-bonding geometry*

O(1) ... O(1 ^{vii})	2.50 (1) Å	N(3) ... O(1 ⁱⁱ)	3.09 (1) Å
O(2) ... O(2 ^{vi})	2.53 (1)	N(3) ... O(2)	3.12 (1)
O(4) ... O(3 ^{iv})	2.49 (1)	N(4) ... O(3 ⁱ)	2.82 (1)
N(1) ... O(2 ^v)	3.08 (1)	N(4) ... O(4 ⁱⁱⁱ)	2.90 (1)
N(2) ... O(1 ⁱ)	2.95 (1)		

NB Also N(1) ... O(3ⁱⁱⁱ) 3.20 (1)

Equivalent positions

(i)	$x, 1 + y, 1 + z$	(v)	$-x, 1 - y, 1 - z$
(ii)	$x, 1 + y, z$	(vi)	$-x, 1 - y, -z$
(iii)	$x, y, 1 + z$	(vii)	$-x, -y, -z$
(iv)	$1 - x, 1 - y, -z$		

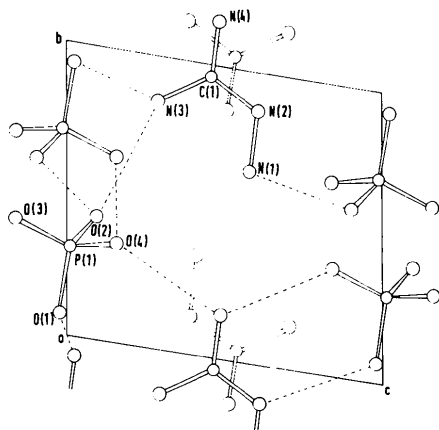


Fig. 2. Projection of the structure down the *a* axis; all of the distinct hydrogen bonds are shown.

O(3^{iv}) direction. The remaining two hydrogen bonds, O(1) ... O(1^{vii}) and O(2) ... O(2^{vi}), are both across centres of symmetry. Their bond lengths of 2.5 Å suggest (Speakman, 1972) that there are two potential minima either side of the centre of symmetry. The H atoms were thus disposed with a site occupancy of 0.5 at 1 Å from O(1) and from O(2). With inclusion of these H atoms (but not their refinement) and with isotropic thermal parameters set equal to the mean value of $U_{11} + U_{22} + U_{33}$ for the atoms to which they are bonded, *R* fell to 0.074 and the e.s.d.'s of the other bonds were reduced [e.g. C(1)–N(2) 0.015 to 0.013 Å]. In the last cycle the average parameter shift/e.s.d. was 0.05 and the maximum was 0.3 [z for N(4)].

Scattering factors were those listed in *International Tables for X-ray Crystallography* (1974) and all cal-

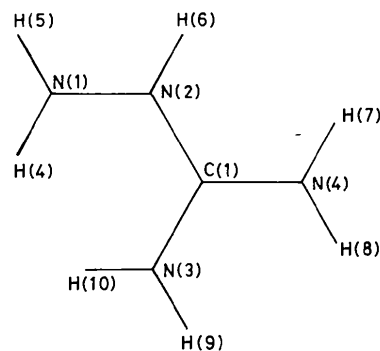


Fig. 3. The numbering scheme used for the aminoguanidinium ion.

culations, except the refinement, were carried out with *MULTAN 76*. *CRYLSQ* of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the least-squares refinement with unit weights.

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