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The Crystal Structure of Bisguanidinium Hydrogen Phosphate Monohydrate

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The structure of $[C(NH_2)_3]_2HPO_4.H_2O$ has been determined from counter intensities. The space group is $P\bar{4}2_1c$ with $a = 16{\cdot}843$ (3), $c = 7{\cdot}251$ (1) Å, $Z = 8$. The guanidinium ions are effectively planar with C–N ranging from 1·315 to 1·335 Å. The phosphate O–H···O hydrogen bond is short at 2·568 (7) Å. Thirteen of the fifteen H atoms are involved in hydrogen bonding.

Introduction

This compound is of interest since it is likely to contain multiple hydrogen bonds to O, the ratio of possible hydrogen-bonding H to O atoms being 3:1. It was also possible that a precise study might throw some light on the apparently significant lengthening of one of the C–N bonds in guanidinium carbonate (Adams & Small, 1974). The crystal data have been given by Adams & Pritchard (1975).

Experimental

Crystals were prepared by addition of guanidinium carbonate to orthophosphoric acid until effervescence ceased, followed by slow evaporation, whereupon hard colourless needles of square cross-section were formed. Photographs were used to obtain the space group, and cell dimensions (Table 1) in satisfactory agreement with those of Adams & Pritchard were obtained by a least-squares procedure based on θ values measured on the diffractometer (Small & Travers, 1961).

Table 1. *Crystal data*

Space group $P\bar{4}2_1c$; $a = 16{\cdot}843(3)$, $c = 7{\cdot}251(1)$ Å
(Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å), $Z = 8$; $d_m = 1{\cdot}51$, $d_c = 1{\cdot}52$ g cm^{-3}

Determination of the structure

Initially the space group was mis-assigned as $P4_22_12$ since the conditions noted were: $h00$, $h = 2n$; $00l$, $l = 2n$. The intensities of the 1365 unique reflexions occurring at $\theta < 82{\cdot}1°$ with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) were collected on a diffractometer at room temperature. Intensities were corrected for Lorentz and polarization effects. A Wilson plot gave the relatively low overall temperature factor of 1·5 Å^2. E values were obtained for all reflexions.

MULTAN (Germain, Main & Woolfson, 1970) was used to solve the structure and since the version available at the time of the investigation was not applicable to symmetries higher than orthorhombic, it was necessary to treat the crystal as orthorhombic. The equivalent reflexions in one octant were generated and the 227 reflexions having $E > 1{\cdot}6$ were used on the basis of space group $P2_12_12$. An E map computed with the phases from the set with the highest figure of merit revealed a chemically reasonable set of peaks.

Inspection of the coordinates of the two equivalent sets of atoms revealed that (110) was a glide plane, a fact inconsistent with $P4_22_12$. A shift of origin by $\mathbf{a}/2 + \mathbf{c}/4$ resulted in symmetry consistent with $P\bar{4}2_1c$ which has conditions, $h00$, $h = 2n$; hhl, $l = 2n$; *i.e.* as for $P4_22_12$ but with inclusion of the more general second condition. The intensities of the hhl reflexions were in almost all cases <3 standard deviations of background intensity. These reflexions were removed and the posi-

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tions of the atoms converted to those for $P\bar{4}2_1c$ and averaged. An absorption correction was computed with *ABSCOR* in the X-RAY 63 system on the Chilton ATLAS.

Refinement was carried out with *FMLS* of Bracher (1967). The 19 reflexions for which the intensity was less than one e.s.d. of the background were left out of the refinement and calculation of R. Ten reflexions considered to be suffering from extinction were also left out of the refinement. The H atoms of the guanidinium ions were found from a difference synthesis although it did not prove possible to locate the H atom of the HPO_4^{2-} group or those of the water molecule. The H atoms were refined isotropically throughout.

In an attempt to correct for extinction in a systematic way the method of Larson (1970) was used. The output from a structure factor calculation was used to obtain an isotropic extinction parameter which was then used to correct the $|F_o|$ values. One cycle of *FMLS* was performed and the procedure repeated. Unit weights were used, and on the last cycle the parameter shifts were of the order of the appropriate standard deviations. The final R was 0·066. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Final atomic and thermal parameters are given in Tables 2, 3 and 4.*

Table 2. *Fractional atomic coordinates and their standard deviations*

	x	y	z
P	0·87102 (7)	0·23599 (7)	0·20606 (19)
O(1)	0·9352 (2)	0·1726 (2)	0·1961 (7)
O(2)	0·9032 (2)	0·3189 (2)	0·1908 (7)
O(3)	0·8163 (3)	0·2191 (3)	0·0282 (5)
O(4)	0·8192 (2)	0‘2222 (3)	0·3747 (5)
O(5)	0·9611 (3)	0·3603 (3)	0·8504 (7)
C(1)	0·6073 (3)	0·1479 (3)	0·2837 (9)
N(1)	0·5505 (3)	0·1032 (3)	0·2150 (9)
N(2)	0·5926 (3)	0·2228 (3)	0·3334 (8)
N(3)	0·6808 (3)	0·1198 (3)	0·2960 (9)
C(2)	0·9826 (3)	0·1559 (3)	0·6967 (9)
N(4)	0·9071 (3)	0·1789 (3)	0·6974 (8)
N(5)	1·0187 (3)	0·1384 (4)	0·8524 (7)
N(6)	1·0209 (3)	0·1477 (4)	0·5389 (7)
H(1)	0·562 (6)	0·057 (7)	0·119 (14)
H(2)	0·505 (7)	0·120 (6)	0·214 (17)
H(3)	0·555 (5)	0·234 (5)	0·349 (12)
H(4)	0·640 (5)	0·261 (5)	0·330 (13)
H(5)	0·733 (5)	0·163 (5)	0·266 (14)
H(6)	0·780 (4)	0·060 (4)	0·258 (10)
H(7)	0·887 (8)	0·204 (7)	0·541 (18)
H(8)	0·880 (4)	0·188 (4)	0·799 (11)
H(9)	0·985 (6)	0·126 (6)	0·1003 (14)
H(10)	1·061 (5)	0·100 (5)	0·802 (13)
H(11)	1·093 (6)	0·128 (6)	0·618 (15)
H(12)	1·011 (6)	0·157 (5)	0·432 (12)

Table 4. *Isotropic temperature factors for the hydrogen atoms* (Å^2)

H(1)	5·6 (2·6)	H(5)	3·8 (2·3)	H(9)	4·6 (2·6)
H(2)	7·1 (3·1)	H(6)	1·0 (1·5)	H(10)	2·4 (1·8)
H(3)	2·4 (1·8)	H(7)	7·3 (3·7)	H(11)	4·7 (2·6)
H(4)	3·4 (2·1)	H(8)	1·0 (1·4)	H(12)	3·1 (2·1)

Description and discussion of the structure

Bond lengths and angles are in Table 5, least-squares planes in Table 6 and details of the hydrogen bonding in Table 7. The guanidinium ions are planar within experimental error; the large standard deviations of the H atoms preclude any detailed discussion of them. The C–N lengths are similar to those found in other guanidinium or substituted guanidinium salts [see *e.g.* Adams & Small (1974), Cotton, Day, Hazen & Larsen (1973), Cotton, Day, Hazen, Larsen & Wong (1974)]. The monohydrogen phosphate ions show one relatively long P–O distance for the P–O–H bond and three shorter distances for the remaining P–O bonds. This contrasts with the case of bis(methylguanidinium) hydrogen phosphate (Cotton *et al.*, 1974) where there are two long and two short P–O bonds, a fact attributed to extensive hydrogen-bonding interactions influencing the electronic distribution of the phosphate.

Table 3. *Temperature factors, with standard deviations for the 'heavy' atoms*

$$T=\exp\,[-10^{-5}(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})]\,.$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P	85 (4)	102 (4)	514 (19)	−6 (6)	56 (19)	−57 (18)
O(1)	155 (12)	221 (14)	773 (67)	156 (21)	50 (60)	−97 (65)
O(2)	225 (14)	152 (12)	1084 (79)	−166 (22)	59 (68)	−88 (63)
O(3)	184 (14)	161 (14)	578 (66)	25 (25)	−95 (54)	−71 (53)
O(4)	143 (14)	218 (15)	693 (67)	−20 (26)	239 (54)	−61 (58)
O(5)	180 (15)	333 (19)	1654 (101)	−37 (28)	31 (67)	461 (78)
C(1)	170 (17)	158 (16)	915 (97)	1 (27)	254 (83)	59 (82)
N(1)	148 (15)	233 (18)	1898 (118)	−44 (26)	146 (86)	−328 (95)
N(2)	162 (16)	219 (17)	1610 (117)	95 (27)	−67 (75)	−469 (81)
N(3)	159 (15)	212 (17)	1810 (115)	54 (27)	99 (90)	60 (96)
C(2)	162 (18)	165 (17)	868 (93)	13 (27)	24 (82)	−236 (85)
N(4)	166 (15)	295 (18)	970 (86)	62 (28)	−95 (79)	−263 (91)
N(5)	211 (19)	358 (23)	799 (88)	132 (35)	−144 (67)	−169 (80)
N(6)	247 (21)	424 (27)	864 (96)	142 (38)	227 (78)	32 (90)

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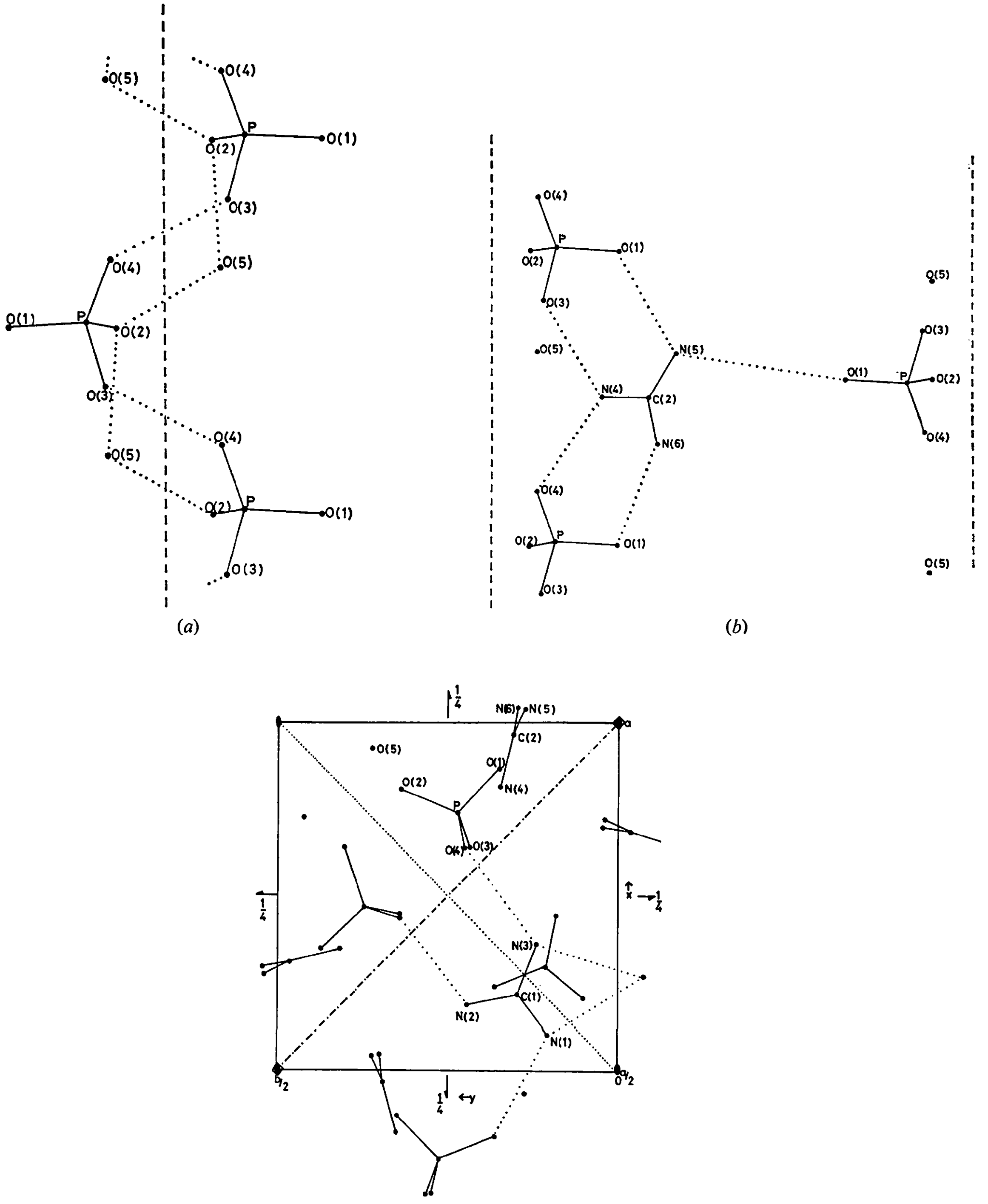
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31272 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The structure [Fig. 1(*a*)-(*c*)] consists of a three-dimensional hydrogen-bonding network in which 13 of the 15 H atoms are used. The phosphate groups related by the *c* glide are joined by hydrogen bonds from the water oxygen, O(5). There are also relatively short hydrogen bonds, O(3)-H···O(4), between them



(*a*)

(*b*)

(*c*)

Fig. 1. (*a*) Projection onto (110) of the hydrogen-bonded phosphate chain. Hydrogen bonds involving water molecules and HPO_4^{2-} ions are shown. (*b*) Projection on to (110) of the hydrogen bonding to the phosphate chains by the guanidinium ion C(2), N(4), N(5), N(6). (*c*) Projection of the structure on to (001) with hydrogen bonds involving the C(1), N(1), N(2), N(3) guanidinium group shown.

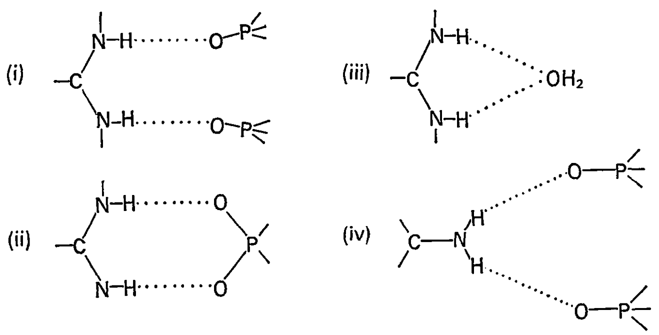


Fig. 2. Schematic drawing of hydrogen-bonding geometry. (i) N(2)-H(4)···O(3), N(3)-H(5)···O(4). (ii) N(4)-H(8)···O(3), N(5)-H(9)···O(1). (iii) N(1)-H(1)···O(5), N(3)-H(6)···O(5). (iv) N(4)-H(8)···O(3), N(4)-H(7)···O(4).

Table 5. *Bond lengths and angles*

P——O(1)	1·521 (5) Å	O(1)—P——O(2)	113·1 (3)°
P——O(2)	1·502 (5)	O(1)—P——O(3)	104·2 (3)
P——O(3)	1·610 (5)	O(1)—P——O(4)	109·8 (3)
P——O(4)	1·520 (5)	O(2)—P——O(3)	108·2 (3)
C(1)–N(1)	1·315 (8)	O(2)—P——O(4)	114·1 (3)
C(1)–N(2)	1·335 (8)	O(3)—P——O(4)	106·8 (3)
C(1)–N(3)	1·329 (8)	N(1)—C(1)–N(2)	120·5 (5)
C(2)–N(4)	1·330 (9)	N(1)—C(1)–N(3)	120·0 (5)
C(2)–N(5)	1·315 (9)	N(2)—C(1)–N(3)	119·4 (5)
C(2)–N(6)	1·320 (9)	N(4)—C(2)–N(5)	120·2 (6)
N(1)–H(1)	1·07 (11)	N(4)—C(2)–N(6)	120·0 (6)
N(1)–H(2)	0·82 (10)	N(5)—C(2)–N(6)	119·7 (6)
N(2)–H(3)	0·66 (11)	H(1)—N(1)–H(2)	115 (9)
N(2)–H(4)	1·02 (8)	C(1)—N(1)–H(1)	122 (6)
N(3)–H(5)	1·16 (9)	C(1)—N(1)–H(2)	119 (7)
N(3)–H(6)	1·05 (8)	H(3)—N(2)–H(4)	124 (10)
N(4)–H(7)	1·26 (14)	C(1)—N(2)–H(3)	119 (9)
N(4)–H(8)	0·88 (9)	C(1)—N(2)–H(4)	116 (4)
N(5)–H(9)	1·25 (11)	H(5)—N(3)–H(6)	124 (7)
N(5)–H(10)	1·03 (14)	C(1)—N(3)–H(5)	118 (5)
N(6)–H(11)	1·38 (10)	C(1)—N(3)–H(6)	109 (5)
N(6)–H(12)	0·86 (9)	H(7)—N(4)–H(8)	123 (8)
		C(2)—N(4)–H(7)	111 (6)
		C(2)—N(4)–H(8)	124 (6)
		H(9)—N(5)–H(10)	121 (9)
		C(2)—N(5)–H(9)	125 (5)
		C(2)—N(5)–H(10)	99 (8)
		H(11)–N(6)–H(12)	139 (8)
		C(2)—N(6)–H(11)	95 (4)
		C(2)—N(6)–H(12)	125 (6)

of length similar to those found in orthophosphoric acid (Furberg, 1955). The chain of glide-related phosphate ions is also linked up with other chains by hydrogen bonds involving bridging guanidinium ions. The water oxygen atom, O(5), accepts two hydrogen bonds, from N(1)-H(1) and N(3)-H(6). O(3) also accepts two hydrogen bonds, but O(1), O(2) and O(4) each accept three hydrogen bonds. H(3) and H(11) bonded to N(2) and N(6) respectively are not involved in hydrogen bonding. The variety of different hydrogen-bonding geometries is schematized in Fig. 2.

Table 6. *Deviations of atoms from the least-squares planes* (Å)

(*a*) Plane through C(1), N(1), N(2), N(3)

$$-0{\cdot}2065x-0{\cdot}3214y+0{\cdot}9242z=-1{\cdot}0276$$

C(1)	0·016	N(2)	−0·005
N(1)	−0·005	N(3)	−0·005

(*b*) Plane through C(2), N(4), N(5), N(6)

$$0{\cdot}3025x+0{\cdot}9506y+0{\cdot}0703z=7{\cdot}8441$$

C(2)	0·012	N(5)	−0·004
N(4)	−0·004	N(6)	−0·004

Table 7. *Hydrogen-bonding geometry*

(*a*) Distances (Å)

O(3)···O(4^{i})	2·568 (7)	H(7)····O(4)	1·69 (13)
N(1)···O(5^{ii})	2·866 (7)	N(4)····O(3^{iv})	2·924 (8)
H(1)···O(5^{ii})	2·08 (11)	H(8)····O(3^{iv})	2·05 (9)
N(1)···O(2^{iii})	2·888 (7)	N(5)····O(1^{iv})	2·918 (8)
H(2)···O(2^{iii})	2·11 (10)	H(9)····O(1^{iv})	1·81 (11)
N(2)···O(3^{i})	3·003 (7)	N(5)····O(1^{v})	2·896 (8)
H(4)···O(3^{i})	2·17 (8)	H(10)···O(1^{v})	1·97 (14)
N(3)···O(4)	2·955 (7)	N(6)····O(1)	2·904 (8)
H(5)···O(4)	1·93 (10)	H(12)···O(1)	2·06 (9)
N(3)···O(5^{ii})	2·958 (7)	O(5)····O(2^{iv})	2·744 (8)
H(6)···O(5^{ii})	1·96 (8)	O(5)····O(2^{i})	2·756 (7)
N(4)···O(4)	2·864 (8)		

(*b*) Angles

N(1)–H(1)···O(5^{ii})	128 (8)	N(4)–H(7)····O(4)	153 (10)
N(1)–H(2)···O(2^{iii})	158 (10)	N(4)–H(8)····O(3^{iv})	176 (8)
N(2)–H(4)···O(3^{i})	137 (6)	N(5)–H(9)····O(1^{iv})	144 (8)
N(3)–H(5)···O(4)	145 (9)	N(5)–H(10)···O(1^{v})	148 (11)
N(3)–H(6)···O(5^{ii})	158 (7)	N(6)–H(12)···O(1)	170 (9)

Symmetry code

(i)	$\frac{1}{2}+y,\ \frac{1}{2}+x,\ \frac{1}{2}+z$;	(iv)	$x,\ y,\ 1+z$
(ii)	$\bar{y},\ x,\ \bar{z}$;	(v)	$y,\ \bar{x},\ \bar{z}$
(iii)	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}-z$;		

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