The Crystal Structures of Guanidinium Phosphonate – Acetone (1/1) and Guanidinium Phenylphosphonate – Water (1/2)

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Summary: All oxygen atoms of the anions and all nitrogen atoms of the cations participate in extended hydrogen bond networks in both $(CH_6N_3)_2HPO_3,(CH_3)_2CO$ [$Pna2_1$, a = 13.888(7), b = 9.658(4), c = 9.561(4) Å, Z = 4] and $(CH_6N_3)_3(C_6H_5PO_3)$, $2H_2O$ [Cc, a = 18.51(1), b = 7.586(3), c = 12.48(1) Å, β = 121.6(1)°, Z = 4]. The lattice solvent molecules are also involved in hydrogen bonding; their presence as spacers is required by the non-planarity of the anions. The N..O distances range from 2.78 to 3.10 Å. The structures were solved from photographic data, with respective residuals 0.055 for 723 reflections and 0.048 for 1268 reflections.†

The present work follows structural studies of phenylphosphonic acid[1] and guanidinium and ammonium phosphinate (hypophosphite)[2]. It was prompted by the finding that in guanidinium carbonate, $(CH_6N_3)_2CO_3$, each nitrogen atom participates in two hydrogen bonds of a three-dimensional network, and each anion oxygen in four.[3] The XO_3 groups in the phosphonate (phosphite) and bulky phenylphosphonate anions also bear a -2 charge, but are non-planar. We thought it of interest to determine the nature of the hydrogen-bond network in the guanidinium salts of these anions, and whether the presence of lattice solvent molecules was necessary.

Experimental

A concentrated aqueous solution of each salt was prepared from stoichiometric amounts of the acid and $(CH_6N_3)_2CO_3$. GPA [$(CH_6N_3)_2HPO_3$, $(CH_3)_2CO$] was precipitated by the addition of acetone, and was recrystallised by the diffusion of acetone vapour into a solution in 1:1 water: methanol. GPPW [$(CH_6N_3)_2(C_6H_5PO_3)$, $2H_2O$] was deposited upon seeding with a drop of acetone and was recrystallised from hot water. It was not found possible to obtain satisfactory unsolvated crystals of either salt from any solvent or mixture of solvents.

Crystal Data – GPA, $C_5H_{19}N_6O_4P$, orthorhombic, $Pna2_1$, a = 13.888(7), b = 9.658(4), c = 9.561(4) Å, Z = 4 (D_c = 1.34 g cm^{-3}; CuKα radiation (λ = 1.5418 Å), μ = 19.4 cm^{-1}.

GPPW, $C_8H_{21}N_6O_5P$, monoclinic, Cc, a = 18.51(1), b = 7.586(3), c = 12.48(1) Å, β = 121.6(1)°, D_m = 1.38, D_c = 1.39 g cm^{-3}, Z = 4; Cu radiation, μ = 18.0 cm^{-1}.

Table 1.
Atomic coordinates (x 10^4) for GPA, $(CH_6N_3)_2HPO_3$, $(CH_3)_3CO$.

P	x	y	z
	1237(3)	2369(2)	2570[a]
O(1)	1244(5)	989(5)	3319(8)
O(2)	2145(5)	2635(5)	1746(9)
O(3)	321(4)	2573(5)	1714(8)
O(4)	3760(5)	1130(6)	7655(9)
N(1)	3802(6)	4352(6)	2703(9)
N(2)	3051(5)	5881(7)	4204(12)
N(3)	4696(5)	5565(7)	4328(11)
N(4)	3690(6)	747(6)	2727(10)
N(5)	2847(5)	–324(7)	4483(10)
N(6)	4495(5)	–634(7)	4323(12)
C(1)	3855(6)	5282(7)	3776(9)
C(2)	3663(6)	–74(7)	3858(8)
C(3)	3809(8)	2057(8)	6804(10)
C(4)	2959(11)	2810(13)	6325(22)
C(5)	4811(11)	2459(10)	6266(19)

[a]Fixed to define origin.

†Structure factor lists are available from the author on request.

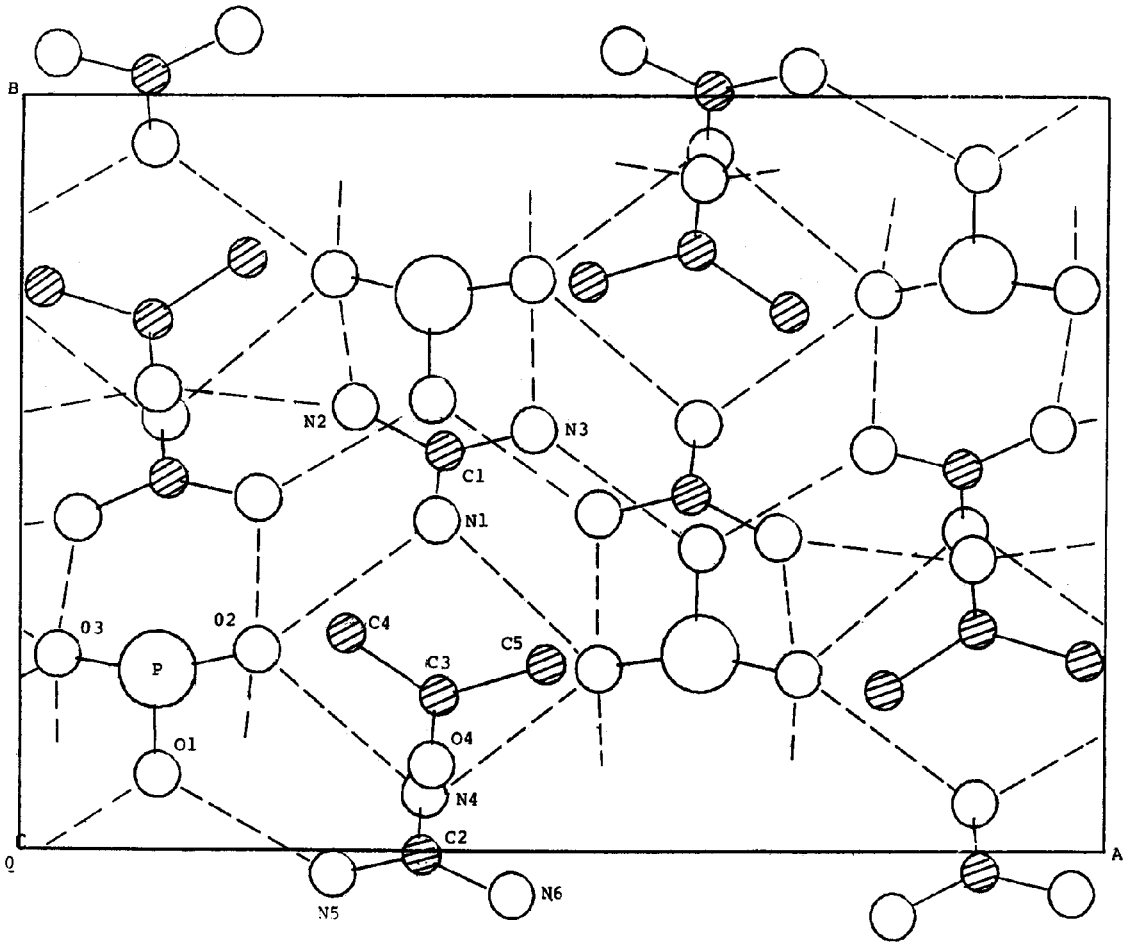

Fig. 1. $(CH_6N_3)_2HPO_3,(CH_3)_2CO$: *c*-axis projection of four asymmetric units.

The levels 0-3*kl* and *hk*0-6 for GPA, and 0-1*kl*, *h*0-7*l* , and *hk*0-3 for GPPW, were recorded as multifilm Weissenberg photographs which were scanned by use of a microdensitometer (Science Research Council, Daresbury Laboratory, England), Absorption corrections were not deemed necessary. Partial structures (phosphorus and adjacent atoms) were obtained from *E*-maps; these were expanded by Fourier syntheses and were refined by full-matrix least-squares by use of SHELX-76.[4] It was clear from the outset that the corresponding centrosymmetric space-groups *Pnam* and C2/*c* were inappropriate, although permitted by the systematic absences. Refinement with anisotropic thermal parameters for all P, O, N, and C atoms and with all data assigned unit weight converged at R 0.055 for GPA (723 unique reflections, 144 parameters) and at R 0.048 for GPPW (1268 reflections, 179 parameters). The majority of the hydrogen atoms, other than the acetone and anion hydrogens in GPA, were then identified among the stronger peaks in difference syntheses (max. 0.3 electron $Å^{-3}$ for each compound), at 1.02-1.08 Å from C, 0.86-1.25 Å from N, and 0.94-1.08 Å from O. However, their inclusion in further cycles of refinement was not considered justified because of their similarity in intensity to the stronger 'noise' peaks and because of the uncertainty raised by the apparent considerable deviation of some cation hydrogens in both compounds from the CN_3 mean planes. Copies of tables of observed and calculated structure factors and of thermal parameters are available from the author.

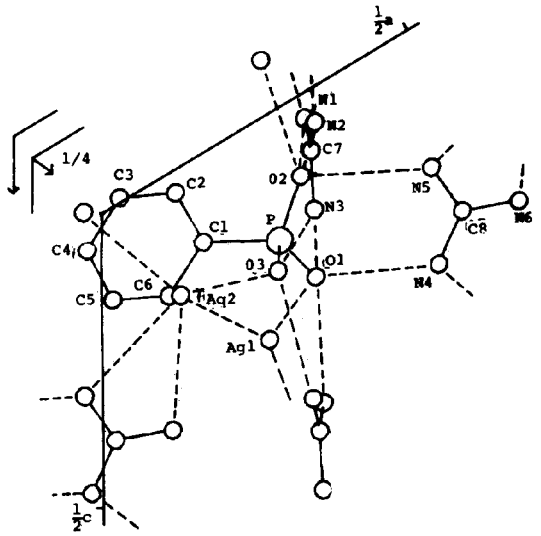

Fig. 2. $(CH_6N_3)_2(C_6H_5PO_3)$, $2H_2O$: *b*-axis projection of one quarter cell. Labelled atoms form one asymmetric unit.

Table 2.
Atomic coordinates (x 10^4) for GPPW,
$(CH_6N_3)_2$ $(C_6H_5PO_3)$, $2H_2O$

P	x	y	z
	2550[a]	1948(2)	2550[a]
O(1)	3046(3)	640(6)	3605(4)
O(2)	2880(3)	2048(6)	1672(4)
O(3)	2510(3)	3783(6)	3063(4)
Aq(1)	2362(5)	7882(7)	4167(5)
Aq(2)	1130(3)	5807(8)	2375(6)
N(1)	2954(3)	5521(7)	695(5)
N(2)	3100(4)	8533(7)	887(5)
N(3)	3054(4)	6933(7)	2413(5)
N(4)	4795(4)	203(10)	4805(7)
N(5)	4733(4)	1149(10)	3026(6)
N(6)	5957(4)	−44(12)	4627(7)
C(1)	1469(4)	1151(8)	1707(5)
C(2)	1098(4)	344(10)	515(6)
C(3)	307(6)	−362(14)	−40(8)
C(4)	−170(5)	−236(14)	510(70)
C(5)	173(5)	529(13)	1669(8)
C(6)	968(4)	1223(10)	2250(6)
C(7)	3032(3)	6983(9)	1339(5)
C(8)	5149(4)	445(11)	4147(8)

[a]Fixed to define origin.

Discussion

Atomic coordinates are given in Tables 1 and 2, and derived dimensions in Tables 3 and 4.

The dimensions of the anion and the two independent cations in both compounds are unremarkable. The substitution of phenyl for hydrogen in HPO_3^{2-} causes no significant change in P-O bond lengths or O-P-O angles. If the roughly-located hydrogen atoms are excluded, the cations in both compounds, the acetone molecule in GPA, and the phenyl ring in GPPW are effectively planar. The chief interest is in the hydrogen bond network. The non-planarity of the anions [unlike the divalent anion in $(CH_6N_3)_2CO_3$], regardless of their size, appears to necessitate the presence of hydrogen-bonding solvent molecules. In GPA (Figure 1) the lattice molecule is the hydrogen acceptor acetone (rather than water or methanol, both of which were also present in solution but which are hydrogen donors as well as accep-

Table 3.
Interatomic distances (Å) and interbond angles (°)
for GPA, $(CH_6N_3)_2HPO_3$, $(CH_3)_2CO$.

P-O(1)	1.513(5)	C(2)-N(4)	1.341(10)
P-O(2)	1.509(7)	C(2)-N(5)	1.304(10)
P-O(3)	1.526(7)	C(2)-N(6)	1.351(10)
C(1)-N(1)	1.367(10)	C(3)-O(4)	1.211(10)
C(1)-N(2)	1.321(10)	C(3)-C(4)	1.460(18)
C(1)-N(3)	1.310(10)	C(3)N-C(5)	1.534(15)
O(1)-P-O(2)	113.1(4)	N(4)-C(2)-N(5)	120.2(9)
O(1)-P-O(3)	111.9(4)	N(4)-C(2)-N(6)	118.5(8)
O(2)-P-O(3)	113.3(3)	N(5)-C(2)-N(6)	121.3(7)
N(1)-C(1)-N(2)	118.2(9)	O(4)-C(3)-C(4)	122.3(1.1)
N(1)-C(1)-N(3)	119.2(8)	O(4)-C(3)-C(5)	117.6(9)
N(2)-C(1)-N(3)	122.5(7)	C(4)-C(3)-C(5)	120.1(9)
Hydrogen bonds:			
O(1)..N(5)	2.79(1)	$O(3^{i})$..N(1)	2.97(1)
$O(1^{i})$..N(3)	2.79(1)	$O(3^{i})$..N(4)	2.95(1)
O(2)..N(1)	2.98(1)	$O(3^{ii})$..N(3)	2.99(1)
O(2)..N(4)	2.97(1)	$O(3^{iii})$..N(6)	2.88(1)
$O(2^{ii})$..N(2)	2.98(1)	$O(4^{iv})$..N(2)	2.93(1)
$O(2^{iii})$..N(5)	2.93(1)	$O(4^{v})$..N(6)	2.94(1)

Symmetry code:
(i) ½ + x, ½ − y, z; (ii) ½ − x, ½ + y, ½ + z;
(iii) ½ − x, − ½ + y, ½ + z; (iv) ½ − x, ½ + y, − ½ + z
(v) 1 − x, − y, − ½ + z

Table 4.

Interatomic distances (Å) and interbond angles (°) for GPPW, $(CH_6N_3)_2(C_6H_5PO_3)$, $2H_2O$

P-O(1)	1.536(4)	C(5)-C(6)	1.368(10)
P-O(2)	1.510(4)	C(6)-C(1)	1.400(8)
P-O(3)	1.528(4)	N(1)-C(7)	1.326(8)
P-C(1)	1.820(6)	N(2)-C(7)	1.339(8)
C(1)-C(2)	1.408(8)	N(3)-C(7)	1.323(7)
C(2)-C(3)	1.367(10)	N(4)-C(8)	1.310(10)
C(3)-C(4)	1.381(10)	N(5)-C(8)	1.310(10)
C(4)-C(5)	1.366(10)	N(6)-C(8)	1.337(9)
O(1)-P-O(2)	111.0(2)	N(1)-C(7)-N(2)	119.1(5)
O(1)-P-O(3)	111.9(2)	N(1)-C(7)-N(3)	121.4(6)
O(1)-P-O(3)	113.7(2)	N(2)-C(7)-N(3)	119.5(6)
C(1)-P-O(1)	104.4(2)	N(4)-C(8)-N(5)	121.7(7)
C(1)-P-O(2)	109.4(2)	N(4)-C(8)-N(6)	119.4(8)
C(1)-P-O(3)	105.9(3)	N(5)-C(8)-N(6)	119.0(7)

Phenyl ring angles: 116.6(6) to 122.0(6), av. 120.0°.

Hydrogen bonds:

O(1)..N(4)	2.78(1)	O(1)..Aq(1)	2.72(1)
O(1)..N(2^{i})	2.86(1)	O(2)..Aq(1^{ii})	2.75(1)
O(2)..N(1)	2.93(1)	O(3)..Aq(2)	2.70(1)
O(2)..N(2^{iii})	2.94(1)	Aq(1)..Aq(2)	2.71(1)
O(2)..N(5)	3.01(1)	Aq(2)..N(4^{iv})	2.94(1)
O(3)..N(1^{i})	2.99(1)	Aq(2)..N(5^{v})	3.10(2)
O(3)..N(3)	2.87(1)	Aq(2)..N(6^{v})	3.06(2)

Symmetry code: (i) x, 1 − y, ½ + z; (ii) x, 1 − y, − ½ + z
(iii) x, -1 + y, z; (iv) -½ + x, ½ − y, -½ + z;
(v) -½ + x, ½ + y, z.

tors). One anion oxygen is the acceptor in two hydrogen bonds, and each of the others is the acceptor in four appreciably longer bonds. Each nitrogen is the hydrogen donor in two bonds. The three-dimensional network inlcudes large voids extending parallel to *b* and centred near x = 0.12, z = 0.57, towards which the non-polar methyl groups are directed.

In GPPW the hydrogen-bond network is also three-dimensional. Its main features (Figure 2) are (i) chains parallel to *b* involving one cation [N(1,2,3)] and the anion; (ii) anion-anion cross-links via this cation and the lattice water Aq(1); and (iii) cross-links along *a* involving the other cation [N(4,5,6)] and water Aq(2). Not all cation H atoms appear to participate. The water molecules act as spacers, permitting the hydrogen-bond network to avoid the large, non-polar phenyl groups.

Anisotropic thermal parameters (x 10^4) for GPA, $(CH_6N_3)_2HPO_3$, $(CH_3)_2CO$*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	227(6)	313(7)	263(9)	15(11)	−26(19)	4(8)
O(1)	324(23)	463(26)	563(35)	198(27)	−56(36)	5(26)
O(2)	306(33)	413(29)	337(60)	75(24)	53(38)	−14(21)
O(3)	207(30)	482(31)	286(55)	51(25)	−9(35)	27(18)
O(4)	420(24)	530(27)	533(32)	215(32)	55(40)	−13(27)
N(1)	350(27)	411(25)	407(36)	−106(32)	40(52)	−3(35)
N(2)	331(32)	440(33)	425(49)	−77(38)	−75(39)	36(27)
N(3)	282(30)	397(29)	399(47)	−117(34)	−63(37)	8(26)
N(4)	345(28)	396(25)	391(37)	114(31)	66(54)	20(34)
N(5)	375(34)	364(32)	402(47)	103(35)	83(38)	31(28)
N(6)	346(30)	457(31)	321(45)	114(33)	10(39)	101(28)
C(1)	338(39)	238(26)	319(43)	62(28)	−37(45)	44(32)
C(2)	305(33)	249(26)	282(39)	−20(28)	−12(48)	−26(33)
C(3)	472(43)	370(30)	399(47)	11(33)	23(51)	−27(42)
C(4)	722(79)	705(57)	772(94)	226(71)	106(78)	258(65)
C(5)	766(77)	682(66)	484(76)	71(46)	276(70)	−242(49)

Anisotropic thermal parameters (x 10^4) for GPPW, $(CH_6N_3)_2(C_6H_5PO_3)$, $2H_2O$*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U13	U12
P	326(5)	250(5)	238(5)	−3(5)	174(4)	2(5)
O(1)	342(16)	410(18)	357(17)	98(14)	196(14)	13(14)
O(2)	417(17)	367(17)	341(16)	−10(14)	247(14)	−31(14)
O(3)	481(19)	357(18)	365(16)	−56(15)	252(15)	−27(15)
Aq(1)	1172(37)	430(23)	423(21)	−67(18)	441(24)	−225(24)
Aq(2)	500(23)	591(25)	795(30)	−187(23)	269(22)	−6(20)
N(1)	456(28)	291(19)	347(19)	−14(16)	238(18)	8(17)
N(2)	651(28)	229(18)	420(22)	−26(17)	350(22)	−14(19)
N(3)	644(26)	374(21)	337(20)	−50(18)	313(20)	−29(21)
N(4)	387(23)	66(34)	687(32)	38(27)	286(24)	42(24)
N(5)	453(29)	845(39)	480(27)	−67(28)	201(23)	81(26)
N(6)	367(25)	1043(45)	788(36)	−144(34)	292(25)	41(28)
C(1)	342(22)	316(23)	300(21)	46(18)	153(19)	3(19)
C(2)	440(27)	582(32)	348(24)	−92(23)	224(22)	−73(25)
C(3)	518(32)	865(51)	432(29)	−213(31)	221(26)	−127(33)
C(4)	351(28)	805(44)	528(33)	−49(31)	184(25)	−859(30)
C(5)	457(33)	880(46)	601(39)	−135(33)	350(32)	−167(32)
C(6)	407(27)	654(34)	395(25)	−123(25)	231(22)	−39(25)
C(7)	299(21)	356(24)	299(22)	54(19)	173(18)	16(19)
C(8)	465(32)	457(34)	621(37)	−188(29)	264(30)	−69(26)

*The temperature factor is in the form $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2klb^*c^*U_{23})]$

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