Preparation, Properties, and Crystal Structure of the Cyclic Compound formed by the Thermal Dehydration of 1-Hydroxyethylidenediphosphonic Acid

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The thermal dehydration of 1-hydroxyethylidenediphosphonic acid at 170—180° produces a compound of formula $C_4H_{12}O_{12}P_4$ which has a multi-acid function. The tetra-ammonium salt of this acid crystallises as the dihydrate in space group *Pbca* with cell dimension *a* = 8·745(15), *b* = 13·24(3), *c* = 16·41(3) Å and *Z* = 4. The structure has been solved by Patterson and Fourier techniques and refined by block-diagonal least-squares methods to *R* = 0·105 for 819 independent reflections. The anion has been shown to contain a $\overline{\mathrm{POCPOC}}$ heterocycle possessing a crystallographic centre of symmetry. The chemical and physical properties of the compound are described.

In recent years 1-hydroxyethylidenediphosphonic acid (EHDP) $CH_3C(OH)[PO(OH)_2]_2$ has attracted attention as a potentially useful material.[1] It has been prepared by a variety of routes, most of which involve reactions of phosphorus(III) compounds (*e.g.* phosphorous acid and phosphorus trichloride) with acetic acid or acetylating agents such as acetyl chloride or acetic anhydride. The reaction conditions have been shown to be important since more complex products, including both linear and cyclic compounds, can be formed under different experimental conditions.[2-4] This subject has recently been reviewed.[5]

As part of a wider investigation we have studied the thermal dehydration of EHDP over a range of temperatures and pressures.

RESULTS AND DISCUSSION

The thermal dehydration of EHDP was performed over a range of conditions using thermogravimetric techniques. The products at each stage of the dehydration were examined by paper chromatography and by i.r., ^1H, and ^{31}P n.m.r. spectroscopy. Some decomposition occurred during the dehydration producing phosphite and phosphate and in order to keep this to a minimum the dehydration was carried out at low pressure so that the water produced could be removed quickly. When EHDP (in its hydrated form, EHDP,$\frac{1}{2}H_2O$) was heated to 100—120° under vacuum, the half mole of water of crystallisation was evolved, leaving the anhydrous material. On further heating at 170—180° under vacuum, one mole of water was liberated per mole of EHDP leaving a white powder. The paper chromatogram of the latter material showed a spot at a low R_F value indicating a more complex compound together with faint spots which identified small quantities of phosphite, phosphate, and unreacted EHDP.

Complete removal of impurities from the powder was difficult because of similarities in physical and chemical properties to those of the main product but most were removed by extraction with methanol, in which the complex material is sparingly soluble. As an aid to further purification, the methyl ester was prepared by reaction of the partially purified product with trimethyl orthoformate.† The empirical formula of this ester was shown by analysis to be $C_5H_{12}O_6P_2$ and its molecular weight in acetone solution was found to be 467 corresponding to the dimeric molecular formula $C_{10}H_{24}O_{12}P_4$. The ^1H n.m.r. spectrum of the compound was complex and consisted of two sets of signals centred on τ 6·1 (OCH_3) and 8·0 (CCH_3) in the intensity ratio 3 : 1. This is consistent with formulation of the compound as the hexamethyl ester $Me_6C_4H_6O_{12}P_4$ related to the parent compound $C_4H_{12}O_{12}P_4$.

The hexa-ammonium salt $[NH_4]_6[C_4H_6O_{12}P_4],2H_2O$ was prepared by dissolving the crude dehydrated product in the minimum amount of water, adding an excess of 0·880 ammonia to the solution and crystallising the product after addition of ethanol. The tetra-ammonium salt $[NH_4]_4[C_4H_8O_{12}P_4],2H_2O$ was readily formed from the hexa-ammonium salt by boiling the latter in water and crystallising the product from ethanol–water.

The above results can be explained if dehydration of EHDP produces a molecule containing four phosphorus atoms. Now the thermogravimetric experiments show that two moles of water are lost per two moles of EHDP hence the formula of the product would be expected to be $C_4H_{12}O_{12}P_4$ according to equation (1). This is in

$$2C_2H_8O_7P_2 \longrightarrow 2H_2O + C_4H_{12}O_{12}P_4 \qquad (1)$$

agreement with the formula deduced from investigation of the methyl ester and the ammonium salts.

Dehydration may occur in several ways which can

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† When diazomethane was used as methylating agent, a second hexamethyl ester (m.p. 452—454 K) was also formed. The fine structure in the ^1H n.m.r. spectra of the two compounds and their *X*-ray diffraction powder photographs differed; this suggests that the two compounds are conformational isomers.

[1] A list of some of the many patents on this material are given in ref. 2. The EHDP used in this work was prepared according to Albright and Wilson, B.P. 1,102,525 (1965).

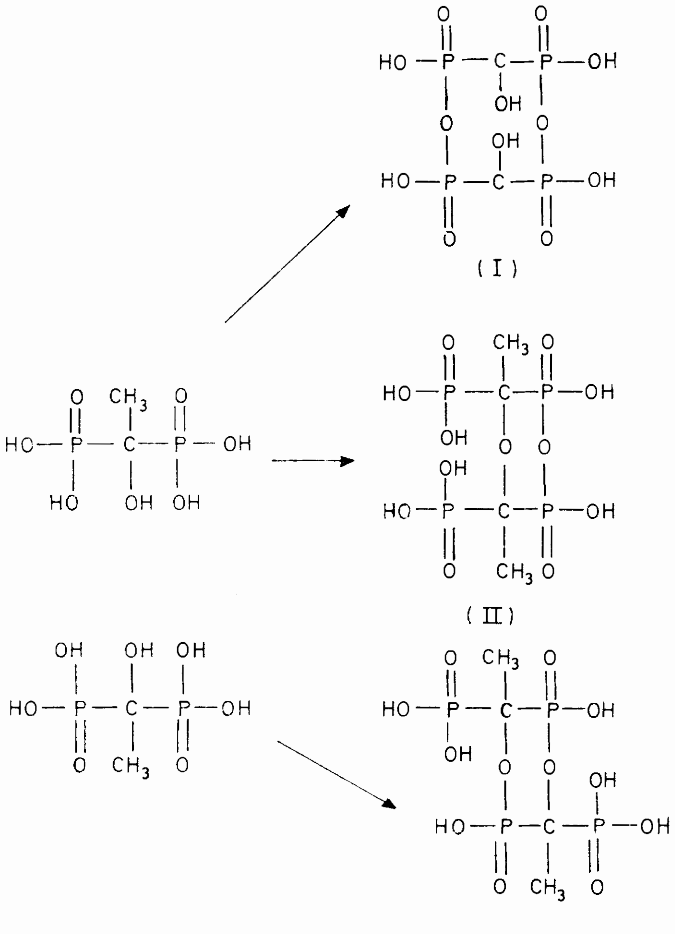
[2] J. B. Prentice, O. T. Quimby, R. J. Grabenstetter, and D. A. Nicholson, *J. Amer. Chem. Soc.*, 1972, **94**, 6119.

[3] B. Blaser, K. H. Worms, A. G. Germscheid, and K. Wollman, *Z. anorg. Chem.*, 1971, **381**, 247.

[4] G. Brun and C. Blanchard, *Comp. rend.*, 1971, **272c**, 2154.

[5] J. D. Curry, D. A. Nicholson, and O. T. Quimby, ‘Topics in Phosphorus Chemistry,’ Interscience, New York, vol. 7, p. 37.

afford compounds with different structures. The three most likely dehydrations are:

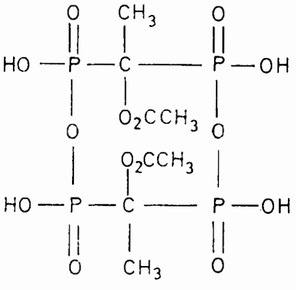


(I)

(II)

(III)

Different compounds which incorporate all three structures have been previously reported. Compound (IV) contains structure (I) and is prepared from phosphorous acid together with a large excess of acetic anhydride.[2] It hydrolyses rapidly in aqueous solution and its ^{1}H and ^{31}P n.m.r. spectra have not been unequivocally assigned although they might be expected to be relatively simple since the phosphorus atoms are equivalent. Further when equivalent quantities of phosphorous acid and acetic anhydride are refluxed for 6 h, a solid is precipitated which has been assigned structure (II). The assignment is based on the ^{31}P n.m.r. spectrum which consists of two complex signals of equal intensity [2] and the authors concluded that the difference in the two chemical shifts showed that the molecule contained a P–O–P link as shown in structure (II) rather than the two PCOP links as in structure (III). It has recently been reported that a compound based on structure (III) is formed from the reaction of acetyl chloride with phosphorous acid in a sealed tube at 120° for 6 h. *X*-Ray analysis of the derived calcium salt showed that the molecule contains a centrosymmetric POCPOC heterocycle.[6]



(IV)

The product formed in the present work from the thermal dehydration of EHDP is only slowly hydrolysed by water and its ^{1}H and ^{31}P n.m.r. spectra show that it contains phosphorus atoms in different environments. These observations are inconsistent with structure (I) but fit to either (II) or (III): the latter are difficult to interdistinguish, however, and hence the crystal structure of the tetra-ammonium salt was determined.

X-*Ray Structure*.—Only the formulation (III) is consistent with a space-group requirement that the $[C_4H_8O_{12}P_4]$ anion have a centre of symmetry. This assignment is confirmed by the structure found for the anion shown in Figure 1.[7] The six-membered POCPOC ring adopts a chair configuration, with the phosphorus and carbon atoms coplanar to within 0·05 Å and the O atoms lying 0·54 Å above and below the plane. The methyl and PO_3 groups attached to the ring carbon atoms adopt axial and equatorial positions, respectively. The distribution of P–O distances suggests that O(23) is associated with the remaining acid hydrogen atom and the close approach of O(21) from a neighbouring anion at 2·50 Å indicates that, in the crystal structure, the anions are linked together by hydrogen bonding to form infinite chains, as seen in Figure 2.[7] A small peak observed between these two oxygen atoms on a difference Fourier summation is considered to be the approximate position of the acid hydrogen atom.

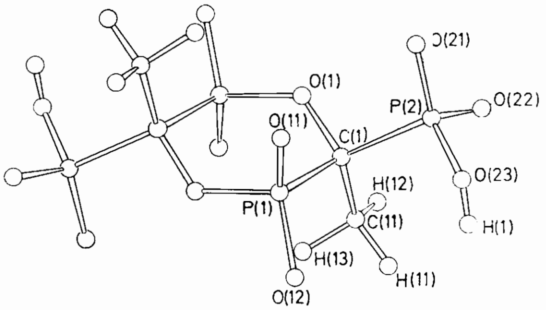


FIGURE 1 The anion $[C_4H_8O_{12}P_4]^{4-}$

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[6] E. Philippot, J. C. Jumas, G. Brun, and M. Maurin, *Cryst. Struct. Comm.*, 1971, **1**, 103.

[7] Produced using ORTEP: A Fortran Thermal-ellipsoid Plot Program for Crystal Structure Illustrations, by C. K. Johnson. Oak Ridge National Laboratory Report, 1965, ORNL 3794.

Assignment of the remaining non-hydrogen atom sites as ammonium ions and water molecules was made from an examination of interatomic distances, shown in Table 3. N(1) is clearly a cation site, having only the negatively charged phosphate O atoms as nearest neighbours. Either O(3) or N(2) could, in fact, be the remaining cation but not both, in view of their mutual interatomic distance of only 2·72 Å. Unfortunately, the attached hydrogen atoms were not clearly resolved on the final difference-Fourier summation. The structural details are in close correspondence with those reported for the dicalcium salt.[6]

The cyclic tetraphosphonic acid (III) can, therefore, be prepared either by reaction of acetyl chloride with phosphorous acid or by the thermal dehydration of EHDP. Its ready formation by the first reaction is of interest, since the method which is reported to produce the compound with structure (II) employs similar reaction conditions, the major difference being the use of acetic anhydride as acetylating agent rather than acetyl chloride. It is also significant that the ^{31}P n.m.r. chemical shifts for the compound shown to have structure (III) are identical with those for the compound with structure (II). A further surprising feature was that treatment of compound (III) with trimethyl orthoformate produced the hexamethyl ester, m.p. 412—414 K, which is very close to the m.p. of the hexamethyl ester of structure (II) (414—417 K).[8]

The above anomalies caused us to reprepare compound (II) by the literature method and compare it, together with some of its derivatives, with the corresponding compounds of structure (III).

Thus, the cyclic tetraphosphonic acids, the tetra-ammonium salts, and the hexamethyl esters of both (II) and (III) were all examined by *X*-ray powder photography. The photographs of the free acids were found to be superimposable, as were those of the tetra-ammonium salts and the hexamethyl esters.

The above results strongly suggest that the compound previously reported to possess structure (II) does in fact have structure (III) and that the cyclotetraphosphonic acid of structure (II) has not so far been synthesised.

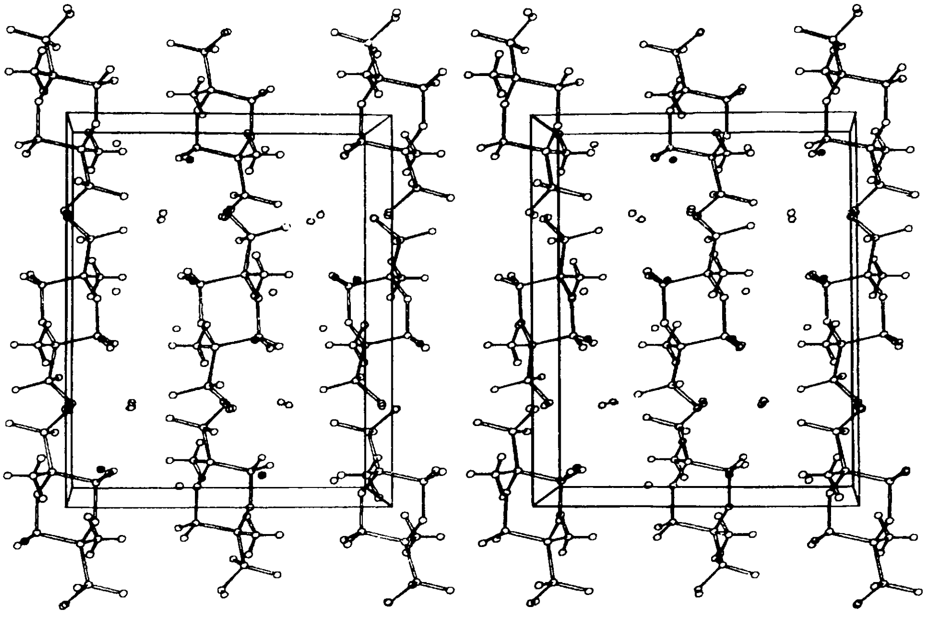

FIGURE 2 Projection of the unit cell contents in the *bc* plane

EXPERIMENTAL

Spectra.—Molecular weight measurements were made on a Mechrolab 301A osmometer. The mass spectra were obtained from an A.E.I. MS 9 mass spectrometer and the ^{1}H and ^{31}P n.m.r. spectra from Perkin-Elmer R10 and R14 spectrometers (at 60 and 100 MHz, respectively, for hydrogen and 24·3 MHz on the R10 for phosphorus). Tetramethylsilane or the sodium salt of trimethylsilylpropanesulphonic acid were used as internal references for the hydrogen spectra and 25% H_3PO_4 was used as external reference for the ^{31}P spectra. The *X*-ray powder diffraction patterns were obtained using a Guinier focussing camera and Cu-K_α radiation.

X-Ray Data Collection.—Crystals grown from aqueous solution were well formed, multifaceted, prisms. Data were collected from a crystal with approximate dimensions 0·2 mm cube using an automated Stoe Weissenberg diffractometer and a graphite crystal monochromator. A stationary background-ω-scan-stationary background measurement cycle was used, with 10 s background and a scan range of $(0{\cdot}9 + 0{\cdot}25\ L)°$, where L is the Lorentz factor, at 1° min^{-1}. A standard reflexion was remeasured every 30 reflexions to check the stability of crystal and equipment. Reciprocal layers 0—7*kl* and *hk*0—3 were collected from the same crystal. 980 Reflexions were used in the structure analysis

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[8] D. A. Nicholson, W. A. Cilley, and O. T. Quimby, *J. Org. Chem.*, 1970, **35**, 3149.

satisfying the criterion $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the reflexion intensity I computed from counting statistics. No averaging of common reflexions was undertaken until refinement was complete. Lattice constants were obtained by accurate measurement of zero-layer precession photographs. No absorption correction was made.

Crystal Data.—$C_4H_{28}N_4O_{14}P_4$, M = 480·2, Orthorhombic, a = 8·745(15), b = 13·24(3), c = 16·41(3) Å, U = 1900 Å^3, D_m = 1·68, Z = 4, D_c = 1·68, $F(000)$ = 1008, Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K) = 4·8 cm^{-1}. Space group *Pbca* from systematic absences.

Structure Solution and Refinement.—Phosphorus atoms were located from a three-dimensional sharpened Patterson synthesis. Remaining non-hydrogen atoms were located from successive cycles of structure factor calculation and difference Fourier syntheses. As it was not possible to locate all hydrogen atoms, an unambiguous assignment of the water molecule and ammonium ion sites could not be made.

Least squares refinement was carried out using the block-diagonal approximation, including the positional and thermal parameters of one atom in a single matrix but no allowance for correlation between the parameters of separate atoms was made. A weight for each reflexion was obtained from the expression $1/W = 10 \pm F_o$, which gave a satisfactorily constant distribution of $w\Delta^2$ when averaged over intervals of $F_o \sin\theta/\lambda$ and the Weissenberg layer. Convergence was obtained at R = 0·103 for 980 reflexions which became R = 0·105 for 819 independent reflexions after averaging [R was 0·089 for the 660 reflexions with $I \geqslant 3\sigma(I)$]. The final structure factor calculation included anisotropic temperature factors for all non-hydrogen atoms. The thermal parameters of O(3), the presumed water oxygen atom, refined to values representing a large amplitude of vibration in the b axis direction. As the average thermal component does not have an unreasonable magnitude, the anisotropy may be due to slight disorder in position of O(3) along the y axis. Three methyl hydrogen atoms and the acidic hydrogen attached to O(23) were also included using co-ordinates obtained from a difference Fourier, and assumed isotropic temperature factors B = 4 Å^2. A final difference Fourier had no peaks greater than 1·0 eÅ^{-3} or less than −0·8 eÅ^{-3}. Scattering factors used were from ref. 9. Observed and calculated structure factors are listed in Supplementary Publication No. 20960 (6 pp.)* Final atomic positional and thermal parameters are in Tables 1 and 2, bond lengths and angles are in Table 3.

TABLE 1

Atomic fractional co-ordinates [a]

Atom	x	y	z
P(1)	0·0466(6)	0·0913(3)	−0·0668(2)
P(2)	0·0631(5)	0·0678(3)	0·1893(2)
C(1)	−0·0305(13)	0·0438(9)	0·0920(8)
C(11)	−0·1906(18)	0·0948(13)	0·0905(9)
O(1)	0·0672(13)	0·0890(7)	0·0316(6)
O(11)	−0·0978(15)	0·1448(7)	−0·0890(6)
O(12)	0·1966(15)	0·1332(9)	−0·0975(8)
O(21)	0·2293(14)	0·0384(8)	0·1832)6)
O(22)	0·0362(14)	0·1744(7)	0·2132(7)
O(23)	−0·0190(13)	−0·0089(8)	0·2486(7)
O(3)	0·0729(20)	0·3978(18)	0·0787(9)
N(1)	0·2876(17)	0·2992(9)	0·2521(8)
N(2)	0·3884(17)	0·1516(11)	0·0488(11)
H(1)	−0·114	−0·003	0·254
H(11)	−0·267	0·069	0·136
H(12)	−0·188	0·171	0·090
H(13)	−0·256	0·065	0·037

[a] In this and subsequent Tables, estimated standard deviations of the last figure are given in parentheses

Paper Chromatography.—The chromatograms were run on Schleicher and Schull 589 orange ribbon special paper or Whatman No. 1 medium flow paper. Ebels acid (pH *ca.* 1·8), consisting of isopropanol (75 ml), water (25 ml), ammonium hydroxide (0·3 ml, 20%), and trichloroacetic acid (5 g), was used as solvent and the developer spray was a solution of perchloric acid (5 ml, 60%), conc. hydrochloric acid (1 ml), and ammonium molybdate (1 g), the mixture being made up to 100 ml with water.

TABLE 2

Atomic thermal parameters [a]/Å^2

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
P(1)	4·7(2)	1·3(1)	0·7(1)	0·0(1)	−0·2(2)	−0·4(2)
P(2)	2·0(2)	1·9(1)	1·1(1)	−0·6(1)	−0·2(1)	0·0(1)
C(1)	0·4(5)	1·6(5)	1·1(4)	−0·1(4)	−0·3(4)	−0·4(4)
C(11)	1·9(6)	4·6(8)	1·0(5)	0·0(7)	−0·2(5)	0·3(6)
O(1)	2·5(5)	2·3(4)	1·6(3)	0·2(3)	0·5(4)	−0·5(4)
O(11)	6·2(7)	1·6(4)	1·1(4)	0·4(4)	−0·8(5)	0·4(4)
O(12)	5·3(7)	3·8(5)	2·2(5)	0·2(5)	−0·3(5)	−2·4(5)
O(21)	3·5(6)	4·0(5)	1·6(4)	0·8(4)	−0·2(5)	0·1(4)
O(22)	3·6(6)	2·6(4)	2·9(5)	−0·6(4)	−0·6(5)	−0·4(5)
O(23)	3·7(6)	3·9(5)	1·7(4)	0·8(5)	0·7(4)	0·2(5)
O(3)	4·4(9)	14·3(1·5)	2·2(7)	−2·4(9)	0·0(7)	−5·5(1·0)
N(1)	6·0(8)	4·1(5)	3·1(5)	1·0(6)	−0·6(6)	0·5(6)
N(2)	3·4(7)	2·5(6)	6·0(1·0)	−0·2(7)	0·9(7)	−0·6(5)

[a] Thermal parameters are coefficients in the expression: $\exp\{-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}kl^*b^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)\}$.

TABLE 3

Some interatomic distances (Å) and angles (°)

(*a*) Atoms	Distance Bond lengths in anion	Atoms	Distance
P(1)–O(1)	1·626(11)	P(1)–O(11)	1·492(13)
P(1)–C(1)	1·841(13)	P(1)–O(12)	1·511(13)
C(1)–O(1)	1·439(16)	P(2)–O(21)	1·508(13)
C(1)–C(11)	1·554(19)	P(2)–O(22)	1·484(11)
P(2)–C(1)	1·821(13)	P(2)–O(23)	1·578(11)
O(21) · · · O(23)	2·50(2)	O(23)–H(1)	0·8(2)
Co-ordination around NH_4^+ and H_2O, less than 3·0 Å.			
N(1) · · · O(12)	2·74(2)	N(2) · · · O(3)	2·72(2)
N(1) · · · O(22)	2·79(2)	N(2) · · · O(11)	2·78(2)
N(1) · · · O(22)	2·82(2)	N(2) · · · O(12)	2·94(2)
N(1) · · · O(11)	2·95(2)	N(2) · · · O(1)	2·94(2)
O(3) · · · N(2)	2·72(2)	O(3) · · · O(11)	2·94(2)
(*b*) Atoms	Angle	Atoms	Angle
O(1)–P(1)–C(1)	102·3(7)	P(2)–C(1)–C(11)	110(1)
O(1)–P(1)–O(11)	110·2(6)	P(1)–O(1)–C(1)	128·8(9)
O(1)–P(1)–O(12)	104·0(7)	C(1)–P(2)–O(21)	109·3(6)
C(1)–P(1)–O(11)	110·0(6)	C(1)–P(2)–O(22)	109·0(6)
C(1)–P(1)–O(12)	110·4(7)	C(1)–P(2)–O(23)	102·9(6)
O(11)–P(1)–O(12)	118·6(7)	O(21)–P(2)–O(22)	114·5(7)
P(1)–C(1)–O(1)	107(1)	O(21)–P(2)–O(23)	108·3(6)
P(1)–C(1)–P(2)	113·6(7)	O(22)–P(2)–O(23)	112·1(7)
P(1)–C(1)–C(11)	110(1)	O(21) · · · H(1)–O(23)	150
O(1)–C(1)–P(2)	105(1)		
O(1)–C(1)–C(11)	110(1)		

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. Items less than 10 pp. are sent as full-size copies.

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

In all cases the paper chromatography experiments employed standard solutions of EHDP (R_F 0·35), phosphorous (R_F 0·71), and phosphoric acid (R_F 0·61) or their ammonium salts (R_F 0·31, 0·57, and 0·62 respectively) on the edges of the paper.

Preparation of the Tetraphosphonic Acid $C_4H_{12}O_{12}P_4$.—A quantity of EHDP,$\frac{1}{2}H_2O$ (23·5 g, Albright and Wilson Ltd.) was heated under vacuum ($<$0·5 mmHg) for 6 h at 443—453 K. A weight loss of 2·8 g resulted giving 20·7 g of crude product. The material evolved during the dehydration of EHDP,$\frac{1}{2}H_2O$ was shown by i.r. spectroscopy to be water, together with traces of phosphine, acetaldehyde, and acetic acid. The crude product was shaken successively with two 20 ml quantities of dry methanol and the remaining solid was filtered and dried (13·6 g, 66%) (Found: C, 12·9; H, 3·3; P, 33·2. Calc. for $C_4H_{12}O_{12}P_4$: C, 12·8; H, 3·2; P, 33·0%). N.m.r.: τ (D_2O) 8·1 [t, 6H, *J*(PH) 16 Hz, 2 × CH_3], and OH (exchangeable in D_2O); ^{31}P n.m.r. (H_2O) −16·0 [m, 2P, $PO(OH)_2$], and −5·5 p.p.m. (m, 2P, ring P).

The compound readily hydrolysed in the acid solvent used in chromatography and hence runs produced a long tail ’: this meant that the R_F value could not be determined accurately.

Preparation of the Hexa-ammonium Tetraphosphonate $[NH_4]_6[C_4H_6O_{12}P_4],2H_2O$.—Dehydration of EHDP,$\frac{1}{2}H_2O$ (71 g) by the method described above was first carried out and the crude product was dissolved in the minimum amount of water. The solution was made alkaline (pH *ca.* 10) by addition of 0·880 ammonia solution: ethanol was then added until the solution became cloudy. It was heated on a steam-bath for 30 min and after cooling, white crystals formed (42 g, 50%) (Found: C, 9·4; H, 6·5; N, 16·2; P, 23·9. $C_4H_{34}N_6O_{14}P_4$ requires C, 9·3; H, 6·6; N, 16·3; P, 24·1%; R_F 0·12).

Preparation of Tetra-ammonium Tetraphosphonate $[NH_4]_4[C_4H_8O_{12}P_4],2H_2O$.—Hexa-ammonium tetraphosphonate (6·2 g) was dissolved in the minimum quantity of boiling water. The solution was cooled and ethanol was added until the solution became cloudy. It was then heated on a steam-bath and allowed to cool when white crystals appeared. They were filtered and dried (4·9 g, 84%) (Found: C, 10·4; H, 6·0; N, 11·8; P, 25·8. $C_4H_{28}O_{14}P_4N_4$ requires C, 10·0; H, 5·8; N, 11·7; P, 25·8%) R_F 0·12, τ (D_2O) 8·2 [t, 6H, *J*(PH) 16 Hz, 2 × CH_3], and OH +NH_4 (exchangeable in D_2O); ^{31}P n.m.r. (H_2O) −16·5 [m, 2P, $PO(OH)_2$] and −8·3 p.p.m. (m, 2P, ring P).

Preparation of Hexamethyl Tetraphosphonate $Me_6C_4H_6O_{12}P_4$.—The tetraphosphonic acid (12·2 g) was added to trimethyl orthoformate (25 ml) and the mixture heated. When the tetraphosphonic acid had dissolved, the solution was refluxed for 30 min and the volatile products removed by distillation at reduced pressure. The resulting solid was recrystallised from ether–ethyl acetate mixture (8·6 g, 58%), m.p. 412—414 K (Found: C, 26·5; H, 5·4; P, 26·9%; *M*, 467. Calc. for $C_{10}H_{24}O_{12}P_4$: C, 26·1; H, 5·2; P, 26·9%; *M*, 460); *m/e* 460 (M^+, 76%); τ ($CDCl_3$) 6·1 (m, 18H, 6 × OCH_3), and 8·0 (m, 6H, 2 × CCH_3, ^{31}P n.m.r. ($CHCl_3$) −16·8 [m, 2P, $PO(OH)_2$] and −7·3 p.p.m. (m, 2P, ring P).

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