Table 1. *Atomic coordinates* (Å)

	x	y	z
Na	0·000	0·000	0·000
P	$1{\cdot}924=\frac{1}{3}a$	$3{\cdot}849=\frac{2}{3}a$	1·882
N	$1{\cdot}924=\frac{1}{3}a$	$3{\cdot}849=\frac{2}{3}a$	3·645
O	0·873	4·479	1·516
H (assumed)	2·81	3·74	3·97

Table 2. *Mean square vibration amplitudes* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Na	0·018	0·018	0·012	0·009	0·000	0·000
P	0·006	0·006	0·011	0·003	0·000	0·000
N	0·016	0·016	0·014	0·008	0·000	0·000
O	0·017	0·011	0·024	0·011	−0·001	−0·007

The coordinate e.s.d.'s given by the least-squares process are 0·008 Å for Na, 0·007 Å for P, 0·018 Å for N and 0·008 Å for O. The e.s.d.'s of the U_{ij} range from 0·001 Å^2 for U_{11} of *P* to 0·007 Å^2 for U_{33} of N. The vibrations of the oxygen and nitrogen atoms in the PO_3NH_3 ion are rather greater than those of the phosphorus and imply molecular angular oscillations about any axis of about 4° r.m.s. amplitude. Correspondingly, the P–O and P–N bond lengths should be increased by about 0·006 Å as compared with those calculated from the coordinates of Table 1.

With these corrections the molecular dimensions are P–O $=1{\cdot}522\pm0{\cdot}011$ Å, P–N $=1{\cdot}769\pm0{\cdot}019$ Å, $\angle$N–P–O $=103°\,58'$ and $\angle$O–P–O′ $=114°\,22'$. The lengths are within 0·016 Å and the angles within 1° 2′ of those given by Hobbs *et al.*

Since the nitrogen is bonded to three hydrogen atoms, there can be no π character in the P–N bond. Consequently we may take $1{\cdot}77\pm0{\cdot}02$ Å as the value of the P–N single-bond length. This is close to the 1·76 Å estimated by the Schomaker–Stevenson method. The P–O length is about 0·02 Å shorter than in the phosphate ion. The increased π-bond order in the phosphoramidate ($2\times\frac{1}{3}$ as against $2\times\frac{1}{4}$) is evidently partially offset by a reduced effective nuclear charge for the 3*d*-orbitals.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N.
II. $Na_4P_2O_7.10H_2O$

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(*Received* 4 *June* 1963)

The crystallographic data given by MacArthur & Beevers (1957) have been used in a structure refinement. The revised molecular dimensions are P–O(bridge) $=1{\cdot}61\pm0{\cdot}015$, P–O(outer) $=1{\cdot}51\pm0{\cdot}015$ Å, $<$P–O–P $=133\,°38'$.

The crystal structure of sodium pyrophosphate decahydrate, $Na_4P_2O_7.10\,H_2O$, was determined by MacArthur & Beevers (1957) by difference syntheses for the three principal zones, which were refined to residuals *R* of about 22%. The interesting results obtained for the dimensions of other isoelectronic X_2O_7 ions, notably $S_2O_7^{2-}$ (Lynton & Truter, 1960) and $Si_2O_7^{6-}$ (Cruickshank, Lynton & Barclay, 1962) suggested that improved dimensions of the pyrophosphate $P_2O_7^{4-}$ ion would be worth seeking.

The space group is *I*2/*c*, with cell dimensions $a=17{\cdot}93$, $b=6{\cdot}96$, $c=14{\cdot}85$ Å and $\beta=118°\,31'$. Each P_2O_7 ion lies on a twofold axis which passes through

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the central oxygen O(1) common to the two phosphate tetrahedra. Two sodium atoms and five water molecules are in general positions.

The data used in the refinement were the 246 non-zero $|F_o|$ for the three zones given by MacArthur & Beevers. Four cycles of least-squares refinement were carried out. Apart from the y coordinate of the water molecule W_2 which shifted by 0·19 Å owing to a change of its sign, the maximum coordinate shift in the refinement was 0·06 Å. The residual R dropped to a final 13·8%. The revised atomic coordinates and their e.s.d.'s are shown in Table 1. The e.s.d.'s are those given by the chain-diagonal least-squares process; they ought to be increased slightly to allow for overlapping in the projections. Anisotropic vibrations were introduced for all atoms, but as these proved neither very large nor very anisotropic it will suffice to record thet the apparent mean-square-vibration amplitudes were approximately 0·01 Å^2 for phosphorus, 0·02 Å^2 for the oxygens of the ion, 0·026 Å^2 for the water molecules and 0·02 Å^2 for the sodiums. The weighting scheme used was

$$w = 1/(6{\cdot}0 + |F_o| + |F_o|^2/106{\cdot}5)\ ,$$

with the $|F_o|$ appropriate to the whole cell, but without the scale factor 1·07 ± 0·03 indicated by the least-squares process.

Table 1. *Atomic coordinates and e.s.d.'s*

	x	y	z
P	1·176 ± 0·005 Å	1·862 ± 0·008 Å	3·226 ± 0·005 Å
Na(1)	4·317 ± 0·010	4·822 ± 0·011	2·008 ± 0·011
Na(2)	6·896 ± 0·010	6·329 ± 0·012	1·242 ± 0·011
O(1)	0	1·232 ± 0·029	3·7125 = $\frac{1}{4}c$
O(2)	0·446 ± 0·015	3·095 ± 0·017	2·297 ± 0·018
O(3)	1·397 ± 0·017	0·769 ± 0·022	2·345 ± 0·018
O(4)	2·584 ± 0·017	2·212 ± 0·019	4·709 ± 0·019
W(1)	1·793 ± 0·018	4·106 ± 0·021	0·725 ± 0·019
W(2)	4·280 ± 0·016	−0·070 ± 0·029	3·211 ± 0·020
W(3)	4·840 ± 0·019	2·885 ± 0·021	0·349 ± 0·019
W(4)	7·008 ± 0·020	5·139 ± 0·021	3·325 ± 0·017
W(5)	7·475 ± 0·018	4·296 ± 0·021	0·402 ± 0·019

The lengths in the pyrophosphate ion calculated from the coordinates of Table 1 are P–O(1) (bridge) = 1·601 Å with a nominal e.s.d. of 0·013 Å, P–O(2) = 1·506, P–O(3) = 1·485 and P–O(4) = 1·520 Å. As the vibrations of the oxygen atoms are greater than those of the phosphorus atoms, a small rotational correction of about 0·01 Å must be added. The corrected dimensions may therefore be taken as P–O(1) (bridge) = 1·61 ± 0·015 Å and mean P–O(outer) = 1·51 ± 0·015 Å. The bridge angle P–O(1)–P is 133° 38′ and the O–P–O angles are

O(1)–P–O(2) = 107°
O(1)–P–O(3) = 103°
O(1)–P–O(4) = 105°
O(2)–P–O(3) = 114°
O(2)–P–O(4) = 111°
O(2)–P–O(4) = 115° .

The averages are ∠O(1)–P–O = 105° and ∠O–P–O = 113°. As compared with MacArthur & Beevers's values the main changes are that P–O(1) is now 0·02 Å shorter and the outer bonds some 0·04 Å longer.

In $K_2S_2O_7$ (Lynton & Truter, 1960), where the e.s.d.'s of the oxygen atom coordinates are as low as 0·007 Å, the pyrosulphate ion has an S–O–S angle of 124° and an S–O(bridge) bond of 1·64$_5$ Å. To get a P–O–P angle of 124° and a corresponding P–O bond of, say, 1·67 Å, the oxygen O(1) would have to be moved about 0·15 Å along the twofold axis. As the e.s.d. of this atom is about 0·03 Å, such a shift is well outside the limits of experimental error, and the larger X–O–X angle and shorter X–O(bridge) bond in the pyrophosphate ion in this crystal must be accepted as definite.

For a description of the crystal structure reference should be made to MacArthur & Beevers (1957). The revised distances for the bonds within the two sodium octahedra are

Na(1)–W(1) = 2·33 Å
–W(2) = 2·40
–W(2′) = 2·42
–W(3) = 2·76
–W(3′) = 2·75
–W(4) = 2·39

Na(2)–O(2) = 2·44 Å
–O(4) = 2·60
–W(1) = 2·46
–W(3) = 2·45
–W(4) = 2·35
–W(5) = 2·37

Apart from the Na(1)–W(2) distance, which has decreased by 0·25 Å, these value are all close to those given by MacArthur & Beevers.

Each of the three water molecules, W(1), W(2), W(4), is coordinated to two sodium atoms and two oxygen atoms, with W–O links of 2·72–2·89 Å. W(3) is coordinated to three sodium atoms, to an O(4) (2·67 Å) and to W(5) (2·97 Å). W(5) is coordinated to Na(2), W(3) (2·97 Å) and to two different O(3) (2·79 and 3·04 Å).

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