given by Davies & Corbridge. The greatest change is an increase of 0·020 Å in the length of P(2)–O(4). Fig. 1 shows the dimensions when the values of the three similar bonds in the P(2) tetrahedron are averaged.

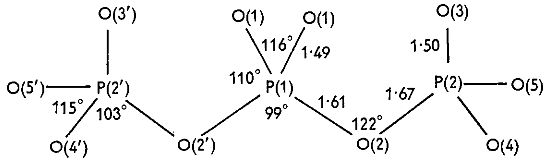

Fig. 1. Dimensions of the triphosphate ion.

Davies & Corbridge found a difference in length of the two long bonds P(2)–O(2) = 1·68 and P(1)–O(2) = 1·61 Å which they considered probably significant. This refinement confirms the dimensions as 1·67 Å and 1·61 Å. As it is an empirical rule (Cruickshank, 1961) that the average of the four bonds in a tetrahedron is roughly constant, the difference is consistent with the fact that the two short bonds in the P(1) tetrahedron are nearly equal to the three short bonds in the P(2) tetrahedron. The P(1)–O(2)–P(2) angle of 122° is the smallest known for linked phosphate tetrahedra.

The crystal structure of $Na_5P_3O_{10}$, phase I, has been determined by Corbridge (1960) from difference syntheses in two zones. Within the rather larger experimental error, the bond lengths are the same in the two P_3O_{10} ions, but some of the angles, particularly in the terminal phosphate tetrahedra, are rather different.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N.
IV. $(NH_4)_4P_4O_{12}$

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The crystallographic data given by Romers, Ketelaar, & MacGillavry (1951) have been used in a structure refinement. In the tetrametaphosphate ion the two types of ring bond have P–O = 1·65 and 1·58 Å, both ±0·03 Å. The exocyclic P–O bonds are 1·47 – 1·52 Å.

The crystal structure of ammonium tetrametaphosphate (ATMP), $(NH_4)_4P_4O_{12}$, was determined by Romers, Ketelaar & MacGillavry (1951) from three electron-density projections along [100] [110] and [010]. As no back-shift corrections seem to have been applied, it appeared worthwhile refining the structure by least squares.

The space group is *Cmca*, with cell dimensions $a = 10{\cdot}42$, $b = 10{\cdot}82$, $c = 12{\cdot}78$ Å. The structure consists of tetramer anions $P_4O_{12}^{4-}$ and NH_4^+ cations. There are four P_4O_{12} groups in the cell clustered around the 4(*a*) positions. Each tetramer has point-group symmetry 2/*m* as shown in Fig. 1. There are eight $(NH_4)_I$ at the 8(*c*) positions and eight $(NH_4)_{II}$ at the 8(*f*) positions.

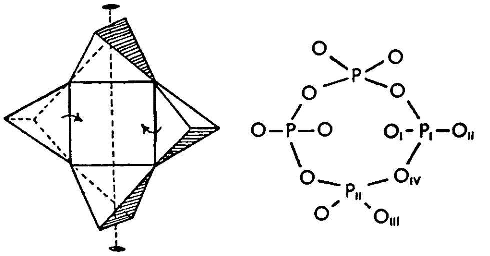

Fig. 1. Position of the P_4O_{12} group with respect to symmetry elements 2 and *m* of the space group *Cmca*.

The data used in the refinement were the 224 nonzero $|F_o|$ for the three zones given by Romers, Ketelaar & MacGillavry (1951) (the listed 003 and 0,6,14 reflexions were omitted because of suspected misprints). Four cycles of least-squares refinement were carried out. These produced coordinate shifts not exceeding 0·02 Å for either phosphorus atom or 0·06 Å for any oxygen or nitrogen atom. The residual *R* dropped from an initial 19·7% to a final 14·7% (hydrogen atoms were not included). The revised atomic coordinates are given in Table 1 and the

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vibration parameters in Table 2. Anisotropic vibrations were introduced for the heavier phosphorus atoms but not for oxygen or nitrogen. If the $|F_o|$ listed by Romers *et al.* are for one eighth of the cell contents, the $|F_o|$ scale factor determined by the LS process was $0{\cdot}88 \pm 0{\cdot}02$. The weighting scheme used was

$$w = 1/(24 + |F_o| + |F_o|^2/200)\ ,$$

with the $|F_o|$ appropriate to the whole cell, but without the factor 0·88.

With some allowance for the effects of overlapping, the coordinate e.s.d.'s given by the least-squares process are about 0·01 Å for phosphorus and 0·03 Å for oxygen or nitrogen. The e.s.d.'s of the anisotropic U_{ij} for phosphorus are about 0·004 Å^2 and of the isotropic U for oxygen or nitrogen about 0·005 Å^2. Since none of the vibration parameters exceeds 0·020 Å^2, possible coordinate corrections for the effects of molecular rotational vibrations can be neglected in comparison with the coordinate e.s.d.'s mentioned above.

Table 1. *Atomic coordinates*

	x (Å)	y (Å)	z (Å)
P_I	0	0·369	1·917
P_{II}	2·188	0	0
O_I	0	−1·094	2·086
O_{II}	0	1·350	3·084
O_{III}	2·938	−1·007	0·812
O_{IV}	1·267	0·838	0·969
$(NH_4)_I$	2·605	2·917	3·195
$(NH_4)_{II}$	0	3·402	−0·558

Table 2. *Mean square vibration amplitudes*

	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)
P_I	0·011	0·006	0·009	−0·004
P_{II}	0·003	0·012	0·010	0·004

	U (Å^2)		U (Å^2)
O_I	0·007	$(NH_4)_I$	0·015
O_{II}	0·014	$(NH_4)_{II}$	0·009
O_{III}	0·020		
O_{IV}	0·017		

The revised molecular dimensions are shown in Table 3 along with those given by Romers *et al.* The only significant change is for P_I–O_{II} which has increased from 1·44 to 1·52 Å. The difference in length between the two long ring bonds, P_I–O_{IV} = 1·65 and P_{II}–O_{IV} = 1·58 Å, is more marked, though the difference need not be taken as significant since O_{IV} has an e.s.d. of 0·03 Å. In a better analysis of the monoclinic form of $Na_4P_4O_{12}.4H_2O$ (Ondik, Block & MacGillavry, 1961) the corresponding lengths are 1·635 and 1·584 Å, with e.s.d.'s of 0·016 Å, and in a still better analysis of the triclinic form of $Na_4P_4O_{12}.4H_2O$ (Ondik, personal communication) the lengths are almost equal at 1·608 and 1·594 Å (±0·005 Å).

Table 3. *Molecular dimensions*

Values of Romers *et al.* in brackets

P_I–O_I	1·47 Å	(1·48 Å)	P_I–O_{IV}–P_{II}	130½°	(132°)
P_I–O_{II}	1·52	(1·44)	O_I–P_I–O_{II}	123½	(122)
P_I–O_{IV}	1·65	(1·63)	O_{III}–P_{II}–O_{III}	120	(120)
P_{II}–O_{IV}	1·58	(1·59)	O_{IV}–P_I–O_{IV}	100½	(100)
P_{II}–O_{III}	1·49	(1·51)	O_{IV}–P_{II}–O_{IV}	108½	(110)
			O_{III}–P_{II}–O_{IV}	108½	
			O_I–P_I–O_{IV}	110½	
			O_{II}–P_I–O_{IV}	105	

Within the P_4O_{12} ion the plane O_{IV}–P_I–O'_{IV}, makes an angle of 67° with the plane of the four O_{IV} atoms; this bending back of the P_I tetrahedron allows a reasonable P_I–O_{IV}–P_{II} angle. The intramolecular O_I–O''_{IV} distance is reduced to 3·32 Å.

As described by Romers *et al.* the crystal structure of ATMP involves a roughly tetrahedral arrangement of $N{-}H \cdots O$ hydrogen bonds around each ammonium ion. The revised $N \cdots O$ distances are

$(NH_4)_I$ to	O_{III}	2·83 Å	(twice)
	O_{II}	3·04 Å	(twice)
$(NH_4)_{II}$ to	O_I	2·77 Å	
	O_{II}	2·83 Å	
	O_{III}	2·84 Å	(twice) .

None of these values differs by more than 0·04 Å from those given earlier.

References

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