Table 3. *Shape of* TeO_6^{6-} *octahedra in some ortho-tellurates*

	Te–O (Å)	O–Te–O |maximum deviation (°) from 90°|
Ca_3TeO_6	1·913 (6)–1·924 (6)	1·6 (3)
Te(OH)$_6$ (monoclinic)	1·907 (1)–1·914 (1)	2·4 (1)
Te(OH)$_6$ (cubic)	1·913 (6)	0·8 (3)
Cu_3TeO_6	1·921 (2)	4·0 (1)
Mg_3TeO_6	1·912 (3)–1·914 (3)	4·6 (1)

The shape of the TeO_6^{6-} octahedron is essentially the same as it is in, *e.g.*, Te(OH)$_6$(monoclinic) (Lindqvist & Lehmann, 1973), Te(OH)$_6$(cubic) (Falck & Lindqvist, 1978*b*), Cu_3TeO_6 (Falck & Lindqvist, 1978*a*) and Mg_3TeO_6 (Schulz & Bayer, 1971) as can be seen in Table 3. The conclusion that the TeO_6^{6-} ion is rigid with bond lengths of about 1·92 Å (Falck & Lindqvist, 1978*a*) is confirmed by this structure determination.

We are grateful to Mr D. Heijdenrijk for his patient efforts to find suitable single crystals from our reaction product.

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Structure of Phosphorus(III,V) Oxide P₄O₇

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Abstract. P_4O_7, monoclinic, $P2_1/n$, $a = 9·808$ (2), $b = 9·966$ (1), $c = 6·852$ (1) Å, $\beta = 96·81$ (1)°, $V = 665·0$ Å³, $Z = 4$, $D_x = 2·35$ Mg m⁻³ (the pycnometric value could not be determined), 1822 reflexions, $R = 0·08$, anisotropic temperature factors. Molecules comprising four P atoms are connected *via* six bridging O atoms to form an adamantane-like cage with one additional O atom in a terminal position at the pentavalent P. Bond lengths and angles involving trivalent phosphorus are P^{III}–O–(P^{III}) 1·64 Å, P^{III}–O–(P^{V}) 1·68 Å, O–P^{III}–O 99°, P^{III}–O–P^{III} 128°, P^{III}–O–P^{V} 124°.

Introduction. The main problem in this investigation was the difficult handling of the very hygroscopic crystals. For X-ray investigations they were selected in a special box under a stream of nitrogen, which had been dried with liquid nitrogen, and enclosed in Mark tubes.

The symmetry of the intensities and the systematic absences were determined by film methods. The symmetry was found to be monoclinic; the systematic absences obeyed the following conditions: reflexions $h0l$ are only present when $h + l$ is even, and $0k0$ when k is even. Therefore the space group is $P2_1/n$. The cell parameters, previously calculated with film data, were refined by least-squares methods from the diffractometer settings of 14 reflexions.

A rod-shaped crystal 0·2 mm in diameter and 0·9 mm in length (direction [102]) was used for the

Table 1. *Atomic parameters*

$$B_{iso} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{iso} (Å^2)
P(1)	−0·1176 (1)	0·3903 (2)	0·6749 (2)	3·5 (1)
P(2)	0·1692 (1)	0·3941 (2)	0·8196 (3)	3·7 (1)
P(3)	0·0506 (2)	0·1660 (2)	0·5906 (3)	3·9 (1)
P(4)	−0·0211 (2)	0·2100 (2)	0·9883 (3)	4·6 (1)
O(12)	0·0227 (4)	0·4678 (4)	0·7279 (6)	3·8 (1)
O(13)	−0·0772 (4)	0·2753 (4)	0·5327 (6)	3·7 (1)
O(14)	−0·1372 (4)	0·3145 (5)	0·8698 (6)	4·3 (1)
O(23)	0·1716 (3)	0·2730 (4)	0·6616 (6)	3·6 (1)
O(24)	0·1109 (4)	0·3136 (5)	0·9988 (6)	4·4 (1)
O(34)	0·0086 (4)	0·1186 (4)	0·8014 (7)	4·2 (1)
O(11)	−0·2304 (4)	0·4726 (5)	0·5943 (7)	5·0 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *of* P$_4$O$_7$

P(1)–O(11)	1·439 (5)	P(3)–O(13)	1·679 (6)
O(12)	1·591 (8)	O(23)	1·635 (9)
O(13)	1·594 (9)	O(34)	1·628 (10)
O(14)	1·575 (9)	P(4)–O(14)	1·685 (6)
P(2)–O(12)	1·674 (6)	O(24)	1·660 (10)
O(23)	1·633 (10)	O(34)	1·636 (10)
O(24)	1·637 (10)		

O(11)–P(1)–O(12)	114·8 (3)	O(14)–P(4)–O(24)	96·7 (2)
O(11)	O(13)	114·5 (3)	O(14)	O(34)	98·1 (2)
O(11)	O(14)	115·9 (3)	O(24)	O(34)	99·9 (2)
O(12)	O(13)	102·7 (2)		
O(12)	O(14)	103·4 (2)		
O(13)	O(14)	103·9 (2)		
O(12)–P(2)–O(23)	99·0 (2)	P(1)–O(12)–P(2)	123·9 (3)
O(12)	O(24)	97·9 (2)	P(1)–O(13)–P(3)	124·1 (3)
O(23)	O(24)	99·9 (2)	P(1)–O(14)–P(4)	124·5 (3)
O(13)–P(3)–O(23)	98·3 (2)	P(2)–O(23)–P(3)	128·3 (3)
O(13)	O(34)	98·0 (2)	P(2)–O(24)–P(4)	128·3 (3)
O(23)	O(34)	100·3 (2)	P(3)–O(34)–P(4)	128·9 (3)

collection of intensity data on a Hilger four-circle diffractometer with Mo $K\alpha$ radiation (graphite monochromator). All 1822 independent reflexions up to $\sin\theta/\lambda = 0.67$ Å^{-1} were measured, of which 533 were unobserved ($I < 3\sigma_B$). The following conditions were used: $\omega/2\theta$ scan for $\theta > 6°$, ω scan for $\theta \le 6°$, Lp correction, no absorption correction, calculation of $\sigma_{F_{obs}}$ for unobserved reflexions according to French & Wilson (1978).

The structure was solved by direct methods and all atoms were found in the first E map. The structure was then refined by full-matrix least-squares methods with unit weights to $R = 0.08$ for all 1822 reflexions. The atomic parameters are given in Table 1,* bond lengths and angles in Table 2. A final difference map gave no

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35646 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hint that there could be more O in the structure than the composition P$_4$O$_7$ demands. This means the crystals investigated form no solid solution with P$_4$O$_8$ or P$_4$O$_9$ molecules. A refinement with the occupancy factor n for the terminal O atom as a free parameter resulted in $n = 0.95$, but this deviates from $n = 1$ only by $2\sigma(n)$ so that probably no P$_4$O$_6$ molecules are in solid solution in the crystal investigated. These facts are of interest because P$_4$O$_9$ and P$_4$O$_8$ form solid solutions with P$_4$O$_8$ and P$_4$O$_7$ respectively.

Discussion. P$_4$O$_7$ was the only molecular phosphorus(III,V) oxide of which the structure was not known. Loeper (1979) successfully prepared crystalline P$_4$O$_7$, and kindly supplied us with a sample. She obtained this compound in accordance with the method described by Walker & Mills (1975).

The geometry of the molecule is shown in Fig. 1. It belongs to the same structural type as the other molecular phosphorus oxides P$_4$O$_6$, P$_4$O$_8$, P$_4$O$_9$ and P$_4$O$_{10}$: an adamantane-like core of composition P$_4$O$_6$ with a different number of terminal O atoms. In Table 3 their bond lengths and valence angles are compared.
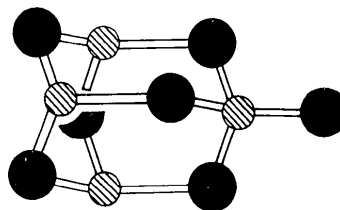

Fig. 1. The P$_4$O$_7$ molecule. Hatched circles: P, black circles: O.

Table 3. *Structural data of molecular phosphorus oxides*

Bond lengths are in Å (e.s.d. 0·003–0·017 Å) and angles in deg (e.s.d. 0·2–1·0°).

	P$_4$O$_6$	P$_4$O$_7$	P$_4$O$_8$	P$_4$O$_9$	P$_4$O$_{10}$
Reference	(a)	(b)	(a)	(c)	(c)
Molecular symmetry	$\bar{4}3m$	$3m$	$2mm$	$3m$	$\bar{4}3m$
P^{III}–O$_{br}$–(P^V)	–	1·68	1·67	1·66	–
P^{III}–O$_{br}$–(P^{III})	1·64	1·64	1·63	–	–
P^V–O$_{br}$–(P^V)	–	–	1·60	1·59	1·60
P^V–O$_{br}$–(P^{III})	–	1·59	1·58	1·60	–
P^V–O$_{term}$	–	1·44	1·41	1·42	1·43
O$_{term}$–P^V–O$_{br}$	–	115	115	117	117
O$_{br}$–P^V–O$_{br}$	–	103	103	102	102
O$_{br}$–P^{III}–O$_{br}$	100	99	98	97	–
P^V–O$_{br}$–P^V	–	–	121	123	124
P^V–O$_{br}$–P^{III}	–	124	124	127	–
P^{III}–O$_{br}$–P^{III}	126	128	130	–	–

References: (a) Beagley, Cruickshank, Hewitt & Jost (1969). (b) This work. (c) Beagley, Cruickshank, Hewitt & Haaland (1967).

Table 4. *Unit cells of phosphorus*(III,V) *oxides*

In the case of P_4O_9 the unit cell according to crystallographic symmetry has been transformed for better comparison.

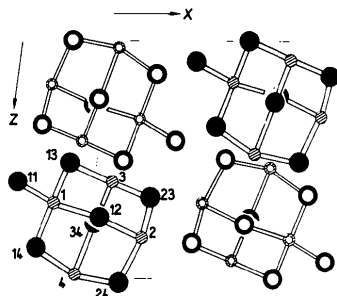|	a (Å)	b (Å)	c (Å)	Monoclinic angle (°)	Space group
P_4O_7	9·808 (2)	9·966 (1)	6·852 (1)	96·81 (1)	$P2_1/n$
P_4O_8	9·66 (4)	10·10 (4)	6·93 (3)	96·8 (3)	$C2/c$
P_4O_9	9·66 (3)	10·05 (3)	2 × 6·95 (3)	93·0 (4)	$R3c$

Fig. 2. Structure of P_4O_7 projected along |010|. Hatched circles: P, black circles: O; filled circles: upper layer of molecules, open circles: lower layer. The numbering of the atoms is according to Table 1.

For P_4O_6 and P_4O_{10} the data given are for the free molecules determined by gas electron diffraction; for the other oxides the data were determined by crystal structure analysis and then averaged according to the pseudosymmetry of the molecules in the crystal.

The pseudosymmetry for the P_4O_7 molecule is accurately fulfilled. Distances and angles, of which average values are given in Table 3, are equal within the 3σ limit. Only the temperature factors of P(4) and its O

neighbours deviate markedly from the pseudosymmetry, probably due to intermolecular forces.

A striking feature of the crystal structures of the phosphorus(III,V) oxides is the similarity of their lattice parameters, which becomes obvious when a unit cell suitable for this comparison is chosen (Table 4). The structures (that of P_4O_7 is shown in Fig. 2) are similar, but they become more open in the row from P_4O_9 over P_4O_8 to P_4O_7. This may be responsible for the very high hygroscopicity of P_4O_7, which exceeds that of molecular P_4O_{10}.

The shortest intermolecular contacts in the P_4O_7 structure are between trivalent P and O. $P(2)\cdots O(13)$ and $P(2)\cdots O(11)$ are 3·21 and 3·25 Å respectively and $O(34)\cdots O(11)$ is 3·24 Å.

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The Structure of TiZn₁₆

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Abstract. $TiZn_{16}$, *Cmcm*, $Z = 4$, $a = 7·720$ (7), $b = 11·449$ (7), $c = 11·755$ (9) Å. $R = 0·11$ for 407 reflexions. The structure is compared to the $TMZn_{13}$ (TM = Mn, Fe, Co) structure.

Introduction. In the course of a study of the intermediate phases formed between transition metals, single crystals of a phase in the Ti–Zn system were obtained. According to a phase-diagram study (Heine