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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. V. P_4O_{10}

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The crystallographic data given by de Decker & MacGillavry (1941) for P_4O_{10} have been used in a structure refinement. The internal P–O = 1·58 Å, ∠ P–O–P = 124°, but one independent external P–O = 1·41 ± 0·02 Å and the other 1·51 ± 0·04 Å. The rhombohedral crystal packing is discussed. The best present estimates of the molecular dimensions are thought to be: external P–O = 1·40 Å, internal P–O = 1·60 Å and ∠ P–O–P = 124½°, in agreement with the electron diffraction study by Akishin, Rambidi & Zasorin (1959).

Introduction

The structure of the P_4O_{10} molecule in the vapour phase was first determined in the electron diffraction investigation of Hampson & Stosick (1938). The molecule has point symmetry $\bar{4}3m$ with the configuration shown in Fig. 1. Hampson & Stosick gave the short external P–O bond as 1·39 ± 0·02 Å, the long internal P–O bond as 1·62 ± 0·02 Å and the P–O–P angle as 123½° ± 1°.

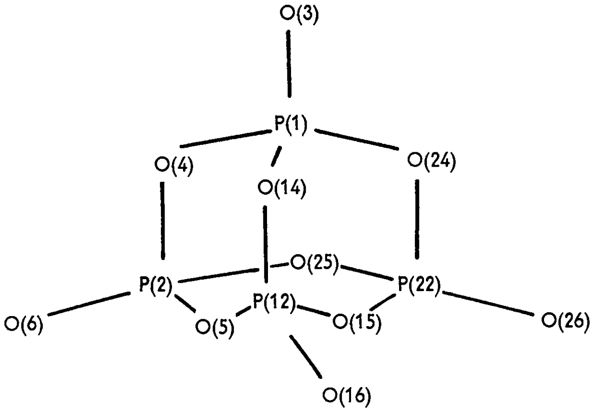

Fig. 1. The configuration of P_4O_{10}.

Relative to the single bond radius of X, for X either Si, P, S or Cl, the external P–O bond of 1·39 Å in P_4O_{10} is the shortest X–O bond known. Since it is a key point in Cruickshank's (1961) theory of π bonding that the unlinked X–O bond in an XO_4 tetrahedron linked to three others should have a high double-bond character, it seemed very desirable to confirm the early electron diffraction value.

The crystal structure of P_4O_{10} (the metastable first form of phosphorus pentoxide) was determined by de Decker & MacGillavry (1941), but they made no attempt to verify precisely the molecular dimensions given by Hampson & Stosick. They recorded the values of 169 independent non-zero $|F_o|$ for the zero and first [001] layers and the zero [11$\bar{1}$] layer. The values are corrected for absorption. It thus seemed likely that their crystal structure could be considerably refined and a check made on the molecular dimensions given by Hampson & Stosick.

Crystalline P_4O_{10} has the rhombohedral space group $R3c$, with dimensions $a = 7·43$ Å and $\alpha = 87°$. The molecules are arranged in a distorted body centred array. In each molecule the bond P(1)–O(3) lies along the crystallographic [111] threefold axis of symmetry and a molecule at (0, 0, 0) is turned about this axis in an opposite sense to a molecule at ($\pm\frac{1}{2}$, $\pm\frac{1}{2}$, $\pm\frac{1}{2}$) by the action of the glide-plane symmetry. In Fig. 1 P(12), P(22), *etc.* denote atoms generated from P(2), *etc.* by the threefold symmetry.

The refinement

The data used in the refinement were the $169|F_o|$ given by de Decker & MacGillavry. They thought that 10 of the larger reflexions were inaccurate, but during the present refinement it was found on comparison with the F_c that only 110 and $\bar{1}$10 seemed in error by more than 25% and only these two reflexions were omitted in the final stages of the refinement. Six cycles of least-squares refinement were carried out. These produced shifts of coordinates of up to 0·09 Å from those given by de Decker & MacGillavry. The residual R dropped from an initial 19% to a final 12·6%. The revised atomic coordinates are given in Table 1, to-

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

	x (Å)	y (Å)	z (Å)
P(1)	0·945 ± 0·009	0·945 ± 0·009	0·945 ± 0·009
P(2)	0·910 ± 0·010	−1·415 ± 0·009	−0·422 ± 0·009
O(3)	1·775 ± 0·033	1·775 ± 0·033	1·775 ± 0·033
O(4)	1·653 ± 0·020	−0·403 ± 0·019	0·437 ± 0·018
O(5)	0·383 ± 0·022	−0·418 ± 0·018	−1·597 ± 0·020
O(6)	1·617 ± 0·024	−2·599 ± 0·018	−0·797 ± 0·024

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Table 2. *Mean square vibration amplitudes and e.s.d.'s* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	0·027 ± 0·003	0·027 ± 0·003	0·027 ± 0·003	−0·001 ± 0·003	−0·001 ± 0·003	−0·001 ± 0·003
P(2)	0·026 ± 0·003	0·020 ± 0·003	0·029 ± 0·004	0·000 ± 0·003	0·001 ± 0·003	0·000 ± 0·004
O(3)	0·06 ± 0·01	0·06 ± 0·01	0·06 ± 0·01	0·00 ± 0·02	0·00 ± 0·02	0·00 ± 0·02
O(4)	0·03 ± 0·01	0·02 ± 0·01	0·02 ± 0·01	0·00 ± 0·01	0·00 ± 0·01	−0·02 ± 0·01
O(5)	0·04 ± 0·01	0·02 ± 0·01	0·02 ± 0·01	0·02 ± 0·01	−0·01 ± 0·01	−0·02 ± 0·01
O(6)	0·05 ± 0·01	0·02 ± 0·01	0·04 ± 0·01	0·01 ± 0·01	−0·02 ± 0·01	0·00 ± 0·01

gether with their e.s.d.'s. Anisotropic atomic vibrations were allowed for, lest the molecular angular oscillations should imply important coordinate corrections. The values of the vibration tensors U_{ij} are given in Table 2, together with their e.s.d.'s. If the $|F_o|$ given by de Decker & MacGillavry are for one-sixth of the cell contents, the $|F_o|$ scale factor determined by the least-squares process was $1{\cdot}01 \pm 0{\cdot}03$. The weighting scheme used was

$$w = 1/(4{\cdot}2 + |F_o| + |F_o|^2/19{\cdot}8)\,,$$

with the $|F_o|$ appropriate to the whole cell, but without the factor 1·01.

The anisotropic atomic vibration amplitudes in Table 2 correspond rather roughly to molecular rigid body vibrations (Cruickshank, 1956*a*) with an isotropic translational mean-square amplitude of 0·02 Å^2 and an isotropic angular oscillation of 3° r.m.s. amplitude. The corresponding radial corrections (Cruickshank, 1956*b*) to the coordinates are about 0·007 Å for the outer oxygens atoms (O(3), O(6)) and 0·004 Å for the inner atoms (P(1), P(2), O(4), O(5)); as these are small in comparison with the e.s.d.'s they have been neglected in the following discussion of the molecular dimensions.

Molecular dimensions

The bond lengths calculated from the coordinates of Table 1 are:

External P(1)–O(3) = 1·51 Å   P(2)–O(6) = 1·41 Å
Internal P(1)–O(4) = 1·58   P(2)–O(4) = 1·60
P(2)–O(5) = 1·59   P(12)–O(5) = 1·53

The e.s.d.'s derived from the least-squares process are all 0·02 Å, except for P(1)–O(3) which has an e.s.d. of 0·04 Å. These error estimates ought probably to be increased slightly to allow for off-diagonal interactions in the least-squares matrix between different atoms, since the $|F_o|$ data are not fully three-dimensional. The four internal bonds average 1·58 Å and agree within experimental error. The two external bonds, P(1)–O(3) and P(2)–O(6), do not agree at all well, though the difference of 0·10 Å is not absolutely outside the possible limits of experimental error. The two values of the P–O–P angle are P(1)–O(4)–P(2) = $122\frac{1}{2}°$ and P(2)–O(5)–P(12) = 126°, which give an average of 124°. The external O–P–O angles, such as ∠ O(6)–P(2)–O(4), average 117° and the internal O–P–O angles, such as ∠ O(4)–P(2)–O(5), average 101°.

By comparison Hampson & Stosick (1938) gave the external P–O = $1{\cdot}39 \pm 0{\cdot}02$ Å, the internal P–O = $1{\cdot}62 \pm 0{\cdot}02$ Å and P–O–P = $123\frac{1}{2}° \pm 1°$; a more recent gas electron-diffraction study by Akishin, Rambidi & Zasorin (1959) gives $1{\cdot}40 \pm 0{\cdot}03$, $1{\cdot}60 \pm 0{\cdot}01$ and $124\frac{1}{2}° \pm 1°$. The agreement of the latter dimensions with those obtained by X-ray crystallography is adequate, except for the present P(1)–O(3) bond of $1{\cdot}51 \pm 0{\cdot}04$ Å. It seems most plausible to treat this large value as due to experimental errors, for the peak shape of O(3) is more diffuse than any other and the implied vibrational amplitude is unreasonably as large in the radial as in the tangential directions. Further from considerations of the crystal packing, as will be shown below, it would be reasonable for O(3) to be about 0·1 Å nearer P(1).

The positions of the phosphorus atoms are considerably more accurate than those of the oxygen atoms. The two independent distances in the inter-phosphorus tetrahedron, with an allowance of 0·01 Å for the rotational oscillation effect, are P(1)–P(2) = 2·80 Å and P(2)–P(12) = 2·79 Å, so that this tetrahedron is regular within experimental error. The accuracy of the cell dimensions is not known, but these values seem sufficiently close to the P–P distance of 2·82 Å implied by the results of Akishin *et al.*, but not to the 2·85 Å implied by Hampson & Stosick.

As Hampson & Stosick's molecular dimensions deviate in one direction and the crystallographic values in the other, it seems reasonable to take the 1·40, 1·60 and $124\frac{1}{2}°$ of Akishin *et al.* as the best present estimates of the dimensions of the P_4O_{10} molecule.

The crystal structure

The way the molecules pack together to form the crystal structure is of some interest. Each molecule has four spikes (O(3), O(6), O(16), O(26)) and four recesses, which are formed between sets of three oxygens (O(5), O(15), O(25) and O(4), O(5), O(14), *etc.*). The spikes of the molecule at (0, 0, 0) protrude into recesses of the four molecules at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$, $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ and $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, and its recesses receive spikes from the four molecules at $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$, $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, *etc.* In the [111] direction the packing is quite symmetrical; the O(3) at the top of the (0, 0, 0) molecule fits symmetrically into the base O(5), O(15), O(25) of the molecule above at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with three equal apparent contacts of 2·89 Å. Similarly the O(3) of the molecule at $(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2})$ fits into the base of the molecule at the origin. In the $[11\bar{1}]$, *etc.* directions the packing is roughly but not at all exactly similar. An O(26) atom of the molecule at $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ fits into the O(4), O(5), O(14) recess of the origin molecule, but does so unsymmetrically with contacts of 3·13 Å to O(4), 3·04 Å to O(5) and 2·97 Å to O(14). (There are no other contacts < 3·2 Å.) If the fit were symmetrical, the crystal structure would be cubic with a space group $I\bar{4}3m$. The latter is the space group of hexamethylenetetramine, where each $(CH_2)_6N_4$ molecule also has $\bar{4}3m$ symmetry and each nitrogen fits into a recess formed by three hydrogens of another molecule. The reason for the rhombohedral space group with P_4O_{10} is that a closer packing can be achieved by the less symmetrical arrangement because of the roughly tetrahedral envelope of the molecule. By twisting adjoining molecules ±25° about their [111] axes, the molecular centres come closer together for the same minimum interatomic distance. In hexamethylenetetramine the molecule has a much more nearly spherical envelope and no packing advantage can be gained by a corresponding distortion of the cubic structure.

With this explanation of the packing in mind, we can return to the problem of the apparently unequal external P–O bonds. It seems unreasonable that the three symmetrical contacts apparently of 2·89 Å formed by O(3) to the molecule above at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ should be appreciably shorter than any of the unsymmetrical contacts, 2·97, 3·04 and 3·13 Å, formed by O(6). This suggests that the true position of O(3) is about 0·1 Å nearer P(1), which fits in well with the other estimates of the external P–O bond length.

I am very grateful to Prof. C. H. MacGillavry for drawing my attention to the crystallographic data for P_4O_{10}.

References

Akishin, P. A., Rambidi, N. G. & Zasorin, E. Z. (1959). *Kristallografiya*, **4**, 360.
Cruickshank, D. W. J. (1956*a*). *Acta Cryst.* **9**, 754.
Cruickshank, D. W. J. (1956*b*). *Acta Cryst.* **9**, 757.
Cruickshank, D. W. J. (1961). *J. Chem. Soc.* 5486.
De Decker, H. C. J. & MacGillavry, C. H. (1941). *Rec. Trav. chim. Pays-Bas*, **60**, 153.
Hampson, G. C. & Stosick, A. J. (1938). *J. Amer. Chem. Soc.* **60**, 1814.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. VI. P_2O_5, Form III

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The crystallographic data measured by MacGillavry, de Decker & Nijland (1949) have been used in a structure refinement. The revised dimensions average P–O(linked) = 1·56 ± 0·015, P–O (unlinked) = 1·49 ± 0·025 Å and ∠P–O–P = 145°.

The crystal structure of the third form of phosphorus pentoxide was determined by MacGillavry, de Decker & Nijland (1949). At Professor MacGillavry's suggestion the data have been used in a least-squares refinement.

The space group is *Pnam*, with cell dimensions $a = 9·23$, $b = 7·18$ and $c = 4·94$ Å. The structure consists of corrugated sheets parallel to (100). One sheet is shown in Fig. 1, projected along the *a* axis. Five of the atoms, P(1), P(2), O(1), O(2), O(3), of the asymmetric unit are fixed in the plane $z = \frac{1}{4}$, the sixth atom O(4) is in a general position but very close to the plane $z = 0$.

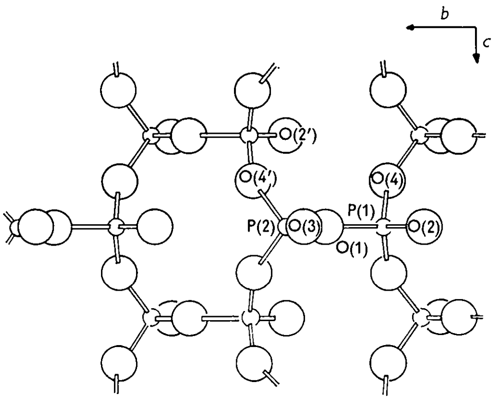

Fig. 1. Structure of a sheet of $(P_2O_5)_\infty$.

The data used in the refinement were 115 non-zero $|F_o|$ for the zero, first and second [001] layers. The scaled $|F_o|$ and final $|F_c|$ are given in Table 1. Six cycles of least-squares refinement were carried out. The maximum shift from the coordinates given by MacGil-

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