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.

Acta Cryst. (1964). **17**, 679

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

By D. W. J. Cruickshank*

School of Chemistry, The University, Leeds 2, England

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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 $a = 9{\cdot}23$, $b = 7{\cdot}18$ and $c = 4{\cdot}94$ 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 $z = 0$.

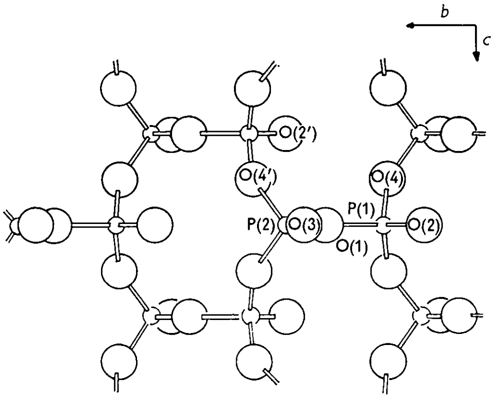

Fig. 1. Structure of a sheet of $(P_2O_5)_\infty$.

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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* Present address: Chemistry Department, The University, Glasgow, W. 2, Scotland.

Table 1. *Observed and calculated structure factors*
($\times 10$)

h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c	h k l	$\lvert F_o \rvert$	F_c
2 0 0	451	-517	1 8 0	429	-458	2 6 1	440	387
4 0 0	246	-322	7 8 0	165	225	4 6 1	125	132
6 0 0	510	-469	2 0 1	528	575	5 6 1	158	155
8 0 0	572	432	4 0 1	73	- 88	3 7 1	404	304
10,0 0	128	-178	6 0 1	429	-383	0 0 2	917	-1022
1 1 0	315	340	8 0 1	220	-234	2 0 2	176	240
2 1 0	591	-648	0 1 1	147	-135	4 0 2	422	-367
3 1 0	143	128	1 1 1	238	352	6 0 2	737	664
6 1 0	312	261	2 1 1	660	669	8 0 2	110	-108
7 1 0	297	-324	3 1 1	293	-298	12,0 2	128	-125
8 1 0	227	257	4 1 1	429	-398	14,0 2	147	176
0 2 0	697	-786	5 1 1	110	118	1 1 2	345	-359
2 2 0	227	256	7 1 1	216	-291	2 1 2	293	-261
3 2 0	389	-362	8 1 1	264	-264	4 1 2	110	146
4 2 0	429	346	10,1 1	378	315	7 1 2	143	198
5 2 0	264	291	1 2 1	539	669	8 1 2	547	-449
6 2 0	110	119	2 2 1	125	-165	0 2 2	143	-102
7 2 0	165	187	3 2 1	139	-183	1 2 2	253	209
8 2 0	470	-411	4 2 1	378	-315	3 2 2	554	461
9 2 0	235	235	5 2 1	393	-300	5 2 2	569	-439
2 3 0	429	441	6 2 1	216	242	6 2 2	396	-314
3 3 0	407	-371	0 3 1	521	500	7 2 2	183	-206
5 3 0	429	350	3 3 1	114	-121	1 3 2	345	260
11,3 0	308	-366	4 3 1	279	242	2 3 2	220	150
1 4 0	183	-225	5 3 1	238	-225	5 3 2	506	-425
2 4 0	532	-471	6 3 1	334	-284	6 3 2	293	-300
3 4 0	572	516	7 3 1	477	352	0 4 2	293	284
4 4 0	308	288	1 4 1	110	-139	2 4 2	521	352
9 4 0	257	-282	2 4 1	216	-203	3 4 2	756	-655
10,4 0	147	-155	3 4 1	213	233	4 4 2	682	-546
1 5 0	183	-225	5 4 1	114	154	5 4 2	415	319
3 5 0	106	86	6 4 1	213	261	2 5 2	279	-260
4 5 0	268	279	0 5 1	150	-167	3 5 2	202	224
8 5 0	220	-213	1 5 1	638	457	4 5 2	187	-193
0 6 0	268	243	3 5 1	213	-210	0 6 2	363	-340
1 6 0	492	462	5 5 1	521	388	1 6 2	150	-155
6 6 0	128	-144	6 5 1	231	248	4 6 2	227	224
7 6 0	205	-278	7 5 1	139	-181	5 6 2	235	-283
						7 6 2	187	206

lavry *et al.* was only 0·05 Å. The residual R dropped to 14·5%. The revised atomic coordinates and their e.s.d.'s are given in Table 2. Anisotropic vibrations were allowed for the phosphorus atoms but not foi the oxygens. There was some indication that the apparent vibrations were least in the **c** direction. The individual variations among the atomic vibrations were not significant and the average apparent m.s. amplitude U was 0·007 Å². The weighting scheme was

$$w = 1/(22 + |F_o| + |F_o|^2/76)\ .$$

Table 2. *Atomic coordinates and e.s.d.'s*

	x (Å)	y (Å)	z (Å)
P(1)	$2{\cdot}225 \pm 0{\cdot}013$	$2{\cdot}095 \pm 0{\cdot}014$	$1{\cdot}235 = \frac{1}{4}c$
P(2)	$3{\cdot}702 \pm 0{\cdot}012$	$4{\cdot}715 \pm 0{\cdot}014$	$1{\cdot}235 = \frac{1}{4}c$
O(1)	$2{\cdot}593 \pm 0{\cdot}025$	$3{\cdot}615 \pm 0{\cdot}032$	$1{\cdot}235 = \frac{1}{4}c$
O(2)	$3{\cdot}349 \pm 0{\cdot}029$	$1{\cdot}111 \pm 0{\cdot}033$	$1{\cdot}235 = \frac{1}{4}c$
O(3)	$5{\cdot}104 \pm 0{\cdot}025$	$4{\cdot}229 \pm 0{\cdot}030$	$1{\cdot}235 = \frac{1}{4}c$
O(4)	$1{\cdot}272 \pm 0{\cdot}017$	$2{\cdot}034 \pm 0{\cdot}020$	$-0{\cdot}004 \pm 0{\cdot}038$

The dimensions within one molecular sheet are listed in Table 3. Each phosphate tetrahedron has three oxygen atoms linked to other tetrahedra and one unlinked oxygen atom. The individual values for the chemically equivalent bonds agree well within their e.s.d.'s of 0·03 to 0·04 Å. The average dimensions are

$$\text{PO(linked)} = 1{\cdot}56 \pm 0{\cdot}015\ ,$$
$$\text{P–O(unlinked)} = 1{\cdot}49 \pm 0{\cdot}025\ \text{Å}$$

and ∠P–O–P = 145°; the two types of O–P–O angle average 116° and 103°.

Table 3. *Dimensions in* $(P_2O_5)_\infty$

P(1)–O(1) = 1·56 Å
P(1)–O(4) = 1·56
P(2)–O(1) = 1·56
P(2)–O(4) = 1·57 Å
P(1)–O(2) = 1·49
P(2)–O(3) = 1·48

∠ P(2)–O(1)–P(1) = 148½°
∠ P(1)–O(4)–P(2) = 141½
∠ O(2)–P(1)–O(1) = 117½
∠ O(2)–P(1)–O(4) = 115½
∠ O(3)–P(2)–O(1) = 116
∠ O(3)–P(2)–O(4) = 114°
∠ O(1)–P(1)–O(4) = 100½
∠ O(4)–P(1)–O(4) = 104
∠ O(1)–P(2)–O(4) = 104
∠ O(4)–P(2)–O(4) = 103

These bond lengths differ considerably from those in P_4O_{10} molecules, for which the best estimates (Cruickshank, 1964) are P–O(linked) = 1·60 Å, P–O(unlinked) = 1·40 Å and ∠P–O–P = 124°. In both structures the P–O–P angles are probably determined by the connectivities of the structures. Within one molecular sheet of the present structure, there are non-bonded contacts between O(2′) and O(4) of 2·94 Å and between O(2′) and O(1) of 3·01 Å, which are typical values for the van der Waals contacts between sheets. If the P–O–P angles were both reduced to the more typical valuc of 132°, O(2′) ··· O(4) would be reduced by about 0·1 Å and O(2′) ··· O(1) by about 0·25 Å. It is thus likely that the P–O–P angles are determined by the need to allow comfortable van der Waals distances within the molecular sheets.

If the P–O–P angles are regarded as determined, the lengths of the P–O bonds in the two structures then fall into an intelligible pattern. For in the opened-out P–O–P angle of $(P_2O_5)_\infty$, the oxygen p orbit lying in the P–O–P plane can play a part in the π-bonding system of the structure. Consequently relative to P_4O_{10} the P–O(linked) bonds are contracted and, owing to the sharing of the π character, the P–O (unlinked) bonds are lengthened.

There are a large number of inter-layer contacts. The O(3) at $z = \frac{1}{4}$ of the layer shown in Fig. 1 makes no less than 12 contacts to atoms in the layer above. These are in sets of six to atoms at $z = -\frac{1}{4}$ or $\frac{3}{4}$ (except O(4) at $z = 0$ or $\frac{1}{2}$), and the distances are O(4′) ··· O(3) = 3·24, O(2′) ··· O(3) = 3·18, P(1′) ··· O(3) = 3·23, O(1′) ··· O(3) = 2·98, P(2′) ··· O(3) = 3·06 and O(3′) ··· O(3) = 2·95 Å. O(3) also contacts the P(1) (3·24) and O(4) (3·05) at the positions $(\frac{1}{2}+x,\ \frac{1}{2}-y, z)$. The shortest contact of the whole structure is 2·86 Å between O(4) at $(\frac{1}{2}+x,\ \frac{1}{2}-y, z)$ and O(2).

I should like to thank Professor MacGillavry for letting me have the $|F_o|$ for this structure.

References

Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 677.
MacGillavry, C. H., de Decker, H. C. J. & Nijland, L. M. (1949). *Nature, Lond.* **164**, 448.