2 and 3 are smaller than those from plane 5, indicating a somewhat more trigonal bipyramidal character of the intermediate molecular geometry.

The benzene rings are both flat within ±0·005 Å, while the five-membered rings are puckered up to ±0·06 Å. The angles between the planes of the two rings are 3·9 and 2·4° in both halves of the molecule. There is a non-crystallographic twofold axis defined by the phosphorus and fluorine atoms. A rotation through this axis of one half of the molecule leads to an r.m.s. distance of 0·052 Å for the corresponding atoms. The packing of the molecules, for which there are no intermolecular distances less than the sum of the van der Waals radii of the respective atoms, is shown in Fig. 2.

We thank Professor R. Schmutzler for encouraging this investigation and for the sample crystals. This work was supported by the Deutsche Forschungsgemeinschaft, which also provided the diffractometer.

A Telefunken TR4 computer at the Computer Center of the University of Stuttgart was used for generation and reduction of diffractometer input and output and a UNIVAC 1108 was used for all calculations with the X-RAY 72 system. Plots and calculations of the program *ORTEP* (Johnson, 1965) were performed on a Telefunken TR440 of the Gesellschaft für Mathematik und Datenverarbeitung m.b.H. at Darmstadt.

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Crystal Structures of Pentacoordinate Phosphorus Compounds. III. 2-Methyl-2,2′-spirobis-(1,3,2-benzodioxaphosphole), $(C_6H_4O_2)_2PCH_3$

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The title compound is monoclinic, space group $P2_1/c$, with $a=14·842$ (10), $b=12·092$ (9), $c=13·711$ (8) Å, $\beta=98·52$ (9)°; $Z=8$. The intensities were measured with a four-circle diffractometer. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to $R=0·05$. The geometry of the pentacoordinate phosphorus group can be described as a rectangular pyramid. The characteristic features of molecule (I) are: the diagonal angles O–P–O are 148·1 and 156·9°, the four bond angles between the apical methyl group and the P–O bonds are similar (105·6, 102·1, 106·1 and 101·1°), and the differences of the P–O bond lengths (1·654, 1·649 *versus* 1·674, 1·672 Å) may be regarded as a small residual character of a bipyramid. The corresponding values of molecule II are: diagonal angles O–P–O 147·7 and 156·2°, the four C–P–O angles are similar (106·4, 102·3, 105·9 and 101·4°); however the four P–O bonds cannot be classified as pairs of short and long bonds (1·650, 1·658 *versus* 1·661 and 1·674 Å). In both molecules the four oxygen atoms show distances from a corresponding least-squares plane of less than 0·06 Å.

This investigation continues the studies of the stereochemistry of pentacoordinate phosphorus atoms. In contrast to part II of the series (Wunderlich & Mootz, 1974) the title compound contains a phosphorus atom surrounded by four electronegative oxygen atoms and one less electronegative carbon atom. *A priori* this should yield the geometry of a tetragonal pyramid (Hoffmann, Howell & Muetterties, 1972); however the chelation should reduce the symmetry to that of a rectangular pyramid (Kepert, 1973). Except for the transition stage during the pseudorotation by the Berry mechanism (Berry, 1960; Gillespie *et al.*, 1971)

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no tetragonal or rectangular pyramids are known for the geometry of pentacoordinate phosphorus atoms. Preliminary results of this investigation are given elsewhere (Wunderlich & Mootz, 1973; Wunderlich, Mootz, Schmutzler & Wieber, 1974).

Experimental

Transparent crystals of $(C_6H_4O_2)_2PCH_3$ were obtained from butyl ether (Wieber & Hoos, 1968). The preparation of the crystals was performed directly in butyl

Table 1. *Atomic parameters with estimated standard deviations, referring to the last significant figure, in parentheses*

U or U_{ij} multiplied by 100. Temperature factor is defined by:

$$\exp\,[-2\pi^2(U_{11}h^2a^{*2}+2U_{23}klb^*c^*+\ldots)]\text{ or }\exp\,[-8\pi^2U(\sin\theta/\lambda)^2]\,.$$

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	0·87774 (6)	0·43931 (8)	0·09090 (6)	4·64 (6)	5·63 (6)	4·15 (5)	−0·26 (5)	−0·24 (4)	0·58 (5)
O(11)	0·9584 (1)	0·5341 (2)	0·1147 (1)	5·7 (1)	7·3 (2)	4·7 (1)	−1·8 (1)	−1·1 (1)	0·7 (1)
O(12)	0·8880 (1)	0·4083 (2)	0·2110 (1)	6·2 (2)	9·0 (2)	4·5 (1)	−1·4 (1)	−0·5 (1)	0·8 (1)
O(13)	0·7708 (1)	0·4034 (2)	0·0924 (1)	5·0 (1)	6·8 (2)	5·1 (1)	−0·7 (1)	−0·0 (1)	1·2 (1)
O(14)	0·8476 (1)	0·5142 (2)	−0·0113 (2)	4·8 (1)	7·7 (2)	5·2 (1)	−1·2 (1)	−1·0 (1)	2·1 (1)
C(10)	0·9309 (3)	0·3241 (5)	0·0426 (4)	6·7 (4)	8·2 (4)	6·7 (4)	1·9 (3)	0·6 (3)	0·2 (3)
H(101)	0·993 (3)	0·344 (3)	0·026 (3)	12 (2)					
H(102)	0·949 (3)	0·280 (4)	0·080 (3)	11 (2)					
H(103)	0·928 (4)	0·316 (4)	−0·032 (4)	19 (3)					
C(11)	0·9655 (2)	0·4516 (3)	0·2625 (3)	5·6 (2)	6·9 (3)	4·4 (2)	1·1 (2)	−0·5 (2)	−0·1 (2)
C(12)	1·0055 (3)	0·5227 (3)	0·2088 (3)	5·3 (3)	6·4 (3)	4·9 (2)	0·3 (2)	−0·2 (2)	−0·9 (2)
C(13)	1·0848 (3)	0·5785 (4)	0·2435 (3)	6·2 (3)	11·4 (4)	6·5 (3)	−1·7 (3)	−0·5 (3)	−1·4 (3)
C(14)	1·1215 (4)	0·5539 (5)	0·3412 (4)	6·9 (4)	12·1 (5)	7·6 (4)	−0·1 (4)	−1·1 (3)	−3·1 (4)
C(15)	1·0797 (4)	0·4846 (5)	0·3954 (4)	8·3 (4)	12·2 (5)	5·4 (4)	3·7 (4)	−2·0 (3)	−1·7 (3)
C(16)	0·9993 (3)	0·4290 (4)	0·3598 (3)	8·3 (4)	9·6 (4)	5·1 (3)	1·1 (3)	−0·9 (3)	0·3 (3)
H(13)	1·120 (2)	0·631 (3)	0·199 (3)	9 (1)					
H(14)	1·179 (3)	0·595 (3)	0·356 (3)	9 (2)					
H(15)	1·102 (3)	0·472 (4)	0·455 (3)	12 (2)					
H(16)	0·966 (3)	0·374 (3)	0·403 (3)	11 (2)					
C(21)	0·7580 (2)	0·4983 (3)	−0·0499 (3)	4·2 (2)	5·7 (2)	4·9 (2)	−0·4 (2)	−0·6 (2)	0·0 (2)
C(22)	0·7143 (2)	0·4364 (3)	0·0079 (2)	4·8 (3)	4·7 (2)	5·2 (2)	−0·4 (2)	−0·2 (2)	−0·2 (2)
C(23)	0·6221 (3)	0·4125 (3)	−0·0124 (3)	4·8 (3)	6·9 (3)	8·3 (3)	−1·1 (2)	0·2 (3)	−0·9 (3)
C(24)	0·5780 (3)	0·4572 (4)	−0·1006 (4)	5·0 (3)	8·5 (4)	8·8 (4)	−0·2 (3)	−1·7 (3)	−2·0 (3)
C(25)	0·6221 (3)	0·5191 (4)	−0·1596 (4)	6·4 (4)	9·4 (4)	6·1 (3)	1·4 (3)	−2·0 (3)	−0·7 (3)
C(26)	0·7154 (3)	0·5432 (3)	−0·1374 (3)	6·4 (3)	8·0 (3)	5·8 (3)	−0·3 (3)	−0·8 (2)	1·1 (2)
H(23)	0·589 (3)	0·370 (3)	0·036 (3)	9 (2)					
H(24)	0·512 (3)	0·439 (3)	−0·111 (3)	10 (1)					
H(25)	0·597 (2)	0·548 (3)	−0·222 (3)	8 (1)					
H(26)	0·757 (2)	0·592 (3)	−0·180 (2)	8 (1)					
P(2)	0·66864(6)	0·44421 (8)	0·37448 (7)	4·67 (6)	5·85 (7)	5·91 (6)	−0·89 (6)	−1·45 (5)	1·24 (6)
O(21)	0·7518 (2)	0·5349 (2)	0·4048 (2)	6·7 (2)	8·0 (2)	7·5 (2)	−3·3 (1)	−3·1 (1)	2·6 (1)
O(22)	0·6393 (1)	0·5100 (2)	0·2671 (2)	5·1 (1)	6·3 (2)	5·7 (1)	−1·4 (1)	−1·9 (1)	1·8 (1)
O(23)	0·5589 (1)	0·4163 (2)	0·3651 (2)	4·9 (1)	7·0 (2)	5·9 (1)	−1·5 (1)	−1·2 (1)	1·7 (1)
O(24)	0·6792 (1)	0·4266 (2)	0·4958 (2)	5·4 (2)	10·5 (2)	5·6 (2)	−2·7 (1)	−1·4 (1)	1·2 (1)
C(20)	0·7214 (4)	0·3234 (5)	0·3359 (4)	6·2 (4)	6·9 (4)	10·5 (4)	0·6 (3)	1·0 (3)	2·0 (3)
H(201)	0·780 (3)	0·324 (4)	0·355 (4)	15 (2)					
H(202)	0·747 (4)	0·322 (5)	0·257 (4)	23 (3)					
H(203)	0·692 (3)	0·269 (4)	0·348 (3)	12 (2)					
C(31)	0·7020 (2)	0·5867 (3)	0·2486 (3)	4·9 (2)	4·3 (2)	6·5 (3)	0·6 (2)	−0·4 (2)	0·6 (2)
C(32)	0·7673 (3)	0·6009 (3)	0·3284 (3)	5·5 (3)	4·9 (3)	7·7 (3)	−0·9 (2)	−0·7 (2)	1·5 (2)
C(33)	0·8365 (3)	0·6741 (4)	0·3275 (4)	7·2 (3)	7·3 (3)	9·4 (4)	−1·8 (3)	−1·7 (3)	1·9 (3)
C(34)	0·8382 (3)	0·7338 (4)	0·2426 (4)	6·0 (3)	6·6 (3)	12·5 (5)	−1·3 (3)	0·5 (3)	1·7 (3)
C(35)	0·7742 (4)	0·7206 (4)	0·1623 (4)	8·5 (4)	5·7 (3)	8·7 (4)	−0·1 (3)	2·1 (3)	1·8 (3)
C(36)	0·7039 (3)	0·6464 (3)	0·1648 (3)	7·2 (3)	5·4 (3)	6·2 (3)	0·5 (3)	−0·2 (3)	1·0 (3)
H(33)	0·869 (3)	0·689 (3)	0·389 (3)	10 (2)					
H(34)	0·888 (3)	0·783 (3)	0·240 (3)	11 (2)					
H(35)	0·787 (2)	0·760 (3)	0·101 (2)	8 (1)					
H(36)	0·664 (2)	0·635 (3)	0·113 (2)	6 (1)					
C(41)	0·6037 (2)	0·3816 (3)	0·5258 (3)	6·5 (3)	6·3 (3)	5·1 (2)	−0·9 (2)	−0·6 (2)	0·2 (2)
C(42)	0·5333 (3)	0·3760 (3)	0·4497 (3)	5·2 (3)	4·0 (2)	6·7 (3)	−1·0 (2)	0·1 (2)	0·5 (2)
C(43)	0·4513 (3)	0·3365 (4)	0·4631 (4)	7·4 (4)	6·5 (3)	7·9 (4)	−1·1 (3)	−0·0 (3)	0·9 (3)
C(44)	0·4400 (4)	0·2996 (3)	0·5553 (5)	7·7 (4)	6·0 (3)	11·5 (5)	−1·3 (3)	2·8 (4)	−0·1 (3)
C(45)	0·5097 (4)	0·3054 (4)	0·6321 (4)	11·0 (5)	8·5 (4)	7·4 (4)	−0·8 (3)	2·2 (4)	−0·6 (3)
C(46)	0·5920 (4)	0·3494 (4)	0·6180 (4)	8·6 (4)	9·6 (4)	6·5 (4)	−2·2 (3)	−0·1 (3)	0·2 (3)
H(43)	0·410 (2)	0·336 (3)	0·415 (2)	6 (1)					
H(44)	0·381 (2)	0·270 (2)	0·566 (2)	6 (1)					
H(45)	0·496 (3)	0·278 (3)	0·698 (3)	11 (2)					
H(46)	0·640 (3)	0·347 (4)	0·661 (3)	11 (2)					

Table 2. *Observed and calculated structure factors*

The columns contain index l, $10F_{\mathrm{meas}}$ and $10F_{\mathrm{calc}}$.

ether to avoid decomposition; thereafter the crystals were sealed into glass capillaries.

The lattice parameters were determined at room temperature by measurement of diffractometer angles of 25 reflexions with Mo $K\alpha$ radiation and by a subsequent least-squares refinement from the θ values. The density determined by flotation is $d_m = 1{\cdot}43$ g cm^{-3} and agrees with the calculated density, $d_x = 1{\cdot}432$ g cm^{-3}, for $Z = 8$. From systematic absences the space group was determined to be $P2_1/c$ with two molecules per asymmetric unit. Probably owing to high thermal motion only the 2291 independent intensities up to $2\theta_{\max} = 40°$ could be measured with Zr-filtered Mo $K\alpha$ radiation and a paper tape controlled four-circle diffractometer (Siemens AED). The instrument scanned in a coupled θ:2θ mode applying the so-called five-value measurement. The observed intensity for 756 reflexions was $I < 3\sigma(I)$ where the standard deviation of the intensity is defined by $\sigma(I) = [\sigma^2_{\rm pk} + (0{\cdot}02I)^2]^{1/2}$ with $\sigma_{\rm pk} = (I_{\rm pk} + I_{\rm bg})^{1/2}$ and $I = I_{\rm pk} - I_{\rm bg}$. To keep systematic errors small (Hirshfeld & Rabinovich, 1973) all data were classified 'observed' and included in the later refinements. The c axis was parallel to the φ axis of the diffractometer. Because of the low linear absorption coefficient $\mu = 2{\cdot}4$ cm^{-1} (Mo $K\alpha$ radiation), no absorption corrections were applied.

Structure determination and refinement

Attempts to solve the structure by location of the two phosphorus atoms from a sharpened Patterson map failed, probably owing to the limited quantity of the data. With direct methods, applying the program *TANGEN* of the X-RAY (1972) system again no solution could be achieved. However with program *PHASE* (the multi-symbolic technique) 247 phases out of the 264 reflexions with $E > 1{\cdot}6$ were determined. Although, in comparison with the final values, 38 of these phases were wrong, a subsequent E map revealed two outstanding high peaks, which were interpreted as the phosphorus atoms. By two steps of structure-factor calculation and Fourier syntheses the complete molecules with the exception of hydrogen atoms, were located. The structure was refined isotropically by full-matrix least-squares calculations to $R = \sum|\Delta F_{\rm meas}|/\sum F_{\rm meas} = 0{\cdot}16$. After three cycles of block-diagonal least-squares refinement with anisotropic temperature factors ($R = 0{\cdot}09$) a difference map showed peaks for all hydrogen atoms. At this stage the observed structure factors of the 30 strongest reflexions showed a very poor agreement with the calculated values. Examination of the diffractometer output suggested that the scan width was too narrow during the data col-

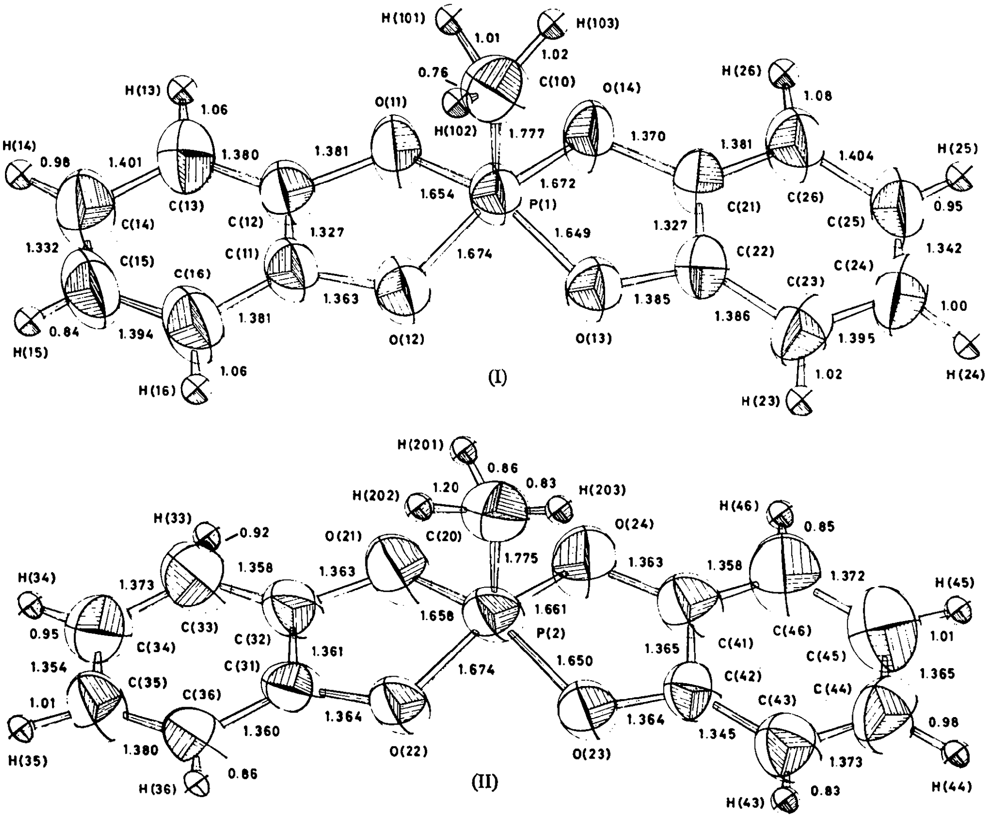

Fig. 1. The two independent molecules of $(C_6H_4O_2)_2PCH_3$ with bond lengths in Å in a comparable arbitrary orientation to the crystallographic axes. The atoms are represented by thermal ellipsoids of 50% probability. An isotropic temperature factor of $B = 1{\cdot}0$ Å^2 was given to all hydrogen atoms. E.s.d.'s are P–O 0·003, P–C 0·006, O–C 0·004, C–C 0·005–0·009, C–H 0·03–0·06 Å.

lection. This affected only the very strong reflexions which were re-collected with an increased scan width and incorporated into the data set. For the final refinement in an anisotropic mode for the heavy atoms and an isotropic mode for the H atoms the 412 atom parameters had to be packed into six blocks: four catechol rings and two phosphorus groups. The refinement converged (maximum shift/error = 0·6) after three cycles at $R=0{\cdot}055$ and $R_w=[\sum w(\Delta F_{\rm meas})^2/\sum wF^2_{\rm meas}]^{1/2}=0{\cdot}037$, including all reflexions. The minimized function was $\sum w(\Delta F_{\rm meas})^2$ with empirical weights derived from $\sigma(I)$ by $w=1/\sigma^2(F)$. Atomic scattering factors for P, O, and C were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). The final atomic coordinates and thermal parameters are given in Table 1. In spite of the good convergence of all other parameters the results for the hydrogen atoms of the methyl groups are unsatisfactory. The high temperature factors may be interpreted as an uncertainty of the location of these atoms. Table 2 contains a list of the observed and calculated structure factors.

Table 3. *Bond angles of molecules* (I) *and* (II)

Molecule (I) is indexed by $m=1$, $n=1$ or $n=2$, molecule (II) by $m=2$, $n=3$ or $n=4$. The second indices of the C and H atoms make use of the assumption of a molecular twofold symmetry axis through the atoms P and C(*m*O). E.s.d.'s are:

∠O–P–O	∠O–P–C	∠P–O–C	∠O–C–C
0·1	0·2	0·2	0·3–0·4
∠C–C–C	∠C–C–H	∠P–C–H	∠H–C–H
0·3–0·5	2–3	2–4	4–5°

	$m=1$	$m=2$
O(*m*1)—P(*m*)—O(*m*3)	148·1°	147·7°
O(*m*2)—P(*m*)—O(*m*4)	156·9	156·2
O(*m*1)—P(*m*)—O(*m*2)	90·2	89·6
O(*m*1)—P(*m*)—O(*m*4)	83·5	83·0
O(*m*2)—P(*m*)—O(*m*3)	82·8	84·4
O(*m*3)—P(*m*)—O(*m*4)	90·8	89·9
O(*m*1)—P(*m*)—C(*m*O)	105·6	105·9
O(*m*2)—P(*m*)—C(*m*O)	102·1	101·4
O(*m*3)—P(*m*)—C(*m*O)	106·2	106·4
O(*m*4)—P(*m*)—C(*m*O)	101·0	102·3
P(*m*)—C(*m*O)–H(*m*O1)	112	112
P(*m*)—C(*m*O)–H(*m*O2)	115	119
P(*m*)—C(*m*O)–H(*m*O3)	119	109
H(*m*O1)–C(*m*O)–H(*m*O2)	95	80
H(*m*O2)–C(*m*O)–H(*m*O3)	125	115
H(*m*O3)–C(*m*O)–H(*m*O1)	72	119

	$n=1$	$n=2$	$n=3$	$n=4$
P(*m*)—O(*m*1)–C(*n*2)	111·5°		113·5°	
P(*m*)—O(*m*2)–C(*n*1)	111·7		113·0	
P(*m*)—O(*m*3)–C(*n*2)		112·2°		113·8°
P(*m*)—O(*m*4)–C(*n*1)		111·9		113·2
O(*m*1)–C(*n*2)–C(*n*1)	112·1		111·3	
O(*m*1)–C(*n*2)–C(*n*3)	124·2		127·1	
O(*m*2)–C(*n*1)–C(*n*2)	112·0		111·1	
O(*m*2)–C(*n*1)–C(*n*6)	125·6		128·2	
O(*m*3)–C(*n*2)–C(*n*1)		111·9		110·8
O(*m*3)–C(*n*2)–C(*n*3)		124·4		128·0
O(*m*4)–C(*n*1)–C(*n*2)		112·3		111·0
O(*m*4)–C(*n*1)–C(*n*6)		125·0		128·3
C(*n*1)–C(*n*2)–C(*n*3)	123·7	123·6	121·6	121·3
C(*n*2)–C(*n*3)–C(*n*4)	114·6	114·5	117·4	118·5
C(*n*3)–C(*n*4)–C(*n*5)	121·3	122·1	121·9	120·8
C(*n*4)–C(*n*5)–C(*n*6)	123·6	122·6	119·9	119·9
C(*n*5)–C(*n*6)–C(*n*1)	114·3	114·6	118·5	118·8
C(*n*6)–C(*n*1)–C(*n*2)	122·4	122·6	120·7	120·5
C(*n*2)–C(*n*3)–H(*n*3)	124	122	114	118
C(*n*4)–C(*n*3)–H(*n*3)	122	123	127	123
C(*n*3)–C(*n*4)–H(*n*4)	107	111	118	119
C(*n*5)–C(*n*4)–H(*n*4)	132	127	120	120
C(*n*4)–C(*n*5)–H(*n*5)	120	126	115	117
C(*n*6)–C(*n*5)–H(*n*5)	116	111	124	123
C(*n*5)–C(*n*6)–H(*n*6)	123	128	121	124
C(*n*1)–C(*n*6)–H(*n*6)	122	117	120	116

Results and discussion

Fig. 1 shows the two independent molecules with thermal ellipsoids of the non-hydrogen atoms and all bond lengths. Bond angles are listed in Table 3. Molecules (I) and (II) reveal essentially the same geometry, which is close to the idealized geometry of a rectangular pyramid with four electronegative oxygen atoms in the base and the less electronegative methyl group at the top. But there exists some distortion from ideality towards the geometry of a bipyramid.

For molecule (I) the two pairs of diagonal P–O bonds show significant (8σ) differences of about 0·02 Å (1·654 and 1·649 *vs.* 1·674 and 1·672 Å), but these differences are small compared with the corresponding values of a trigonal bipyramid (Spratley, Hamilton & Ladell, 1967). The bond angles reveal the characteristic values of a rectangular pyramid. The four similar C–P–O angles (101·0, 102·1, 105·6 and 106·2, average 103·8°) and the two diagonal O–P–O angles (148·1 and 156·9°, average 152·5°) are characteristic of a rectangular pyramid. Zemann (1963) calculated theoretical values of 104·1 and 151·9° for these two representative angles in a square pyramid with symmetry C_{4v} on the basis of pure electrostatic interactions between the ligands. Although this is only a hypothetical model, it is in excellent agreement with the observed angles.

Table 4(i), containing distances of atoms from various least-squares planes, shows the geometry of the pentacoordinate phosphorus atom in a different way. Plane 1 and 4 must be satisfied for a trigonal bipyramid as well as a tetragonal pyramid. But the distances from planes 2, 3, and 5 are sensitive to deviations from these two ideal geometries. For the trigonal bipyramid planes 2 and 3 must be exactly satisfied by the defining atoms, in the other case plane 5 is relevant. The average distances are 0·113 Å from planes 2 and 3 and 0·059 Å from plane 5. These values confirm the description in terms of a rectangular pyramid. In the preceding article (Wunderlich & Mootz, 1974) the corresponding distances of 0·057 and 0·152 Å gave preference to the description of that structure in terms of a bipyramid.

In the case of molecule (II) the differences in the two pairs of diagonal P–O bond lengths (1·650, 1·658 and 1·661, 1·674 Å) are almost insignificant (4σ). Again the four C–P–O angles are similar (101·4, 102·3, 105·9 and 106·4, average 104·0°) and the two diagonal O–P–O angles (147·7 and 156·2°, average 152·0°) differ by only about 4° from the theoretical values of Zemann (1963). The average distances of the atoms from least-squares planes 2, 3, and 5 [see Table 4(ii)] of 0·115, 0·116, and 0·059 Å respectively, are again more characteristic of a rectangular pyramid than a trigonal bipyramid.

Table 4. *Atomic distances* (Å) *from several least-squares planes in molecules* (I) *and* (II)

Only distances of atoms defining the planes are listed.

(i) Central part of molecule(I)

	Plane 1	2	3	4	5
P(1)	−0·003	0·219	−0·219	−0·001	
C(10)	0·001			0·000	
O(11)	0·001	0·007			0·059
O(12)		−0·113	0·113	0·000	−0·059
O(13)	0·001		−0·007		0·059
O(14)		−0·113	0·113	0·000	−0·058

(ii) Five-membered rings of molecule(I)

	n=1	*n*=2
P(1)	0·088	−0·051
O(11)	−0·085	
O(12)	−0·085	
O(13)		0·049
O(14)		0·049
C(*n*1)	0·041	−0·024
C(*n*2)	0·040	−0·022

(iii) Benzene rings of molecule(I)

	n=1	*n*=2
C(*n*1)	−0·012	0·004
C(*n*2)	0·003	−0·006
C(*n*3)	0·009	0·004
C(*n*4)	−0·014	−0·001
C(*n*5)	0·006	−0·001
C(*n*6)	0·007	0·000

(iv) Central part of molecule(II)

	Plane 1	2	3	4	5
P(2)	−0·003	0·221	−0·226	−0·009	
C(20)	0·001			0·001	
O(21)	0·001	0·009			0·059
O(22)		−0·115	0·115	0·004	−0·058
O(23)	0·001		−0·005		0·058
O(24)		−0·116	0·116	0·004	−0·059

Table 4 (*cont.*)

(v) Five-membered rings of molecule(II)

	n=3	*n*=4
P(2)	0·068	−0·065
O(21)	−0·066	
O(22)	−0·064	
O(23)		0·061
O(24)		0·063
C(*n*1)	0·030	−0·032
C(*n*2)	0·032	−0·027

(vi) Benzene rings of molecule(II)

	n=3	*n*=4
C(*n*1)	0·002	−0·014
C(*n*2)	0·001	−0·003
C(*n*3)	0·000	0·013
C(*n*4)	−0·002	−0·007
C(*n*5)	0·004	−0·009
C(*n*6)	−0·004	0·020

In both molecules as well as in the corresponding fluorine compound (Wunderlich & Mootz, 1974) the five-membered rings show similar bond lengths and angles. Differences in C–O bond lengths are paralleled by opposite differences of the adjacent P–O bond lengths. The benzene rings show some irregularities in bond lengths as well as in bond angles. In all rings the C–C–C angle at C(*n*3) and C(*n*6) is less than 120°, thus causing a reasonable squeezing of the rings towards the central phosphorus atom. These irregularities may reflect the condensation of the six- and five-membered rings, as well as the high thermal motions of the atoms. All C–H bond lengths vary in a range normally expected for X-ray data.

Additional least-squares planes (Table 4) show that the benzene rings are flat within 0·02 Å while the five-membered rings are puckered up to 0·09 Å. The angles between the two kinds of rings are 5·3, 1·2, 3·4, and 3·6°.

Both molecules reveal a non-crystallographic two-fold axis defined by the methyl group and the phosphorus atom. A rotation through this axis of one half

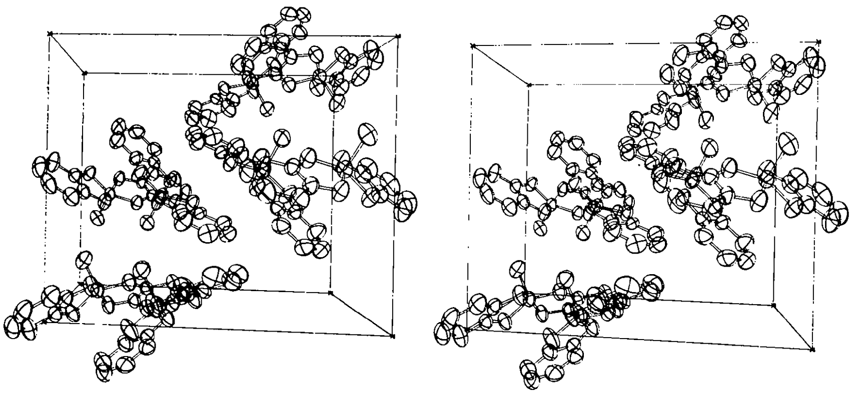

Fig. 2. Stereo plot (*ORTEP*, Johnson, 1965) of the molecular packing of $(C_6H_4O_2)_2PCH_3$ viewed parallel to c on ½,½,0. The lower right molecules represent the asymmetric unit as listed in Table 1.

of the molecule leads to r.m.s. distances for the corresponding atoms of 0·120 and 0·094 Å for molecule (I) and (II), respectively. The molecular packing of the compound, Fig. 2, displays no intermolecular approaches with distances less than the sum of the van der Waals radii.

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The Two-Dimensional Tunnel Structures of $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$*

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The structures of $K_3Sb_5O_{14}$ and $K_2Sb_4O_{11}$ have been solved by the single-crystal X-ray direct method and the heavy-atom method, respectively. The structure of $K_3Sb_5O_{14}$ is orthorhombic, with space group *Pbam* and cell parameters $a=24{\cdot}247$ (4), $b=7{\cdot}157$ (2), $c=7{\cdot}334$ (2) Å, $Z=4$. The structure of $K_2Sb_4O_{11}$ is monoclinic, with space group $C2/m$ and cell parameters $a=19{\cdot}473$ (4), $b=7{\cdot}542$ (1), $c=7{\cdot}198$ (1) Å, $\beta=94{\cdot}82$ (2)°, $Z=4$. A full-matrix least-squares refinement gave $R=0{\cdot}072$ and $R=0{\cdot}067$, respectively. In both structures, oxygen atoms form an octahedron around each Sb atom and an irregular polyhedron around each K atom. By sharing corners and edges, the octahedra form a skeleton network having intersecting *b*-axis and *c*-axis tunnels. The K^+ ions, which have more than ten oxygen near neighbors, are located in these tunnels. Evidence for K^+-ion transport within and between tunnels comes from ion exchange of the alkali ions in molten salts and anisotropic temperature factors that are anomalously large in the directions of the tunnels.

Introduction

Unlike Nb^{5+} and Ta^{5+}, the Sb^{5+} ion does not form structures having 180° Sb–O–Sb linkages (Goodenough & Kafalas, 1973). Thus $KSbO_3$ does not form the cubic perovskite structure. At atmospheric pressure it generally has the rhombohedral ilmenite structure. However, Spiegelberg (1940) reported synthesizing two cubic phases of $KSbO_3$ by annealing the ilmenite $KSbO_3$ for 3 weeks at 1000°C in a porcelain crucible. The structure of one of these, *Pn*3, was determined by him. The structure of the other, *Im*3, was elucidated by the present author (Hong, Kafalas & Goodenough, 1973). Both cubic structures contain Sb_2O_{10} edge-shared octahedra. These octahedral-site pairs share corners to form a three-dimensional skeleton structure containing empty tunnels of face-shared octahedra that run parallel to the cubic diagonals. In the *Pn*3 structure, the K^+ ions are ordered on the

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