References

BOLZ, L. H., BOYD, M. E., MAUER, F. A. & PEISER, H. S. (1959). *Acta Cryst.* **12**, 247–248.

BROOKEMAN, J. R., MCENNAN, M. M. & SCOTT, T. A. (1971). *Phys. Rev.* **B4**, 3661–3676.

BROOKEMAN, J. R. & SCOTT, T. A. (1972). *Acta Cryst.* **B28**, 983–984.

ENGLISH, C. A. & VENABLES, J. A. (1971). *Proceedings of the 25th Anniversary Meeting of the Electron Microscopy and Analysis Group*, pp. 48–49. To be published (1973). London: Institute of Physics.

GANNON, D. J. & MORRISON, J. A. (1973). *Canad. J. Phys.* **51**, 1590–1592.

GOODINGS, D. A. & HENKELMAN, M. (1971). *Canad. J. Phys.* **49**, 2902–2910.

HIRSCH, P. B., HOWIE, A., NICHOLSON, R. B., PASHLEY, D. W. & WHELAN, M. J. (1965). *Electron Microscopy of Thin Crystals*, pp. 201–202. London: Butterworths.

HÖRL, E. M. & MARTON, L. (1961). *Acta Cryst.* **14**, 11–19.

JORDAN, T. H., SMITH, H. W., STREIB, W. E. & LIPSCOMB, W. N. (1964). *J. Chem. Phys.* **41**, 756–759.

LA PLACA, S. J. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 984–985.

RUHEMANN, M. (1932). *Z. Phys.* **76**, 368–375.

SCHUCH, A. F. & MILLS, R. L. (1970). *J. Chem. Phys.* **52**, 6000–6008.

STEEDS, J. W., TATLOCK, G. J. & HAMPSON, J. (1973). *Nature, Lond.* **241**, 435–439.

VEGARD, L. (1929). *Z. Phys.* **58**, 497–501.

VENABLES, J. A. (1970). *Phil. Mag.* **21**, 147–166.

WATCHEL, E. J. (1972). *J. Chem. Phys.* **57**, 5620–5621.

Acta Cryst. (1974). **B30**, 935

Crystal Structures of Pentacoordinate Phosphorus Compounds. II.* 2-Fluoro-2,2′-spirobis-(1,3,2-benzodioxaphosphole), $(C_6H_4O_2)_2PF$

BY HARTMUT WUNDERLICH† AND DIETRICH MOOTZ†

Max-Planck-Institut für Festkörperforschung, 7 *Stuttgart* 1, *Postfach* 1099, *Germany* (*BRD*)

(*Received* 19 *November* 1973; *accepted* 21 *November* 1973)

The title compound is orthorhombic, space group $P2_12_12_1$, with a = 11·338 (5), b = 14·725 (5), c = 6·750 (3) Å; Z = 4. The intensities were measured on an automatic off-line four-circle diffractometer. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares calculations to R = 0·04. The geometry of the pentacoordinate phosphorus atom is considerably distorted from the idealized trigonal bipyramid and may be regarded as intermediate between this and a square pyramid. The axial angle O–P–O is 168·2°, the equatorial angles are 107·3, 106·6, and 146·1°. The P–O bond lengths are 1·659 and 1·658 Å (axial) and 1·628 and 1·625 Å (equatorial). Each catechol residue is connected to one axial and one equatorial oxygen atom, thus leaving an equatorial position for the fluorine atom.

The stereochemistry of pentacoordinate phosphorus is usually associated with the geometry of a trigonal bipyramid [see for example Ugi & Ramirez (1972)]. This model has been established for free molecules with five equal and independent ligands at the phosphorus atom, *e.g.* PF_5 (Hansen & Bartell, 1965). Packing forces, unequal ligands and steric interaction of some of the ligands as a consequence of chelation can be expected to cause deviations from the idealized D_{3h} ($\bar{6}m2$) symmetry. Such deviations have, in fact, often been observed since the first accurate crystal structure determinations of more complex compounds such as pentaphenylphosphorus (Wheatley, 1964), the *N*-methyltrichlorophosphinimine dimer (Hess & Forst, 1966) and a cyclic oxyphosphorane (Spratley, Hamilton & Ladell, 1967).

The title compound is also a cyclic oxyphosphorane, with two bidentate catechol residues and a fluorine atom at the phosphorus atom. Considerations of angular strain and ^{19}F n.m.r. data are consistent with the fluorine atom in the equatorial plane of a trigonal bipyramid and each catechol residue bridging one equatorial and one axial position (Doak & Schmutzler, 1970, 1971). However the fluorine atom, as the ligand with the highest electronegativity, should tend to an axial position (Ugi & Ramirez, 1972); thus the applicability of the trigonal bipyramid model to this molecule seems questionable and the alternative of a square pyramid geometry (Hoffmann, Howell & Muetterties, 1972) may be considered. The structure determination was undertaken in order to settle this point. In the structure presented in the following paper (Wunderlich, 1974) the fluorine atom is replaced by a methyl group. Preliminary accounts of both investigations have appeared elsewhere (Wunderlich & Mootz, 1973; Wunderlich, Mootz, Schmuztler & Wieber, 1973).

---

* Part I: Wunderlich, Mootz, Schmutzler & Wieber (1974).

† Present address: Lehrstuhl für Strukturchemie und anorganische Chemie, Universität Düsseldorf, 4 Düsseldorf, Germany.

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

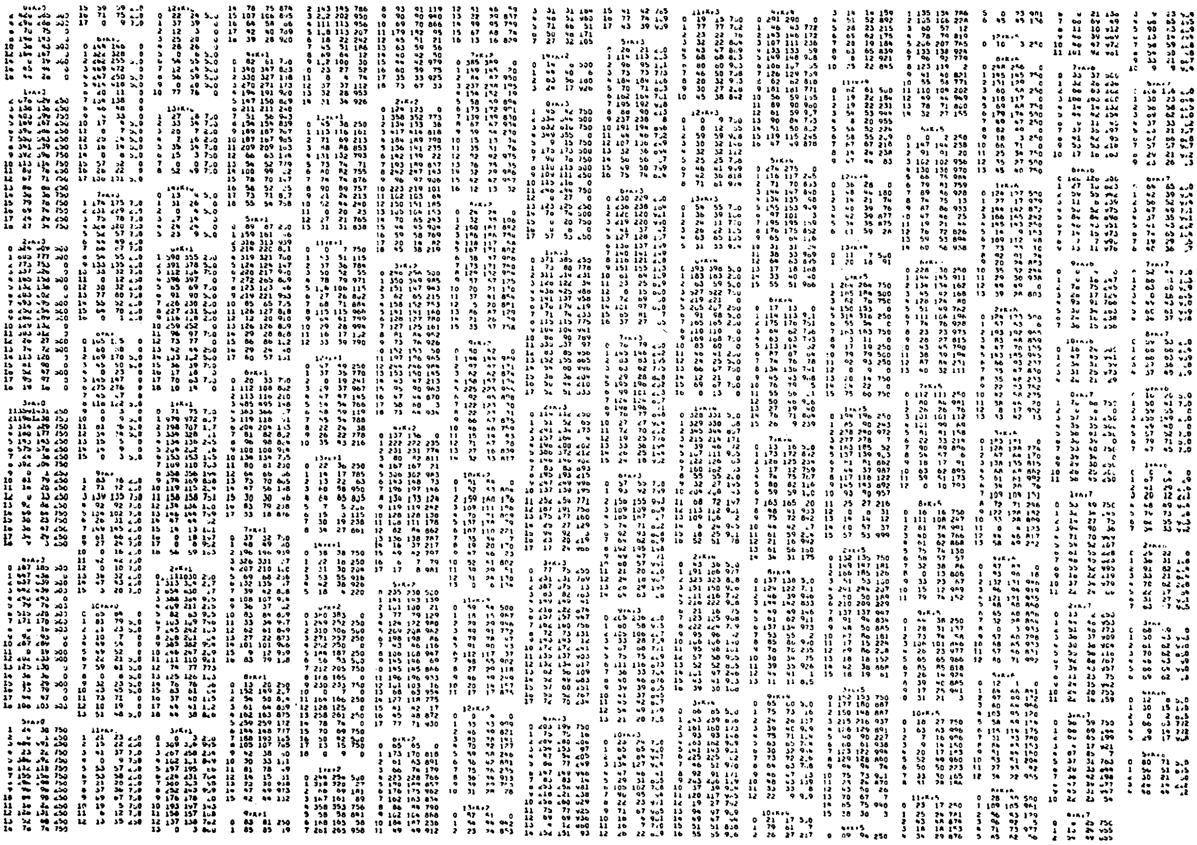
U or U_{ij} multiplied by 100. Temperature factor is defined by:

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

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0·12014 (6)	0·16163 (4)	0·08791 (10)	5·14 (4)	3·76 (3)	3·61 (3)	−0·44 (4)	0·02 (4)	0·41 (3)
F	−0·0051 (1)	0·2028 (1)	0·0779 (2)	5·6 (1)	5·9 (1)	6·5 (1)	0·4 (1)	−0·7 (1)	0·2 (1)
O(1)	0·1534 (2)	0·1264 (1)	−0·1339 (2)	6·5 (1)	4·1 (1)	3·7 (1)	−1·0 (1)	0·3 (1)	0·1 (1)
O(2)	0·0775 (2)	0·0582 (1)	0·1539 (3)	7·2 (1)	4·3 (1)	4·2 (1)	−1·6 (1)	0·5 (1)	0·4 (1)
O(3)	0·1643 (2)	0·1724 (1)	0·3158 (2)	5·9 (1)	4·2 (1)	3·4 (1)	−0·8 (1)	0·1 (1)	0·5 (1)
O(4)	0·1902 (2)	0·2556 (1)	0·0209 (3)	7·8 (1)	4·0 (1)	3·7 (1)	−1·6 (1)	−0·0 (1)	0·3 (1)
C(11)	0·0707 (2)	−0·0001 (2)	−0·0051 (4)	5·0 (2)	4·3 (2)	4·3 (1)	−0·2 (2)	−0·2 (1)	−0·1 (1)
C(12)	0·1153 (2)	0·0385 (2)	−0·1722 (4)	4·3 (2)	3·5 (1)	5·2 (1)	0·1 (1)	−0·4 (1)	0·4 (1)
C(13)	0·1198 (3)	−0·0056 (2)	−0·3505 (4)	5·5 (2)	4·7 (1)	4·4 (1)	0·3 (2)	0·2 (2)	−0·3 (1)
C(14)	0·0752 (3)	−0·0928 (2)	−0·3532 (5)	5·5 (2)	4·9 (2)	6·1 (2)	0·7 (1)	−0·3 (2)	−1·2 (2)
C(15)	0·0301 (3)	−0·1324 (2)	−0·1855 (6)	6·0 (2)	4·1 (2)	7·7 (2)	−0·7 (2)	−0·3 (2)	−0·5 (2)
C(16)	0·0266 (3)	−0·0873 (2)	−0·0060 (5)	6·4 (2)	4·8 (2)	6·2 (2)	−1·5 (2)	0·6 (2)	0·3 (2)
H(13)	0·148 (2)	0·025 (2)	−0·458 (4)	5 (1)					
H(14)	0·078 (2)	−0·124 (2)	−0·474 (4)	4 (1)					
H(15)	0·003 (3)	−0·188 (2)	−0·190 (4)	7 (1)					
H(16)	−0·007 (2)	−0·106 (2)	0·114 (4)	6 (1)					
C(21)	0·2319 (3)	0·3030 (2)	0·1800 (4)	4·8 (2)	3·9 (1)	3·9 (1)	−0·0 (1)	0·6 (1)	−0·0 (1)
C(22)	0·2186 (2)	0·2551 (2)	0·3519 (4)	4·3 (1)	3·6 (1)	4·4 (1)	−0·0 (1)	0·3 (1)	−0·1 (1)
C(23)	0·2574 (3)	0·2860 (2)	0·5307 (4)	6·2 (2)	5·2 (2)	4·2 (2)	−0·2 (2)	−0·2 (1)	−0·1 (1)
C(24)	0·3115 (3)	0·3714 (2)	0·5309 (5)	6·1 (2)	6·2 (2)	5·1 (2)	−0·4 (2)	−0·5 (2)	−1·4 (2)
C(25)	0·3236 (3)	0·4203 (2)	0·3569 (5)	5·4 (2)	4·8 (2)	6·4 (2)	−1·0 (2)	0·8 (2)	−1·4 (2)
C(26)	0·2847 (3)	0·3877 (2)	0·1786 (5)	5·8 (2)	4·4 (2)	5·1 (2)	−0·6 (1)	1·0 (2)	0·1 (1)
H(23)	0·253 (2)	0·253 (2)	0·645 (4)	6 (1)					
H(24)	0·342 (2)	0·392 (2)	0·652 (4)	5 (1)					
H(25)	0·358 (2)	0·476 (2)	0·362 (4)	6 (1)					
H(26)	0·294 (3)	0·412 (2)	0·057 (5)	7 (1)					

Table 2. *Observed and calculated structure factors*

The columns contain index h, $10F_{\text{meas}}$, $10F_{\text{calc}}$ and the phases in millicycles.



Experimental

Crystals of $(C_6H_4O_2)_2PF$, prepared by the method of Doak & Schmutzler (1970, 1971), were received from R. Schmutzler, Technische Universität Braunschweig, Germany. Because of moisture sensitivity the white irregular crystals were enclosed under argon in thin-walled capillaries.

The lattice parameters were determined at room temperature by measurement of diffractometer angles of 40 reflexions with Cu $K\alpha$ radiation and a subsequent least-squares refinement from the θ values. With $Z=4$ the calculated density is $d_x = 1·569$ g cm^{-3}. Weissenberg and precession photographs contained systematic absences of odd orders of $h00$, $0k0$, and possibly $00l$, which were subsequently confirmed during data collection. Consequently the space group is $P2_12_12_1$. The intensities of all 1485 independent reflexions up to $2\theta = 55°$ were determined on a paper-tape controlled diffractometer (Siemens AED) with Zr-filtered Mo $K\alpha$ radiation and a coupled θ:2θ scan for the so-called five-value measurement. There were 432 weak reflexions with $I < 3\sigma(I)$, where the standard deviation of the intensity is defined by $\sigma(I) = [\sigma^2_{\text{pk}} + (0·02I)^2]^{1/2}$ with $\sigma_{\text{pk}} = (I_{\text{pk}} + I_{\text{bg}})^{1/2}$ and $I = I_{\text{pk}} - I_{\text{bg}}$. The dimensions of the crystal were approximately 0·20 × 0·38 × 0·47 mm and

Table 3. *Bond angles of the molecule*

The numbering scheme (second index) for C and H atoms in the two halves of the molecule is based on the assumption of a molecular twofold symmetry axis through atoms P and F. E.s.d.'s are:

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

O(1)–P——O(2)	91·2°
O(3)–P——O(4)	91·7
O(1)–P——O(3)	146·1
O(2)–P——O(4)	168·2
O(1)–P——O(4)	84·5
O(2)–P——O(3)	85·7
O(1)–P——F	107·3
O(2)–P——F	96·0
O(3)–P——F	106·6
O(4)–P——F	95·8
P——O(1)—C(12)	113·3
P——O(2)—C(11)	112·3
P——O(3)—C(22)	112·9
P——O(4)—C(21)	112·2
O(1)–C(12)–C(11)	110·5
O(1)–C(12)–C(13)	126·5
O(2)–C(11)–C(12)	111·5
O(2)–C(11)–C(16)	127·2
O(3)–C(22)–C(21)	110·7
O(3)–C(22)–C(23)	126·3
O(4)–C(21)–C(22)	111·5
O(4)–C(21)–C(26)	127·3

	$n=1$	$n=2$
C(n6)–C(n1)–C(n2)	121·4°	121·2°
C(n1)–C(n2)–C(n3)	123·0	123·0
C(n2)–C(n3)–C(n4)	116·1	116·2
C(n3)–C(n4)–C(n5)	121·4	120·7
C(n4)–C(n5)–C(n6)	122·0	122·0
C(n5)–C(n6)–C(n1)	116·2	116·8
C(n2)–C(n3)–H(n3)	118	123
C(n4)–C(n3)–H(n3)	125	120
C(n3)–C(n4)–H(n4)	117	117
C(n5)–C(n4)–H(n4)	122	122
C(n4)–C(n5)–H(n5)	120	119
C(n6)–C(n5)–H(n5)	118	119
C(n5)–C(n6)–H(n6)	115	115
C(n1)–C(n6)–H(n6)	129	128

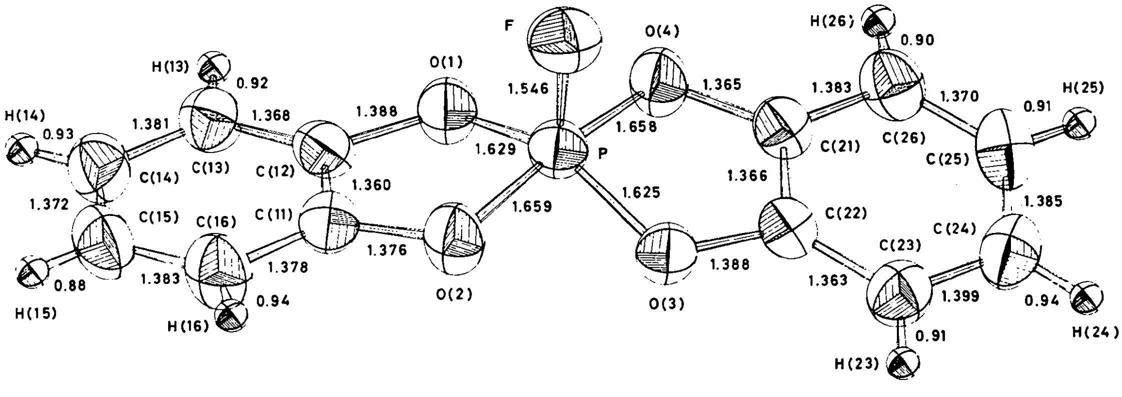


Fig. 1. The molecule of $(C_6H_4O_2)PF$ in arbitrary orientation to the crystallographic axes. Heavy atoms are represented by thermal ellipsoids of 50% probability and an isotropic temperature factor of $B = 1·0$ Å^2 was given to all hydrogen atoms. Bond lengths are given in Å. E.s.d.'s are: P–F,O 0·002, C–O 0·003, C–C 0·005 and C–H 0·03 Å.

c was parallel to the φ axis of the instrument. In view of the low linear absorption coefficient, $\mu_{\mathrm{Mo}\,K\alpha}=2{\cdot}7$ cm^{-1}, no absorption corrections were applied.

Structure determination and refinement

The coordinates of the phosphorus atom were derived from a sharpened Patterson map and the structure was completed by structure-factor calculations and Fourier syntheses. All hydrogen atoms were located in a difference map. The final full-matrix least-squares refinement, with anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogen atoms (195 parameters), converged at $R=\sum|\Delta F_{\mathrm{meas}}|/\sum|F_{\mathrm{meas}}|=0{\cdot}041$ and $R_w=[\sum w(\Delta F_{\mathrm{meas}})^2/\sum wF^2_{\mathrm{meas}}]^{1/2}=0{\cdot}030$ for all reflexions. The function minimized was $\sum w(\Delta F)^2$ with weights derived from $\sigma(I)$ through $w=1/\sigma^2(F)$. Atomic scattering factors for P, F, O, and C were taken from Cromer & Mann (1968), and those for H from Stewart, Davidson & Simpson (1965). The X-RAY (1972) system was used for all calculations. The final atomic coordinates and thermal parameters are given in Table 1; observed and calculated structure factors are listed in Table 2.

Results and discussion

Fig. 1 shows the molecule with thermal ellipsoids of the non-hydrogen atoms and all bond lengths; bond angles are given in Table 3. As speculated in the introduction the molecular structure is intermediate between trigonal bipyramidal and square pyramidal. A similar result was reported recently for the corresponding tetrathio compound $(C_6H_4S_2)_2PF$ (Eisenhut, Schmutzler & Sheldrick, 1973). The two axial oxygen atoms are moved away from the fluorine atom so as to reduce the O(2)–P–O(4) angle from 180° of an ideal bipyramid to 168·2°. Furthermore the difference between the longer axial P–O bond lengths, 1·659 and 1·658 Å, and the shorter equatorial ones, 1·629 and 1·625 Å, is less than usual for trigonal bipyramidal bonding (see for example the structural studies cited in the Introduction). However this difference is still significant (16σ) and is paralleled by an opposite, though smaller, difference between the adjacent C–O bonds in the five-membered rings. The distortion from trigonality caused by the unequal substitution and the chelation is shown by the differences of the equatorial angles (106·6, 107·3 and 146·1°). Bond lengths and bond angles in the two phosphole ring systems are discussed in the following article (Wunderlich, 1974).

Table 4, containing the distances of the atoms from various least-squares planes, shows the amount of distortion from idealized geometry in a different way. In a trigonal bipyramid the appropriate atoms forming the first four planes of Table 4(i) must be coplanar, whereas in an idealized square pyramid the appropriate atoms defining planes 1, 4 and 5 must be coplanar. Thus only atomic distances from planes 2, 3 and 5 are sensitive to a change from trigonal bipyramidal to square pyramidal geometry. The distances from plane

Table 4. *Atomic distances* (Å) *from several least-squares planes*

Only distances of atoms defining the planes are listed.

(i) Central part of the molecule

	Plane 1	2	3	4	5
P	−0·003	−0·107	−0·112	0·007	
F	0·001			−0·001	
O(1)	0·001	−0·004			0·153
O(2)		0·055	0·057	−0·003	−0·152
O(3)	0·001		−0·002		0·151
O(4)		0·056	0·057	−0·003	−0·153

(ii) Five-membered rings

	$n=1$	$n=2$
P	−0·061	−0·059
O(1)	0·056	
O(2)	0·060	
O(3)		0·053
O(4)		0·058
C(n1)	−0·031	−0·032
C(n2)	−0·024	−0·021

(iii) Benzene rings

	$n=1$	$n=2$
C(n1)	−0·001	0·005
C(n2)	−0·002	−0·005
C(n3)	0·003	0·001
C(n4)	−0·002	0·003
C(n5)	0·000	−0·003
C(n6)	0·002	−0·001

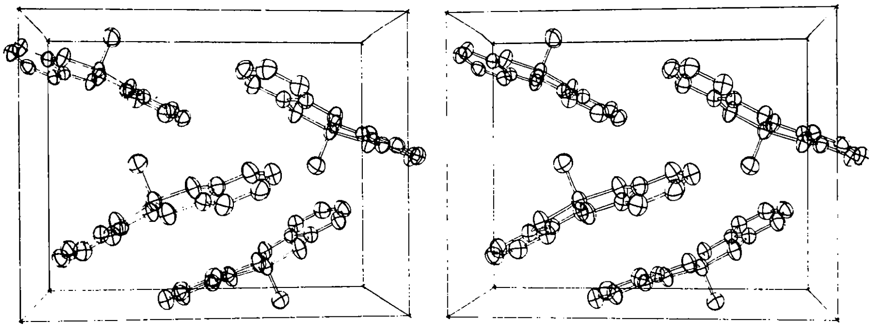


Fig. 2. Stereoview of the molecular packing of $(C_6H_4O_2)PF$ parallel to **c** on $\frac{1}{2},\frac{1}{2},0$ [program ORTEP by Johnson (1965)]. Upper left molecule represents the asymmetric unit, as listed in Table 1.

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.

References

Cromer, D. & Mann, J. (1968). *Acta Cryst.* A**24**, 321–324.
Doak, G. O. & Schmutzler, R. (1970). *Chem. Commun.* pp. 476–477.
Doak, G. O. & Schmutzler, R. (1971). *J. Chem. Soc.* (*A*), pp. 1295–1299.
Eisenhut, M., Schmutzler, R. & Sheldrick, W. S. (1973). *Chem. Commun.* pp. 144–145.
Hansen, K. W. & Bartell, L. S. (1965). *Inorg. Chem.* **4**, 1775–1776.
Hess, H. & Forst, D. (1966). *Z. anorg. allgem. Chem.* **342**, 240–252.
Hoffmann, R., Howell, J. M. & Muetterties, E. L. (1972). *J. Amer. Chem. Soc.* **94**, 3047–3058.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
Spratley, R. D., Hamilton, W. C. & Ladell, J. (1967). *J. Amer. Chem. Soc.* **89**, 2272–2278.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Ugi, I. & Ramirez, F. (1972). *Chem. Brit.* **8**, 198–210.
Wheatley, P. J. (1964). *J. Chem. Soc.* pp. 2206–2222.
Wunderlich, H. (1974). *Acta Cryst.* B**30**, 939–945.
Wunderlich, H. & Mootz, D. (1973). First European Crystallographic Meeting, Bordeaux, Group C6.
Wunderlich, H., Mootz, D., Schmutzler, R. & Wieber, M. (1974). *Z. Naturforsch.* In the press.
X-RAY (1972). Technical Report TR-192 of the Computer Science Center, Univ. of Maryland, June 1972.

Acta Cryst. (1974). B**30**, 939

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

By Hartmut Wunderlich*

Max-Planck-Institut für Festkörperforschung, 7 *Stuttgart* 1, *Postfach* 1099, *Germany* (*BRD*)

(*Received* 19 *November* 1973; *accepted* 21 *November* 1973)

The title compound is monoclinic, space group $P2_1/c$, with $a=14{\cdot}842$ (10), $b=12{\cdot}092$ (9), $c=13{\cdot}711$ (8) Å, $\beta=98{\cdot}52$ (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 $R=0{\cdot}05$. 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)

---

* Present address: Lehrstuhl für Strukturchemie und anorganische Chemie, Universität Düsseldorf, 4 Düsseldorf, Germany.