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2-Hydrido-2,2′-spirobi(1,3,2-benzodioxaphosphole)*

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Abstract. $(C_6H_4O_2)_2PH$, orthorhombic, $P2_12_12_1$; a = 21·141 (8), b = 17·514 (5), c = 5·844 (1) Å; M_r = 248·2, Z = 8, D_x = 1·52 g cm^{-3}, μ(Mo $K\alpha$) = 2·6 cm^{-1}. The structure was determined by direct methods and refined to R = 0·05. The two symmetry independent molecules of the asymmetric unit are related by a non-crystallographic twofold screw axis. The geometry of the pentacoordinated phosphorus atoms in both molecules can be described as 97% trigonal bipyramidal with H atoms in equatorial positions. The axial angles O—P—O are 179°, the equatorial angles O—P—O and H—P—O show deviations less than 3° from 120°.

Introduction. The title compound was prepared and crystallized from ether by Wieber, Foroughi & Klingl (1974). The needle-shaped crystals are air sensitive and had to be sealed in capillaries for X-ray investigations. Photographs showed the systematic absences of the space group $P2_12_12_1$. A comparison of the volume of the unit cell (V = 2164 Å^3) with the volume of the corresponding fluorooxyphosphorane (V = 1127 Å^3; Z = 4) yielded Z = 8 for this compound and thus two molecules in the asymmetric unit. The intensities of all 3587 symmetry-independent reflections up to 2θ = 60° were measured with Mo $K\alpha$ radiation. The computer-controlled diffractometer (Syntex $P2_1$) was operated in an ω-scan mode with a crystal monochromator. 2210 reflections were classified as observed [$I > 1{\cdot}96\sigma(I)$] and were used for the structure determination.

The phase problem was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) using 318 reflections with $|E| > 1{\cdot}55$ and 32 sets of starting phases. A subsequent E map with the most reliable set of phases yielded 32 of the 34 non-H atoms. All 18 H atoms, located in a difference Fourier synthesis, were included in the final refinement (379 parameters) with isotropic temperature factors. Convergence was obtained at R = 0·052 (0·094) and R_w = 0·047 (0·055) for the observed (all) reflections. The weighting scheme applied was $1/w = \sigma_F^2 + (0{\cdot}02F_o)^2$; scattering factors were taken from Cromer & Waber (1974). The anomalous scattering of the P atoms was applied to determine the absolute configuration of the molecules of the crystal under study. The final positional parameters including isotropic B values of all H atoms

Table 1. *Positional parameters* ($\times 10^4$) *for non-hyrogen atoms, with e.s.d.'s in parentheses*

	x	y	z
Molecule I			
P(1)	4925 (1)	4418 (1)	4072 (2)
O(11)	4544 (1)	4333 (2)	1664 (5)
O(12)	4475 (2)	5182 (2)	4865 (6)
O(13)	4665 (1)	3960 (2)	6292 (5)
O(14)	5385 (2)	3660 (2)	3252 (6)
C(11)	3999 (2)	5318 (2)	3335 (8)
C(12)	4035 (2)	4839 (2)	1472 (8)
C(13)	3608 (3)	4853 (3)	−288 (9)
C(14)	3129 (3)	5394 (3)	−158 (10)
C(15)	3093 (3)	5890 (3)	1696 (11)
C(16)	3525 (3)	5855 (3)	3481 (10)
C(21)	5336 (2)	3065 (2)	4757 (8)
C(22)	4921 (2)	3226 (2)	6519 (8)
C(23)	4797 (2)	2735 (3)	8286 (9)
C(24)	5116 (3)	2028 (3)	8189 (10)
C(25)	5531 (3)	1860 (3)	6443 (11)
C(26)	5650 (2)	2376 (3)	4655 (10)
Molecule II			
P(2)	6525 (1)	3530 (1)	9007 (2)
O(21)	6884 (1)	3578 (2)	6556 (5)
O(22)	6953 (2)	2742 (2)	9779 (6)
O(23)	6818 (1)	3983 (2)	11191 (6)
O(24)	6085 (2)	4309 (2)	8215 (6)
C(31)	7396 (2)	2564 (3)	8184 (9)
C(32)	7359 (2)	3033 (2)	6272 (9)
C(33)	7757 (2)	2967 (3)	4453 (9)
C(34)	8209 (2)	2384 (3)	4556 (11)
C(35)	8247 (2)	1912 (3)	6417 (12)
C(36)	7835 (3)	1988 (3)	8255 (12)
C(41)	6140 (2)	4885 (3)	9764 (9)
C(42)	6566 (2)	4714 (3)	11506 (9)
C(43)	6692 (3)	5191 (3)	13271 (10)
C(44)	6359 (3)	5894 (3)	13291 (11)
C(45)	5933 (3)	6064 (3)	11599 (12)
C(46)	5811 (3)	5567 (3)	9783 (10)

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* Crystal Structures of Pentacoordinate Phosphorus Compounds. VI. Part V: Wunderlich (1978*b*).

Table 2. *Positional parameters* ($\times 10^3$) *and temperature factors* (Å^2) *for the hydrogen atoms with e.s.d.'s in parentheses*

The H atoms are bonded to C and P atoms of identical numbering.

	x	y	z	B
Molecule I				
H(1)	541 (2)	487 (2)	433 (6)	1 (1)
H(13)	364 (2)	452 (2)	−148 (7)	1 (1)
H(14)	281 (2)	543 (2)	−148 (8)	4 (1)
H(15)	278 (3)	623 (3)	182 (10)	6 (1)
H(16)	352 (2)	614 (2)	469 (8)	3 (1)
H(23)	450 (2)	283 (2)	953 (9)	3 (1)
H(24)	505 (2)	169 (2)	915 (8)	3 (1)
H(25)	573 (2)	140 (3)	642 (10)	5 (1)
H(26)	597 (2)	222 (2)	347 (8)	3 (1)
Molecule II				
H(2)	597 (2)	312 (2)	931 (8)	4 (1)
H(33)	775 (2)	332 (2)	325 (8)	3 (1)
H(34)	854 (2)	230 (3)	335 (10)	6 (1)
H(35)	856 (3)	152 (3)	646 (12)	8 (2)
H(36)	787 (3)	169 (3)	927 (10)	5 (2)
H(43)	696 (2)	508 (2)	1450 (8)	3 (1)
H(44)	647 (2)	620 (2)	1466 (9)	4 (1)
H(45)	572 (2)	653 (3)	1154 (10)	6 (1)
H(46)	549 (2)	568 (2)	841 (8)	3 (1)

are given in Tables 1 and 2.* All calculations were carried out on a 32 K computer (ECLIPSE, Data General) using the program system *EXTL* (Syntex).

Discussion. Different arrangements of the ligands of pentacoordinate P atoms are discussed frequently to describe transition stages of reactions of tetracoordinate P atoms (Luckenbach, 1973). Spirocyclic oxyphosphoranes are a class of compounds with constraints on the stereochemistry of pentacoordination; thus knowledge of their structures is of interest. Two idealized forms characterize the range of possible geometries: the trigonal bipyramid (tbp, symmetry D_{3h}) and the tetragonal pyramid (tp, symmetry C_{4v}). Within this range the particular structure formed is expected to be determined by differences of electronegativities and steric hindrances of the unequal ligands. Further influence may be exerted by the chelation of the spiro system, *e.g.* reducing the possible tp to a rectangular pyramid (rp, symmetry C_{2v}).

A series of crystal structures of related spirocyclic oxyphosphoranes $(C_6H_4O_2)_2PR$ with different fifth substituents R is known: F (Wunderlich & Mootz, 1974), CH_3 (Wunderlich, 1974), OPh (Sarma, Ramirez & Marecek, 1976), Ph (Brown & Holmes, 1977*a*; Wunderlich, 1978*a*), Cl (Brown & Holmes, 1977*b*), *tert*-butyl (Wunderlich, 1978*b*). All these substituents impose medium to large steric requirements on the P atom in its spiro environment, resulting in geometries of 60 to 90% rp character (criterion by Holmes, 1974; Wunderlich, 1978*a*). The series of known structures is now extended to the molecule with the substituent R = H of minimal size.

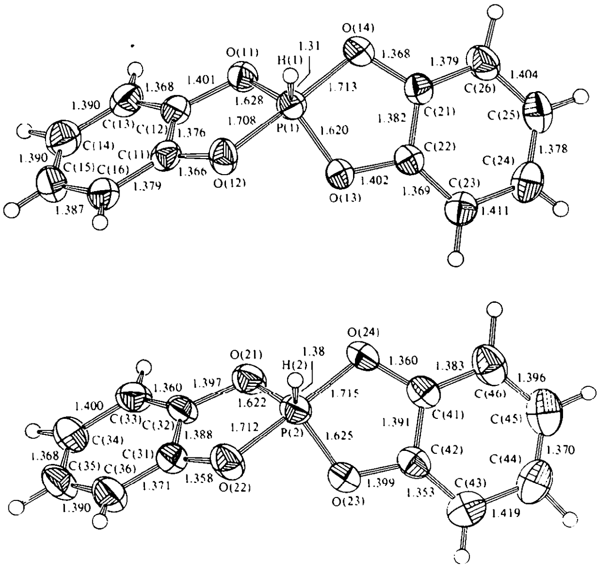

Fig. 1. The two symmetry-independent molecules of $(C_6H_4O_2)_2PH$ in arbitrary crystallographic orientation with bond lengths (Å). The e.s.d.'s are: P—O 0·003–0·004, C—O 0·005–0·006, C—C 0·006–0·009, and P—H 0·03–0·04 Å. The heavy atoms are represented by thermal ellipsoids of 50% probability (*ORTEP* II, Johnson, 1976).

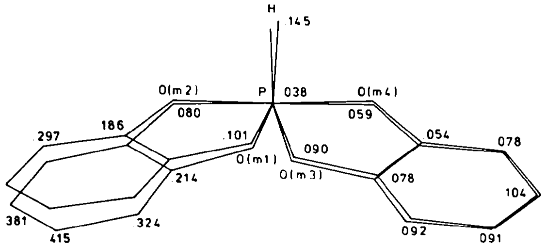

Fig. 2. Transformation of molecule II by a non-crystallographic 2_1 screw axis onto molecule I. The deviations from coincidence of corresponding atoms are given in Å (Wussow, 1977).

Fig. 1 shows the two independent molecules with main bond lengths; bond angles are listed in Table 3. The C—H distances range from 0·79 to 1·07 Å with C—C—H angles between 111 and 128°. Both molecules agree to within 3σ; thus the averaged values will be used in the discussion. The geometry of the pentacoordination is an almost perfect tbp with the H atom

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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 33566 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles in* $(C_6H_4O_2)_2PH$ *for molecule* I (m = 1) *and molecule* II (m = 2)

(i) Angles (°) at P atoms

The e.s.d.'s are O—P—O 0·2° and H—P—O 2°.

	m = 1	m = 2
O(m2)—P(m)—O(m4)	179·1	179·0
O(m2)—P(m)—O(m1)	91·7	91·5
O(m2)—P(m)—O(m3)	88·9	89·2
O(m2)—P(m)—H(m)	86	89
O(m4)—P(m)—O(m1)	88·2	88·6
O(m4)—P(m)—O(m3)	91·9	91·7
O(m4)—P(m)—H(m)	93	90
O(m1)—P(m)—O(m3)	118·5	119·2
O(m1)—P(m)—H(m)	123	122
O(m3)—P(m)—H(m)	118	119

(ii) Other angles (°) in the five-membered rings and exocyclic angles (°)

The e.s.d.'s are 0·3–0·5°.

	m = 1		m = 2	
	n = 1	n = 2	n = 3	n = 4
P(m)—O(m1)—C(n2)	113·1		114·0	
O(m1)—C(n2)—C(n1)	111·4		110·5	
C(n2)—C(n1)—O(m2)	111·8		112·1	
C(n1)—O(m2)—P(m)	111·7		111·7	
O(m1)—C(n2)—C(n3)	125·4		126·6	
O(m2)—C(n1)—C(n6)	128·0		128·0	
P(m)—O(m3)—C(n2)		113·4		113·9
O(m3)—C(n2)—C(n1)		111·3		110·4
C(n2)—C(n1)—O(m4)		111·7		112·4
C(n1)—O(m4)—P(m)		111·6		111·4
O(m3)—C(n2)—C(n3)		125·1		126·1
O(m4)—C(n1)—C(n6)		127·1		127·1

(iii) Angles (°) in the benzene rings

The e.s.d.'s are 0·4–0·6°.

	n = 1	n = 2	n = 3	n = 4
C(n6)—C(n1)—C(n2)	120·3	121·2	119·9	120·5
C(n1)—C(n2)—C(n3)	123·2	123·6	122·9	123·5
C(n2)—C(n3)—C(n4)	116·9	115·5	116·8	116·3
C(n3)—C(n4)—C(n5)	120·6	121·5	121·1	120·7
C(n4)—C(n5)—C(n6)	121·4	121·8	121·2	122·3
C(n5)—C(n6)—C(n1)	117·6	116·4	118·2	116·8

equatorial; averaged lengths are: $(P—O)_{axial}$ 1·712 Å *vs* $(P—O)_{equatorial}$ 1·624 Å. The large difference (0·088 Å) agrees with the corresponding value (0·081 Å) for pentaphenoxyphosphorane (Sarma, Ramirez, McKeever, Marecek & Lee, 1976) where there is no chelation and only a slightly distorted tbp. The axial angle at the P atom is 179·1°, the equatorial values are 118·9, 123, 119°, all in agreement with a description as a 97% tbp. From this result it is evident, for the series, that the stereochemistry of the P atom is not influenced by chelation of the spiro systems. Thus in principle the whole range between tbp and rp should be accessible by compounds of this class.

The large difference between axial and equatorial P—O bond lengths is accompanied by opposite unequal C—O bond lengths in the five-membered rings: $C—O_{ax}$ 1·363 *vs* $C—O_{equ}$ 1·400 Å. The rings are planar within 0·04 Å; the condensed benzene rings deviate less than 0·01 Å from planarity. Bond lengths and angles of the benzene rings show an influence of chelation which compresses the rings towards the central P atom.

Both molecules adopt the same absolute configuration, *i.e.* after applying a rotation and translation the first molecule coincides with the second. From the atomic coordinates this operation corresponds to a local non-crystallographic 2_1 axis parallel to [001] at x = 0·5725, y = 0·3974. Fig. 2 shows the second molecule superposed on the first; no atomic deviation is larger than 0·45 Å.

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