

Tableau 4. Angles de torsion endocycliques ($^{\circ}$)

- (1) Cycle des atomes 1, 2, 3, 4, 5 (cycle spirannique)
 1-2 = +22; 2-3 = 0; 3-4 = -23;
 4-5 = +35; 1-5 = -35
- (2) Cycles des atomes 5, 6, 7, 8, 9, 10
 5-6 = -57; 6-7 = +56; 7-8 = -54;
 8-9 = +55; 9-10 = -56; 5-10 = +56
- (3) Cycle des atomes 8, 9, 11, 12, 13, 14
 8-9 = -54; 9-11 = +54; 11-12 = -55;
 12-13 = +57; 13-14 = -61; 8-14 = +58
- (4) Cycle des atomes 13, 14, 15, 16, 17
 13-14 = +43; 14-15 = -38; 15-16 = +18;
 16-17 = +9; 13-17 = -32

La conformation de la molécule est décrite par les angles de torsion endocycliques repris au Tableau 4. La vue stéréoscopique de la Fig. 2 en donne également une idée.

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2-Phenyl-2,2'-spirobi(1,3,2-benzodioxaphosphole)*

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Abstract. (C₆H₄O₂)₂PC₆H₅, monoclinic, $P2_1/c$, $a = 6.663$ (1), $b = 17.254$ (2), $c = 13.347$ (2) Å, $\beta = 91.27$ (1) $^{\circ}$, $M_r = 324.26$, $Z = 4$, $D_x = 1.40$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 2.0$ cm⁻¹. The structure was solved by direct methods (*MULTAN*) and refined to $R_w = 0.07$. The stereochemistry of the P atom can be described as a 76% rectangular pyramid with *trans* basal angles O-P-O of 145.2 and 160.1 $^{\circ}$. Preliminary results have been given elsewhere [Wunderlich, Third European Crystallographic Meeting, Zurich, Switzerland (1976), Abstract 0 54 D].

Introduction. The title compound was prepared and crystallized by Wieber, Foroughi & Klingl (1974). The crystals had to be sealed in capillaries for the X-ray investigations. From systematic absences the space group was determined as $P2_1/c$. The intensities of all 2708 symmetry-independent reflexions up to $2\theta = 50^{\circ}$ were collected with a $\theta/2\theta$ scan by a computer-controlled diffractometer (Syntex $P2_1$) using Mo $K\alpha$

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Table 1. Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

	x	y	z
P	2066 (4)	82 (2)	2141 (2)
O(1)	-231 (8)	56 (4)	1651 (5)
O(2)	2756 (10)	-644 (4)	1356 (5)
O(3)	4383 (9)	387 (4)	1987 (5)
O(4)	1385 (10)	971 (4)	2540 (5)
C(11)	1158 (16)	-974 (6)	854 (8)
C(12)	-608 (17)	-577 (6)	1012 (7)
C(13)	-2404 (15)	-785 (7)	582 (9)
C(14)	-2358 (18)	-1435 (8)	-35 (8)
C(15)	-605 (20)	-1833 (7)	-201 (8)
C(16)	1223 (17)	-1601 (7)	255 (8)
C(21)	2992 (17)	1479 (7)	2621 (8)
C(22)	4706 (17)	1138 (7)	2315 (7)
C(23)	6463 (15)	1547 (8)	2255 (8)
C(24)	6414 (18)	2323 (8)	2516 (9)
C(25)	4671 (20)	2651 (7)	2855 (9)
C(26)	2887 (18)	2236 (7)	2908 (9)
C(31)	1972 (20)	-440 (6)	3289 (8)
C(32)	173 (22)	-618 (9)	3716 (12)
C(33)	143 (35)	-1015 (11)	4632 (16)
C(34)	1848 (45)	-1203 (11)	5058 (15)
C(35)	3622 (33)	-1060 (13)	4716 (17)
C(36)	3640 (23)	-653 (9)	3764 (12)

* Crystal Structures of Pentacoordinate Phosphorus Compounds. IV. Part III: Wunderlich (1974).

Table 2. *Calculated positional parameters ($\times 10^3$) of the hydrogen atoms*

The H atoms are labelled according to the C atoms to which they are attached.

	x	y	z
H(13)	-372	-49	72
H(14)	-371	-161	-40
H(15)	-65	-232	-65
H(16)	254	-189	13
H(23)	777	129	204
H(24)	768	266	242
H(25)	472	323	311
H(26)	158	248	314
H(32)	-114	-48	332
H(33)	-126	-113	492
H(34)	173	-150	574
H(35)	495	-122	509
H(36)	503	-52	345

radiation and a crystal monochromator. Because of the low percentage (37%) of observed reflexions ($I > 1.96\sigma_I$) the set of data was later reduced to $2\theta = 41.6^\circ$, containing 1036 (64%) observed reflexions (lowered level: $F_o > 2.5\sigma_F$) out of a total of 1618. Preliminary phases of 198 reflexions were determined by *MULTAN* (Germain, Main & Woolfson, 1971); a subsequent *E* map revealed seven connected atoms. The structure was completed by structure factor calculations and Fourier syntheses in the usual way. Owing to very high thermal motion of the phenyl group and the correspondingly poor quality of the data no H atoms could be localized by the difference Fourier technique. All 13 H atoms were generated and included as fixed-atom contributions in the final refinement converging at $R = 0.086$ (0.144) and $R_w = 0.072$ (0.079) for the observed (all) data. The weighting scheme applied was $1/w = \sigma_F^2 + (0.02F_o)^2$; atomic scattering factors were taken from Cromer & Waber (1974). All calculations were carried out with the program system *XTL* (Syntex) on a NOVA 1200 computer. The final positional parameters are given in Tables 1 and 2.*

Discussion. This series deals with crystal structures of a class of spirocyclic oxyphosphoranes with different fifth substituents: F (Wunderlich & Mootz, 1974), CH_3 (Wunderlich, 1974), C_6H_5 (this paper), and $\text{C}(\text{CH}_3)_3$ and H (both to be published). The variation of the fifth ligand involves differences in electronegativity and steric hindrance; both effects influence the geometry of the pentacoordinate P atom. The complete range between an ideal trigonal bipyramid (tbp, symmetry D_{3h}) and an ideal tetragonal pyramid (tp, symmetry

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33067 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

C_{4v}) has to be considered for the environment of the P atom. Of these limiting geometries, the latter should be substituted by a rectangular pyramid (rp, symmetry C_{2v}) in the spiro systems under study.

Bond lengths are given in Fig. 1, and bond angles in Table 3. The P—O bond lengths are significantly different and they indicate a tendency towards a pair of equatorial (1.652 and 1.648 Å) and a pair of axial

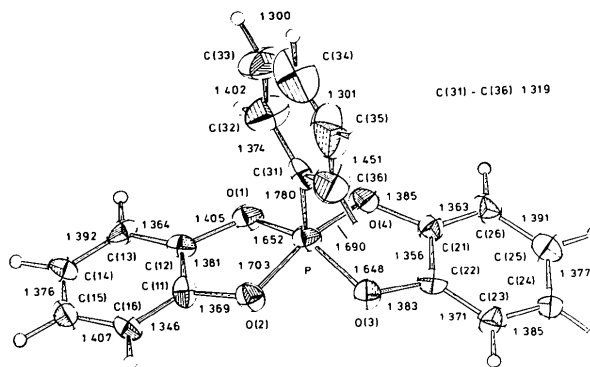


Fig. 1. The molecule of $(\text{C}_6\text{H}_4\text{O}_2)_2\text{PC}_6\text{H}_5$ with bond lengths (Å). Owing to high thermal motion the atoms are represented by ellipsoids of 30% probability only. H atoms are in calculated positions. Estimated standard deviations are: P—O 0.006–0.007, P—C 0.010, C—O 0.012–0.013, C—C (benzo rings) 0.015–0.018, and C—C (phenyl ring) 0.020–0.037 Å.

Table 3. *Bond angles in $(\text{C}_6\text{H}_4\text{O}_2)_2\text{PC}_6\text{H}_5$*

The e.s.d.'s are: 0.3–0.5° at P, 0.6° at O, and 1–2° at C.

(i) Angles (°) at the P atom

	O(1)	O(2)	O(3)	O(4)
O(2)	89.8			
O(3)	145.2	83.8		
O(4)	84.1	160.1	90.5	
C(31)	106.1	99.9	108.7	100.0

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

P—O(1)—C(12)	114.4	P—O(3)—C(22)	113.5
O(1)—C(12)—C(11)	109.7	O(3)—C(22)—C(21)	112.1
C(12)—C(11)—O(2)	112.1	C(22)—C(21)—O(4)	110.9
C(11)—O(2)—P	112.9	C(21)—O(4)—P	112.7

(iii) Angles (°) in the six-membered rings

	n = 1	n = 2	n = 3
C(n1)—C(n2)—C(n3)	123	121	120
C(n2)—C(n3)—C(n4)	115	117	118
C(n3)—C(n4)—C(n5)	122	120	126
C(n4)—C(n5)—C(n6)	121	122	115
C(n5)—C(n6)—C(n1)	116	115	122
C(n6)—C(n1)—C(n2)	122	123	118

(iv) Exocyclic angles (°)

O(1)—C(12)—C(13)	127	O(4)—C(21)—C(26)	126
O(2)—C(11)—C(16)	126	P—C(31)—C(32)	121
O(3)—C(22)—C(23)	126	P—C(31)—C(36)	121

bonds (1.703 and 1.690 Å) of a tbp. But the angles O(1)–P–O(3) (145.2°) and O(2)–P–O(4) (160.1°) give priority to a description of this geometry in terms of an rp. A simple consideration (Holmes, 1974) of the size of these two angles in relation to the values of the idealized geometries yields a 75% rp for this compound. An analogous criterion for a quantification of the geometry (Wunderlich, 1976) can be gained from a least-squares plane defined by the atoms O(1), O(2), O(3), and O(4). This is the basis of an ideal rp or tp with the four atoms coplanar (average distance $\langle d \rangle = 0$). In the case of an ideal tbp these atoms occupy the top, the bottom and two equatorial sites and cannot be coplanar. But they will all have identical distances from a best plane of exactly $\frac{1}{4}$ the averaged equatorial bond lengths. With these as two ends of a scale ($\langle d \rangle = 0$ and a maximum of $\langle d \rangle = \frac{1}{4}\langle P-O \rangle_{eq}$) it is possible to classify every intermediate geometry by a criterion involving the positions of four ligands of the central atom. In the title compound, the four O atoms have an averaged distance of 0.100 Å from the corresponding least-squares plane and the averaged equatorial bond length is 1.650 Å. Thus, this geometry is 0.100/0.4125 = 0.24 away from the ideal rp and can be called 76% rp.

Many of the bond lengths and bond angles of the five-membered rings, the condensed benzene rings and the extra phenyl group show considerable deviations from standard values but they agree with those of other structures of this type, e.g. the analogous phenoxyphosphorane (Sarma, Ramirez & Marecek, 1976).

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Bond distances in rhodium tribromide, RhBr₃, by the X-ray absorption technique. By JOSEPH REED* and P. EISENBERGER, *Bell Laboratories, Murray Hill, New Jersey 07974, USA*

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The interatomic bond distances in RhBr₃ have been determined by extended X-ray absorption fine structure (EXAFS) measurements of the K-shell absorption edges of rhodium and bromine. The analysis yields a Rh–Br distance of 2.49 (1) Å based on the Rh edge data. The Br edge data yield 2.48 (1) Å for the Br–Rh bond and a Br–Br distance of 4.85 (1) Å.

Introduction

In soluble transition-metal catalysts, the strength of the interatomic metal-to-ligand bond is of the utmost importance. A ligand, *L*, must frequently be dissociated in order to make a coordination site available, and the important factor then is the stability of the interatomic *M–L* bond (Henrici-Olivé & Olivé, 1971). Rhodium trihalides have been shown to be active catalysts in the reduction of fumaric acid in aqueous acetate solutions at 25 °C and 1 atm hydrogen (Ipatieff & Tronev, 1935). Nevertheless, structural determinations which would help to elucidate the way in which rhodium trihalides

function as catalysts have not been attempted to date. One possible reason could be the extreme difficulty in obtaining X-ray quality single crystals owing to the deliquescent nature of RhX₃, where X = Cl, Br.

This study reports on the interatomic bond distances in RhBr₃, where a novel technique, extended X-ray absorption fine structure (EXAFS), was used. This technique does not rely on single crystals and has been used previously to determine interatomic distances in iron–sulfur proteins (Shulman, Eisenberger, Blumberg & Stombaugh, 1975), in copper salts in aqueous solutions (Eisenberger & Kincaid, 1975), and in polymer-bound rhodium(I) catalysts (Reed, Eisenberger, Teo & Kincaid, 1977). This present study is part of a larger effort in developing structural confidence in the use of EXAFS as a complement to single-crystal X-ray crystallography.

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