

2-*tert*-Butyl-2,2'-spirobi(1,3,2-benzodioxaphosphole)\*

BY HARTMUT WUNDERLICH

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1,  
4000 Düsseldorf, Federal Republic of Germany

(Received 3 January 1978; accepted 27 January 1978)

**Abstract.**  $(C_6H_4O_2)_2PC(CH_3)_3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 13.223$  (3),  $b = 6.783$  (1),  $c = 16.832$  (5) Å,  $M_r = 304.3$ ,  $Z = 4$ ,  $D_m = 1.33$ ,  $D_x = 1.34$  g cm $^{-3}$ ,  $\mu(Mo K\alpha) = 2.0$  cm $^{-1}$ ; final  $R = 0.07$ . The stereochemistry of the pentacoordinate P atom can be described as an 87% rectangular pyramid with the *tert*-butyl group at the apical site. The two *trans* basal angles O–P–O are 154.9 and 147.0°. Preliminary results have been given [Wunderlich, Third European Crystallographic Meeting, Zurich, Switzerland (1976), Abstract O 54 D].

**Introduction.** The preparation of the title compound is described by Wieber, Foroughi & Klingl (1974). The crystals, received from these authors, were very air sensitive and had to be sealed in capillaries for X-ray investigations. Systematic absences were unique for the space group  $P2_12_12_1$ . The intensities of all 1564 symmetry-independent reflections up to  $2\theta = 50^\circ$  were measured on a computer-controlled diffractometer (Syntex P2<sub>1</sub>) with Mo  $K\alpha$  radiation, a crystal monochromator and a  $\theta/2\theta$  scan mode. From this set five reflections had intensities too high with respect to dead-time losses of the counter and, in addition, a series of 121 reflections had to be removed later because the operation of the shutter had failed. From the resulting 1543 reflections, 1210 were classified as observed ( $F_o > 2.5\sigma_F$ ) and were used for the structure determination. The phase problem was solved from the Patterson function, and the solution completed by Fourier syntheses. The eight H atoms connected to the benzene rings could be located in a difference synthesis, but the nine H atoms of the *tert*-butyl group could be found from a subsequent difference synthesis only with difficulty. Due to high thermal motion in this group their positions remain questionable. During the final refinement with anisotropic thermal parameters for all non-hydrogen atoms, fixed temperature factors for the H atoms of the benzene rings and fixed positional and thermal parameters for the H atoms of the *tert*-butyl group 214 parameters were refined to  $R = 0.071$  (0.094) and  $R_w = 0.068$  (0.070) for the ob-

served (all) reflections. The weighting scheme was  $1/w = \sigma_F^2 + (0.02F_o)^2$ ; scattering factors were taken from Cromer & Waber (1974). Tables 1 and 2 contain the final positional parameters.† All calculations were carried out with the systems XTL and EXTL (Syntex) on NOVA 1200 and ECLIPSE computers respectively.

**Discussion.** In the past many discussions about the trigonal-bipyramidal (tbp) orientation of the ligands of the P atom and transitions from one such orientation to another by pseudorotation (Berry, 1960) or turnstile rotation (Gillespie *et al.*, 1971; Marquarding, Ramirez, Ugi & Gillespie, 1973) have appeared. But only recently has the alternative orientation of a tetragonal-pyramidal (tp) environment of the P atom been found in crystal structures (Wunderlich & Mootz,

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33369 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
P	2280 (2)	1698 (3)	2272 (1)
O(1)	2252 (4)	4065 (7)	2529 (3)
O(2)	2745 (4)	1166 (7)	3180 (3)
O(3)	1745 (4)	−517 (7)	2357 (3)
O(4)	1376 (4)	2354 (7)	1624 (3)
C(11)	3003 (5)	2778 (10)	3609 (5)
C(12)	2725 (6)	4446 (11)	3240 (4)
C(13)	2881 (6)	6308 (11)	3559 (5)
C(14)	3354 (7)	6365 (13)	4292 (5)
C(15)	3632 (8)	4652 (14)	4686 (6)
C(16)	3449 (7)	2805 (13)	4346 (5)
C(21)	756 (6)	867 (11)	1416 (4)
C(22)	972 (5)	−838 (11)	1828 (4)
C(23)	455 (6)	−2580 (13)	1736 (5)
C(24)	−331 (6)	−2563 (14)	1182 (5)
C(25)	−572 (6)	−856 (15)	755 (5)
C(26)	−36 (6)	890 (13)	862 (5)
C(31)	3390 (5)	1376 (13)	1626 (5)
C(32)	3721 (8)	3335 (18)	1310 (7)
C(33)	4269 (7)	441 (20)	2061 (5)
C(34)	3145 (7)	97 (23)	928 (8)

\* Crystal Structures of Pentacoordinate Phosphorus Compounds. V. Part IV: Wunderlich (1978).

Table 2. Positional parameters ( $\times 10^3$ ) with e.s.d.'s in parentheses of the H atoms bonded to C atoms (with identical first two digits of the labelling)

The H atoms of the *tert*-butyl group were used as fixed-atom contributions during the final refinement. The temperature factor was fixed at  $B = 8.0 \text{ \AA}^2$  for these atoms and at  $B = 6.0 \text{ \AA}^2$  for the remaining H atoms.

	x	y	z
H(13)	271 (6)	753 (12)	328 (5)
H(14)	350 (6)	754 (12)	458 (5)
H(15)	373 (6)	468 (12)	519 (5)
H(16)	364 (6)	174 (12)	456 (5)
H(23)	58 (6)	-387 (12)	204 (4)
H(24)	-67 (6)	-390 (12)	106 (5)
H(25)	-117 (6)	-92 (11)	43 (5)
H(26)	-26 (6)	202 (12)	52 (4)
H(321)	294	384	98
H(322)	393	434	173
H(323)	431	331	92
H(331)	439	119	253
H(332)	479	18	161
H(333)	419	-85	246
H(341)	385	-57	68
H(342)	278	92	49
H(343)	263	-98	106

1973; Howard, Russell & Trippett, 1973; Wunderlich, 1974). The geometries of these molecules show only small deviations from the ideal *tp* calculated by Zemmann (1963) with a simple point-charge model. Several other crystal structures with pentacoordinate P atoms cover the complete range between the ideal *tpb* and *tp*.

The crystal structure under study extends a series of spirocyclic oxyphosphoranes (Wunderlich, 1978) in which the fifth substituent is altered with regard to electronegativity and steric hindrance. Both effects influence the geometry at the P atom and the whole range of geometries between *tpb* and *tp* has to be considered. Due to the chelation in the compounds of this series the *tp* has to be replaced in this discussion by a rectangular pyramid (*rp*, symmetry  $C_{2v}$ ).

Fig. 1 shows the molecule with bond lengths between non-hydrogen atoms. The bond angles are given in Table 3. Distances and angles concerning the H atoms of the benzene rings are in the expected range (0.86–1.03 Å and 114–128°); those involving the uncertain methyl groups vary over a wider range (0.9–1.2 Å and 99–125°). The four P–O bonds show only a residual character of a *tpb* with enlarged axial [P–O(2) 1.687, P–O(4) 1.678 Å] and shortened equatorial [P–O(1) 1.663, P–O(3) 1.667 Å] lengths. However, the average distance between these pairs (0.018 Å) is small compared with the corresponding values in pentaphenoxyphosphorane (0.081 Å; Sarma, Ramirez, McKeever, Marecek & Lee, 1976) and in the hydrido compound  $(C_6H_4O_2)_2PH$  of this series (0.087 Å; Wussow, 1977; Wunderlich & Wussow, 1978), both revealing an only slightly distorted *tpb*. In terms of an

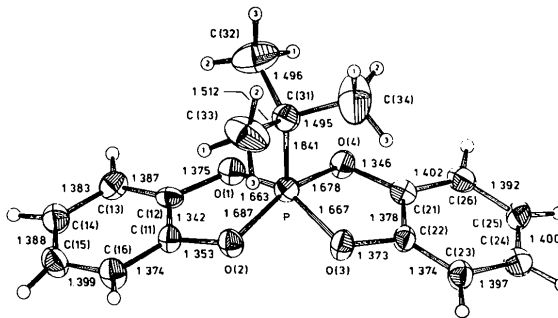


Fig. 1. The molecule of  $(C_6H_4O_2)_2PC(CH_3)_3$  in an arbitrary crystallographic orientation. Thermal ellipsoids are at a level of 30% probability (ORTEP II, Johnson, 1976). All bond lengths are in Å. The e.s.d.'s are: P–O 0.005, P–C 0.008, C–O 0.008, C–C (benzene rings) 0.010–0.013, and C–C (*tert*-butyl) 0.013–0.016 Å. The H atoms of the *tert*-butyl group are identified by the last digit of their labelling.

Table 3. Bond angles in  $(C_6H_4O_2)_2PC(CH_3)_3$

(i) Angles (°) at the P atom. The e.s.d.'s are 0.3°.

	O(1)	O(2)	O(3)	O(4)
O(2)	88.8			
O(3)	147.0	83.4		
O(4)	84.1	154.9	89.6	
C(31)	106.6	102.7	106.4	102.5

(ii) Other angles (°) in the five-membered rings. The e.s.d.'s are 0.4–0.6°.

P–O(1)–C(12)	113.5	P–O(3)–C(22)	113.8
O(1)–C(12)–C(11)	111.6	O(3)–C(22)–C(21)	110.3
C(12)–C(11)–O(2)	111.5	C(22)–C(21)–O(4)	111.8
C(11)–O(2)–P	113.7	C(21)–O(4)–P	113.8

(iii) Angles (°) in the benzene rings. The e.s.d.'s are 0.7–0.8°.

	n = 1	n = 2
C(n1)–C(n2)–C(n3)	123.2	124.2
C(n2)–C(n3)–C(n4)	116.0	116.0
C(n3)–C(n4)–C(n5)	121.5	121.3
C(n4)–C(n5)–C(n6)	120.5	121.4
C(n5)–C(n6)–C(n1)	117.2	117.2
C(n6)–C(n1)–C(n2)	121.6	119.9

(iv) Exocyclic angles (°). The e.s.d.'s are 0.7°.

O(1)–C(12)–C(13)	125.2	O(3)–C(22)–C(23)	125.4
O(2)–C(11)–C(16)	126.9	O(4)–C(21)–C(26)	128.3

(v) Angles (°) of the *tert*-butyl group. The e.s.d.'s are 0.6–0.8°.

P–C(31)–C(32)	109.7	C(32)–C(31)–C(33)	108.6
P–C(31)–C(33)	112.1	C(32)–C(31)–C(34)	107.5
P–C(31)–C(34)	111.1	C(33)–C(31)–C(34)	107.7

*rp* there are two *trans* basal O–P–O angles of similar size (147.0 and 154.9°) and four apical basal angles C–P–O with small differences (106.6, 102.7, 106.4, and 102.5°). Thus, the bond lengths as well as the bond angles give preference for a description in terms of an *rp* with the *tert*-butyl group in the apical position. The four O atoms have to be coplanar in an *rp*, but they cannot be coplanar in a *tpb*. The average deviation from coplanarity of these atoms is only 0.054 Å and

this can be used for a quantification of the geometry (Wunderlich, 1978) giving an 87% rp for this structure.

Due to the chelation and probable packing effects the benzene rings show some deviations from standard geometries. As in all spirocyclic oxyphosphoranes the benzene rings are squeezed towards the center of the molecule. The five- and six-membered rings are planar within 0.05 and 0.01 Å respectively. The condensed rings at each side of the P atom are coplanar within 2°.

#### References

- BERRY, R. S. (1960). *J. Chem. Phys.* **32**, 933–938.  
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–98. Birmingham: Kynoch Press.  
 GILLESPIE, P., HOFFMANN, P., KLUSACEK, H., MARQUARDING, D., PFOHL, S., RAMIREZ, F., TSOLIS, E. A. & UGI, I. (1971). *Angew. Chem.* **83**, 691–721.  
 HOWARD, J. A., RUSSELL, D. R. & TRIPPETT, S. (1973). *J. Chem. Soc. Chem. Commun.* pp. 856–857.  
 JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.  
 MARQUARDING, D., RAMIREZ, F., UGI, I. & GILLESPIE, P. (1973). *Angew. Chem.* **85**, 99–127.  
 SARMA, R., RAMIREZ, F., MCKEEVER, B., MARECEK, J. F. & LEE, S. (1976). *J. Am. Chem. Soc.* **98**, 4691.  
 WIEBER, M., FOROUGH, K. & KLINGL, H. (1974). *Chem. Ber.* **107**, 639–643.  
 WUNDERLICH, H. (1974). *Acta Cryst.* **B30**, 939–945.  
 WUNDERLICH, H. (1976). Third European Crystallographic Meeting, Zurich, Switzerland. Abstract 0 54 D.  
 WUNDERLICH, H. (1978). *Acta Cryst.* **B34**, 342–344.  
 WUNDERLICH, H. & MOOTZ, D. (1973). First European Crystallographic Meeting, Bordeaux, France. Group C6.  
 WUNDERLICH, H. & WUSSOW, H.-G. (1978). *Acta Cryst.* **B34**. In the press.  
 WUSSOW, H.-G. (1977). Diplomarbeit, Universität Düsseldorf.  
 ZEMANN, J. (1963). *Z. Anorg. Allg. Chem.* **324**, 241–249.

*Acta Cryst.* (1978). **B34**, 2017–2020

## Acétyl-1 *O*-Acétyl-6 Laurelliptine

PAR R. ROQUES

*Laboratoire de Cristallographie, Faculté des Sciences d'Abidjan, BP 4322, Abidjan, Côte d'Ivoire*

ET J. P. DECLERCQ ET G. GERMAIN

*Laboratoire de Chimie-Physique et de Cristallographie, Université de Louvain, B-1348, Louvain-la-Neuve, Belgique*

(Reçu le 21 octobre 1977, accepté le 27 octobre 1977)

**Abstract.** C<sub>22</sub>H<sub>23</sub>NO<sub>6</sub>, *M<sub>r</sub>* = 397, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 15.88<sub>8</sub>, *b* = 11.52<sub>9</sub>, *c* = 21.47<sub>2</sub> Å, *V* = 3927.7 Å<sup>3</sup>, *Z* = 8 (two independent molecules), *D<sub>m</sub>* = 1.32<sub>2</sub>, *D<sub>c</sub>* = 1.34 g cm<sup>-3</sup>, *F*(000) = 1680, 2448 observed reflexions, λ(Cu *K*α) = 1.54178 Å, *T* = 294 K. Agreement between the bond distances in the two independent molecules is good.

**Introduction.** Cet alcaloïde, dérivé de la laurelliptine extraite de *Monodora tenuifolia* de la famille des Annonaceae de la flore ivoirienne, nous a été donné par le Laboratoire de Chimie Organique de l'Université d'Abidjan pour identifier et préciser sa structure qui, par voie chimique, présentait de grandes difficultés. En effet, l'alcaloïde de base, la laurelliptine, n'était pas identifié. Cette identification n'a pu s'effectuer qu'après

détermination de sa structure cristalline (Roques, Djakoure & Rossi, 1978).

La laurelliptine a été purifiée par chromatographie sur colonne d'alumine neutre par élution au chlorure de méthylène à 0,5% de méthanol. Ce composé a été obtenu par acétylation de l'alcaloïde laurelliptine, et cristallisé dans le chlorure de méthylène. Les cristaux obtenus sont parallélépipédiques; celui utilisé pour les mesures d'intensité diffractée avait les dimensions suivantes: 0,50 × 0,30 × 0,25 mm.

Une étude sur chambre de Weissenberg et de précession nous a permis de déterminer le groupe spatial, ainsi qu'une première valeur des paramètres. Les intensités de diffraction ont été enregistrées à l'aide d'un diffractomètre automatique CAD-3 Enraf-Nonius. Ces mesures ont été effectuées à 294 K en