References

Barrio, J. R., Secrist, J. A. & Leonard, N. J. (1972). *Biochem. Biophys. Res. Commun.* **46**, 597–604.

Biernat, J., Ciesiołka, J., Górnicki, P., Adamiak, R., Krzyżosiak, W. J. & Wiewiórowski, M. (1978). *Nucleic Acids Res.* **5**, 789–804.

Biernat, J., Ciesiołka, J., Górnicki, P., Krzyżosiak, W. J. & Wiewiórowski, M. (1978). *Nucleic Acids Res. Spec. Publ.* **4**, 203–206.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. 1. New York: Plenum.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Groth, P. (1971). *Acta Chem. Scand.* **25**, 118–128.

Jaskólski, M. (1979). PhD dissertation. A. Mickiewicz Univ., Poznań, Poland.

Krzyżosiak, W. J., Biernat, J., Ciesiołka, J., Górnicki, P. & Wiewiórowski, M. (1979*a*). *Pol. J. Chem.* **53**, 243–252.

Krzyżosiak, W. J., Biernat, J., Ciesiołka, J., Górnicki, P. & Wiewiórowski, M. (1979*b*). *Tetrahedron Lett.* pp. 2647–2648.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Singh, C. (1965). *Acta Cryst.* **19**, 861–864.

Tsernoglou, D. (1966). PhD dissertation. Yale Univ., New Haven, USA.

Wang, A. H. J., Barrio, J. R. & Paul, I. C. (1976). *J. Am. Chem. Soc.* **98**, 7401–7408.

Acta Cryst. (1980). B**36**, 974–977

Structure of Triphenylphosphine Oxide Hemiperhydrate

By Dieter Thierbach, Friedo Huber* and Hans Preut

Lehrstuhl für Anorganische Chemie II, *Universität Dortmund, D*-4500 *Dortmund* 50,
Federal Republic of Germany

(*Received* 7 *November* 1979; *accepted* 2 *January* 1980)

Abstract. $2[C_{18}H_{15}OP.\frac{1}{2}H_2O_2]$, M_r = 590·6, orthorhombic, *Fdd*2, a = 32·277 (1), b = 19·786 (4), c = 9·546 (2) Å, $Z = 8$, V = 6096·4 Å^3, D_c = 1·30, D_m = 1·33 Mg m^{-3} (flotation), μ(Mo $K\alpha$) = 0·137 mm^{-1}, $F(000)$ = 2256, R = 0·083. The crystallographically dependent $(C_6H_5)_3PO$ units and H_2O_2 molecules are linked by hydrogen bonds. Some bond parameters are: P–O(1) = 1·477 (10), O(1)···O(2) = 2·759 (24), O(2)–O(2′) = 1·443 (14) Å, P–O(1)–O(2) = 134·7 (7), O(1)–O(2)–O(2′) = 99·9 (12)°.

Introduction. Recently, we have found short hydrogen bonds in $Ph_3PO.HCl$ (Haupt, Huber, Krüger, Preut & Thierbach, 1977), $Ph_3PO.HF$ (Thierbach & Huber, 1979*a*) and $(Ph_3PO)_2.H_2O.HBr$ (Thierbach & Huber, 1979*b*). In our efforts to determine structures of other hydrogen-bonded derivatives of phosphine oxides, we first tried to prepare crystals of hydrates, described as 1:1 (Michaelis & Gleichmann, 1882; Michaelis & von Soden, 1885) and 2:1 adducts (Halman & Pinchas, 1958). We obtained, however, in all cases, only the monoclinic modification of Ph_3PO. We then turned to investigate other adducts of Ph_3PO with HOX ligands and succeeded in determining the structure of $(Ph_3PO)_2.H_2O_2$. This compound was first prepared by Temple, Tsuno & Leffler (1963), and was proposed as a polymerization catalyst (Rudolph & Reinking, 1967).

Suitable colourless single crystals were obtained by shaking a solution of 2·0 g $(C_6H_5)_3PO$ and 3·1 g 30% H_2O_2 in 24 g ethanol (yield 96%). Analysis: C (found/calc.) 73·18/72·21%, H 5·36/5·46%; TGA (maximum temperature 460 K): total weight loss 6·1% (calculated for loss of H_2O_2 5·8%).

Precession and Weissenberg photographs indicated an orthorhombic lattice with systematic absences (hkl, $h + k = 2n + 1$, $k + l = 2n + 1$ and $l + h = 2n + 1$; $0kl$, $k = 2n + 1$, $l = 2n + 1$ and $k + l = 4n + 1$; $h0l$, $h = 2n + 1$, $l = 2n + 1$ and $h + l = 4n + 1$; $hk0$, $h = 2n + 1$ and $k = 2n + 1$; $h00$, $h = 4n + 1$; $0k0$, $k = 4n + 1$; $00l$, $l = 4n + 1$) consistent with the space group *Fdd*2. The crystal used for data collection was 0·48 × 0·24 × 0·19 mm. The intensity measurements were made on a Hilger & Watts four-circle diffractometer (Mo $K\alpha$ radiation, λ = 0·70926 Å, graphite monochromator and scintillation counter). The cell dimensions and orientation matrix were determined by least squares from the angular positions of 20 reflections. A complete set of symmetry-independent reflections was

---

* To whom correspondence should be addressed.

0567-7408/80/040974-04$01.00

collected within the angular range $2 \le 2\theta \le 32°$ in an ω–2θ scan mode with 70 steps [scan width $\Delta 2\theta = (1{\cdot}34 + 0{\cdot}34 \times \tan\theta)°$ from background to background], an ω step rate of $0{\cdot}01°\ \mathrm{s}^{-1}$ and 2θ step rate of $0{\cdot}02°\ \mathrm{s}^{-1}$. Backgrounds were measured at each end of the scan range for 7s. Three standard reflections showed no significant change in intensity. Background, Lp and absorption corrections were applied. Of the 1317 independent reflections measured, 211 were unobserved and not included in the $[|F_o| < 3\sigma(F_o)]$ refinement.

The structure was solved by Patterson and Fourier methods and refined by blocked full-matrix least squares. Phenyl H atoms were found from a difference synthesis, but it was not possible to locate the H atoms of the H_2O_2. During the refinement the phenyl rings were treated as rigid hexagons (C—C—C 120°; C—C 1·395, C—H 1·080 Å) with individual anisotropic temperature factors for the P, O and C atoms and one common temperature factor for the H atoms. The refinement converged to $R = \sum\Delta/\sum F_o = 0{\cdot}087$ and $R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}F_o) = 0{\cdot}083$ for 154 refined parameters.

Table 1. *Final atomic positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

Numbers in parentheses here and throughout the paper give e.s.d.'s in the least significant digits.

	x	y	z
P	4336 (1)	1269 (2)	2500 (0)
O(1)	4673 (3)	835 (5)	1965 (13)
O(2)	4777 (3)	32 (13)	−371 (20)
C(1)	4474 (3)	2143 (5)	2550 (10)
C(2)	4499 (3)	2499 (5)	1291 (10)
C(3)	4647 (3)	3161 (5)	1278 (10)
C(4)	4771 (3)	3468 (5)	2525 (10)
C(5)	4747 (3)	3112 (5)	3785 (10)
C(6)	4598 (3)	2450 (5)	3797 (10)
H(2)	4401 (3)	2262 (5)	326 (10)
H(3)	4666 (3)	3436 (5)	302 (10)
H(4)	4889 (3)	3979 (5)	2513 (10)
H(5)	4847 (3)	3348 (5)	4747 (10)
H(6)	4582 (3)	2174 (5)	4771 (10)
C(7)	4215 (3)	1042 (5)	4286 (16)
C(8)	3865 (3)	1307 (5)	4944 (16)
C(9)	3787 (3)	1157 (5)	6347 (16)
C(10)	4058 (3)	742 (5)	7091 (16)
C(11)	4408 (3)	477 (5)	6433 (16)
C(12)	4486 (3)	627 (5)	5030 (16)
H(8)	3655 (3)	1630 (5)	4374 (16)
H(9)	3520 (3)	1363 (5)	6866 (16)
H(10)	4003 (3)	623 (5)	8173 (16)
H(11)	4621 (3)	151 (5)	6987 (16)
H(12)	4755 (3)	418 (5)	4495 (16)
C(13)	3869 (3)	1180 (3)	1516 (12)
C(14)	3781 (3)	539 (3)	984 (12)
C(15)	3414 (3)	428 (3)	248 (12)
C(16)	3135 (3)	958 (3)	44 (12)
C(17)	3223 (3)	1598 (3)	577 (12)
C(18)	3590 (3)	1709 (3)	1312 (12)
H(14)	3996 (3)	129 (3)	1147 (12)
H(15)	3345 (3)	−70 (3)	−159 (12)
H(16)	2851 (3)	871 (3)	−533 (12)
H(17)	3009 (3)	2009 (3)	398 (12)
H(18)	3660 (3)	2208 (3)	1704 (12)

Table 2. *Bond distances* (Å) *and angles* (°)

P—O(1)	1·477 (10)	P—C(1)	1·787 (11)
O(1)···O(2)	2·759 (24)	P—C(7)	1·806 (15)
O(2)—O(2′)	1·443 (14)	P—C(13)	1·785 (10)
		P—C (mean)	1·793 (15)
P—O(1)···O(2)	134·7 (7)	C(1)—P—C(7)	105·7 (5)
O(1)···O(2)—O(2′)	99·9 (12)	C(1)—P—C(13)	108·7 (4)
		C(7)—P—C(13)	106·8 (5)
P—C(1)—C(2)	118·6 (7)	C—P—C (mean)	107·1 (5)
P—C(1)—C(6)	121·0 (7)		
P—C(7)—C(8)	120·5 (9)	O(1)—P—C(1)	112·8 (5)
P—C(7)—C(12)	119·5 (9)	O(1)—P—C(7)	109·9 (6)
P—C(13)—C(14)	117·0 (7)	O(1)—P—C(13)	112·5 (5)
P—C(13)—C(18)	123·0 (7)	O(1)—P—C (mean)	111·7 (6)
P—C—C (mean)	119·9 (9)		

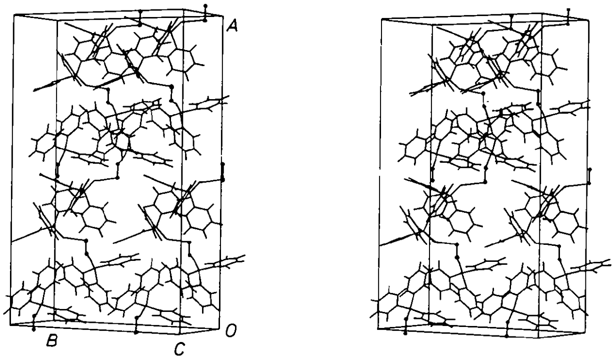

Fig. 1. Unit cell of $[(C_6H_5)_3PO]_2.H_2O_2$.

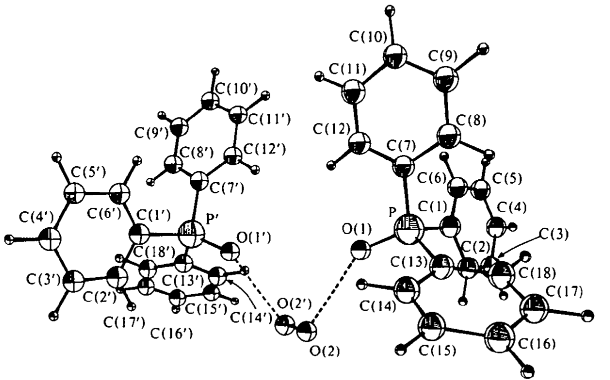

Fig. 2. Perspective view of one coordination unit of $[(C_6H_5)_3PO]_2.H_2O_2$. Numbers of H atoms (omitted for clarity) correspond to numbers of the C atoms to which they are bound.

The final positional parameters are listed in Table 1 and bond distances and angles in Table 2.* Fig. 1

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35005 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Planes, distances* (Å) *of the* P *atoms therefrom and dihedral angles* (°)

Planes are defined in terms of Cartesian coordinates by $Ax + By + Cz = D$; x parallel to a, y in the plane ab, and z parallel to c^*; A, B and C are the direction cosines of the normal to the plane and D is the distance of the plane from the origin. The values for A, B and C are multiplied by 10^4.

Plane†		A	B	C	D (Å × 10^2)
(I)	C(1)–C(6)	9299	−3407	−1389	11·6
(II)	C(7)–C(12)	−5276	−8026	−2783	−10·0
(III)	C(13)–C(18)	4621	2385	−8542	5·1
(IV)	C(1), P, O(1)	−3460	1150	−9312	−6·8
(V)	C(7), P, O(1)	−6750	−6606	−3287	1·9
(VI)	C(13), P, O(1)	2939	7357	−6102	4·5
(VII)	C(1), P, C(7)	−9559	2508	−1527	3·1
(VIII)	C(1), P, C(13)	5349	−1148	−8371	5·2
(IX)	C(7), P, C(13)	2346	−9519	−1973	0·4
(X)	P, O(1), O(2)	3807	7791	−4981	6·1
(XI)	O(1), O(2), O(2′)	718	8172	−5718	1·4
(XII)	O(1′), O(2′), O(2)	−718	−8172	−5718	−1·0

Distances of P from planes (Å × 10^2)

(I)	0·181 (3)	(XI)	0·331 (3)
(II)	−0·092 (3)	(XII)	−3·465 (3)
(III)	−0·063 (2)		

Dihedral angles (°) (mean e.s.d. 2·1 °)

(I)/(II)	100·3	(II)/(IX)	46·0
(I)/(III)	62·2	(III)/(VI)	33·6
(I)/(IV)	103·4	(III)/(VII)	104·6
(I)/(VIII)	49·3	(X)/(XI)	18·4
(II)/(III)	101·4	(X)/(XII)	112·3
(II)/(V)	12·1	(XI)/(XII)	110·2

† Sequence of atoms in planes (I) to (III) is according to Table 1.

shows the arrangement of molecules in the asymmetric unit. Fig. 2 is a perspective view of the coordination unit, also showing the numbering.

The structure solution and refinement were carried out with *SHELX* (Sheldrick, 1976). Figures were drawn with *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978). Scattering factors were taken from Cromer & Mann (1968).

Discussion. The title compound consists of two symmetrically dependent Ph_3PO molecules bound to H_2O_2 by hydrogen bonds. The hydrogen-bond length, 2·759 (24) Å, is significantly longer than the O–H···O bridges in $(Ph_3PO)_2.H_2O.HBr$ of 2·398 (8) and 2·470 (7) Å (Thierbach & Huber, 1979*b*), which can be considered as very short O–H···O bonds (Speakman, 1967). The relatively high thermal stability of $(Ph_3PO)_2.H_2O_2$ is not reflected by the length of the hydrogen bond, as distances found in perhydrates of much lower stability are appreciably shorter, *e.g.* 2·588 (6) Å in $Na_2C_2O_4.H_2O_2$ (Pedersen & Pedersen, 1964) or 2·60 Å in $(NH_4)_2C_2O_4.H_2O_2$ (Pedersen, 1969, 1972*a*).

The O(2)–O(2′) length in the H_2O_2 unit [1·443 (14) Å] is shorter than in crystalline H_2O_2, 1·49 (2) Å (Abrahams, Collin & Lipscomb, 1951). This effect has been noted previously (Pedersen, 1972*b*) and was ascribed to thermal motion or to a small degree of random substitution of H_2O_2 by H_2O. Thus the mean O–O distance in sodium carbonate perhydrate is 1·43 (3) Å (Carrondo, Griffith, Jones & Skapski, 1977) and in guanidium pyrophosphate monoperhydrate sesquihydrate 1·402 (16) and 1·45 (2) Å (Adams & Ramdas, 1978).

The mean C–P–C angles are smaller and the O(1)–P–C angles greater than the ideal tetrahedral angle. The P–O distance, 1·477 (10) Å, corresponds to the values in the uncoordinated compounds: 1·46 (1) Å in the orthorhombic modification (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970), 1·487 (2) Å in the monoclinic modification (D. Thierbach & F. Huber, unpublished).

If we assume the H atoms of the H_2O_2 molecule to be located along the hydrogen-bond directions then the dihedral angle (planes XI and XII, Table 3) is 110·2 (2·1)°. For H_2O_2 in the gas phase a value of 115° was found (Hunt, Lencock, Peters & Hecht, 1965) and in crystalline H_2O_2 94° was calculated (Penney & Sutherland, 1934; Abrahams, Collin & Lipscomb, 1951). The angle O(1)···O(2)–O(2′) in $(Ph_3PO)_2.H_2O_2$ [99·9 (12)°] is comparable to that in solid H_2O_2 [96° 52′ (1·5°)] (Abrahams, Collin & Lipscomb, 1951).

We thank the Fonds der Chemie for financial support.

References

Abrahams, S. C., Collin, R. L. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 15–20.

Adams, J. M. & Ramdas, V. (1978). *Acta Cryst.* B**34**, 2150–2156.

Bandoli, G., Bortolozzo, G., Clemente, D. A., Croatto, U. & Panattoni, C. (1970). *J. Chem. Soc. A*, pp. 2278–2780.

Carrondo, M. A. A. F. de C. T., Griffith, W. P., Jones, D. P. & Skapski, A. C. (1977). *J. Chem. Soc. Dalton Trans.* pp. 2323–2327.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Halman, M. & Pinchas, S. (1958). *J. Chem. Soc.* pp. 3264–3267.

Haupt, H.-J., Huber, F., Krüger, C., Preut, H. & Thierbach, D. (1977). *Z. Anorg. Allg. Chem.* **436**, 229–236.

Hunt, R. H., Lencock, A., Peters, C. W. & Hecht, K. T. (1965). *J. Chem. Phys.* **42**, 1931–1946.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Michaelis, A. & Gleichmann, L. (1882). *Chem. Ber.* **15**, 801–804.

Michaelis, A. & von Soden, H. (1885). *Justus Liebigs Ann. Chem.* **229**, 295–334.
Motherwell, S. & Clegg, W. (1978). *PLUTO*. Univ. of Cambridge, England.
Pedersen, B. F. (1969). *Acta Chem. Scand.* **23**, 342.
Pedersen, B. F. (1972*a*). *Acta Cryst.* B**28**, 746–754.
Pedersen, B. F. (1972*b*). *Acta Cryst.* B**28**, 1014–1016.
Pedersen, B. F. & Pedersen, B. (1964). *Acta Chem. Scand.* **18**, 1454–1468.
Penney, W. G. & Sutherland, G. B. B. M. (1934). *J. Chem. Phys.* **2**, 492–498.
Rudolph, H. & Reinking, K. (1967). German Patent 1268619 (13.1.1967/22.5.1968).
Sheldrick, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
Speakman, J. C. (1967). *Chem. Commun.* pp. 32–33.
Temple, R. D., Tsuno, Y. & Leffler, J. E. (1963). *J. Org. Chem.* **28**, 2495.
Thierbach, D. & Huber, F. (1979*a*). *Z. Anorg. Allg. Chem.* **451**, 137–142.
Thierbach, D. & Huber, F. (1979*b*). *Z. Anorg. Allg. Chem.* **457**, 189–196.

Acta Cryst. (1980). B**36**, 977–979

The Structures of (*E*)- and (*Z*)-2-Chloro-2-ethynyl-5-phenyladamantane*

By Y. Okaya, S. Y. Lin, D. M. Chiou and W. J. le Noble

Chemistry Department, State University of New York, Stony Brook, NY 11794, *USA*

(*Received* 17 *April* 1979; *accepted* 4 *September* 1979)

Abstract. $C_{18}H_{19}Cl$, *E* isomer: monoclinic, $P2_1/c$, $a = 15{\cdot}308\,(2)$, $b = 7{\cdot}229\,(2)$, $c = 14{\cdot}305\,(3)$ Å, $\beta = 113{\cdot}5\,(3)^\circ$, $V = 1452$ Å^3, $Z = 4$ ($\rho_{\text{obs}} = 1{\cdot}25$ Mg m^{-3}). $R = 0{\cdot}038$ for 1900 ($>3\sigma$) reflections. *Z* isomer: orthorhombic, $P2_12_12_1$, $a = 6{\cdot}773\,(1)$, $b = 10{\cdot}043\,(2)$, $c = 21{\cdot}130\,(4)$ Å, $V = 1437$ Å^3, $Z = 4$ ($\rho_{\text{obs}} = 1{\cdot}26$ Mg m^{-3}). $R = 0{\cdot}050$ for 2439 ($>3\sigma$) reflections. All the data were measured using Cu $K\alpha$ radiation on a diffractometer. The Cl atom is in the *anti* configuration with respect to the phenyl group in the *E* isomer; for the *Z* isomer the relationship is *syn*. The results confirm the retention of configuration in a stereospecific return reaction during methanolysis, to give (*E*)- and (*Z*)-2-chlorovinylidene-5-phenyladamantane.

Introduction. This report is part of our systematic configurational study of bridge-head phenyl-substituted adamantanes. The present compounds, (*E*)- and (*Z*)-2-ethynyl-2-chloro-5-phenyladamantane, are converted stereospecifically into (*E*)- and (*Z*)-2-chlorovinylidene-5-phenyladamantane, $Cl{-}CH{=}C{=}C_{10}H_{13}.C_6H_5$, respectively, by neutral solvolysis in CH_3OH (le Noble, Chiou & Okaya, 1979). Since the stereochemistry of the chlorovinylidene compound was established by a crystallographic study of its *E* isomer (Okaya, Małuszyńska, Chiou & le Noble, 1978), it seemed worthwhile to determine unambiguously the molecular structures of the *E* and *Z* chloro compounds by the X-ray method. The diffraction data of both compounds were obtained on an Enraf–Nonius CAD-4 diffractometer controlled by a PDP-8 computer which was in turn under the supervision of a PDP-11/45 computer in a resource-sharing mode (Okaya, 1978). Cu $K\alpha$ was used and the data were collected up to 50° (in *E*) and 65° (in *Z*) with the θ–2θ scan method. The structures were solved by using sharpened Patterson functions, and refined by a full-matrix least-squares program using the Enraf–Nonius structure determination package on the PDP-11/45 computer. The function minimized in the refinements was $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma c F_o^2 + (pF_o^2)^2$, where σc is the deviation based on counting statistics and *p*, the adjustment factor, was 0·03 and 0·04 for the *E* and *Z* data, respectively. All H atoms were located in difference Fourier maps and refined with isotropic temperature factors. The final *R* factors $[= \sum (|F_o| - |F_c|)/\sum |F_o|]$ are 0·038 and 0·050 for the *E* and *Z* structures, respectively. The atomic scattering factors used are derived from data of Cromer & Waber (1974). Because of the relatively small absorption of the specimen, no absorption correction was applied to the diffraction data. The positional parameters of all the atoms are given in Table 1.†

Discussion. The present study has unambiguously assigned the *E* (m.p. = 366 K, acetylenic proton NMR shift = 7·32 τ) and *Z* (m.p. = 364 K, NMR shift 7·30

---

* Crystallographic Studies on Adamantanes. III.

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34739 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/80/040977-03$01.00