*Refinement*

Refinement on $F^2$
$R(F) = 0.0424$
$wR(F^2) = 0.1113$
$S = 1.189$
1459 reflections
169 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.7356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.645$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.485$ e Å$^{-3}$
Extinction correction: *SHELXL*93
Extinction coefficient: $1.28 (4) \times 10^4$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for dap*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| P | 0.32933 (9) | 0.12033 (5) | 0.67981 (6) | 0.0192 (5) |
| O*L* | 1/2 | 0.1539 (2) | 3/4 | 0.0307 (9) |
| O*E*1 | 0.2291 (3) | 0.1984 (2) | 0.6609 (2) | 0.0299 (7) |
| O*E*2 | 0.3557 (3) | 0.0860 (2) | 0.5756 (2) | 0.0301 (7) |
| O*E*3 | 0.2697 (3) | 0.0549 (2) | 0.7446 (2) | 0.0317 (7) |
| O*W*1 | 1/2 | 0.4714 (2) | 3/4 | 0.0341 (9) |
| O*W*2 | 1/2 | −0.2425 (3) | 3/4 | 0.087 (3) |
| O*W*3 | 0.1138 (4) | 0.4051 (2) | 0.6673 (3) | 0.0481 (8) |
| N1 | 0.8399 (3) | 0.4329 (2) | 0.4667 (2) | 0.0255 (7) |
| N2 | 0.3734 (4) | 0.3383 (2) | 0.5957 (3) | 0.0244 (7) |
| C1 | 0.7551 (4) | 0.3614 (2) | 0.5017 (3) | 0.0285 (8) |
| C2 | 0.5996 (4) | 0.3878 (2) | 0.5248 (3) | 0.0290 (9) |
| C3 | 0.5229 (4) | 0.3136 (2) | 0.5678 (3) | 0.0255 (8) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| P—O*E*1 | 1.504 (2) | N2—C3 | 1.474 (4) |
| P—O*E*3 | 1.507 (2) | C1—C2 | 1.502 (5) |
| P—O*E*2 | 1.519 (3) | C2—C3 | 1.528 (5) |
| P—O*L* | 1.613 (1) | P—P$^{\rm i}$ | 3.042 (2) |
| N1—C1 | 1.487 (4) | | |
| O*E*1—P—O*E*3 | 114.0 (2) | O*E*2—P—O*L* | 107.4 (1) |
| O*E*1—P—O*E*2 | 111.4 (2) | P—O*L*—P$^{\rm i}$ | 141.0 (2) |
| O*E*3—P—O*E*2 | 112.6 (1) | N1—C1—C2 | 111.9 (3) |
| O*E*1—P—O*L* | 102.7 (2) | C1—C2—C3 | 109.9 (3) |
| O*E*3—P—O*L* | 108.1 (1) | N2—C3—C2 | 111.2 (3) |

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O*W*1—H*W*1···O*E*3$^{\rm i}$ | 0.83 (5) | 1.87 (5) | 2.695 (3) | 170 (5) |
| O*W*2—H*W*2···O*E*1$^{\rm ii}$ | 0.77 (5) | 1.97 (5) | 2.690 (3) | 156 (6) |
| O*W*3—H1*W*3···O*E*3$^{\rm iii}$ | 0.89 (6) | 1.96 (6) | 2.734 (4) | 145 (5) |
| O*W*3—H2*W*3···O*W*2$^{\rm iv}$ | 0.86 (7) | 2.06 (6) | 2.863 (5) | 156 (6) |
| N1—H1N1···O*E*3$^{\rm v}$ | 0.93 (5) | 1.86 (5) | 2.780 (4) | 167 (4) |
| N1—H2N1···O*E*2$^{\rm vi}$ | 0.95 (6) | 1.92 (6) | 2.823 (4) | 160 (5) |
| N1—H3N1···O*E*2$^{\rm i}$ | 0.99 (5) | 1.81 (5) | 2.809 (4) | 179 (4) |
| N2—H1N2···O*E*2$^{\rm vii}$ | 0.76 (6) | 2.11 (6) | 2.838 (4) | 160 (5) |
| N2—H2N2···O*E*1 | 0.73 (5) | 2.07 (5) | 2.791 (5) | 178 (4) |
| N2—H3N2···O*W*1 | 0.84 (6) | 2.11 (6) | 2.932 (5) | 168 (5) |
| H*W*1—O*W*1···H*W*1$^{\rm viii}$ | – | – | – | 111 (7) |
| H*W*2—O*W*2···H*W*2$^{\rm viii}$ | – | – | – | 107 (9) |
| H1*W*3—O*W*3···H2*W*3 | – | – | – | 101 (5) |

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$; (vii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (viii) $1 - x, y, \frac{3}{2} - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

The authors would like to express their gratitude to Dr T. Jouini, Département de Chimie, Faculté des Sciences, Campus Universitaire, Tunisia, for the X-ray data collection.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DU1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Averbuch-Pouchot, M. T. & Durif, A. (1992). *Eur. J. Solid State Inorg. Chem.* **29**, 993–999.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Kamoun, S., Jouini, A. & Daoud, A. (1992). *J. Solid State Chem.* **99**, 18–28.
Larbot, A. Norbert, A. & Cot, L. (1979). *C. R. Acad. Sci. Ser. C*, **289**, 185–187.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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*Acta Cryst.* (1997). C**53**, 465–467

# 1,4-Phenylenebis(diphenylphosphine oxide)

NATALYA C. ALEXANDER, BRIAN H. ROBINSON AND JIM SIMPSON

*Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. E-mail: jsimpson@alkali.otago.ac.nz*

(*Received 25 October 1996; accepted 26 November 1996*)

## Abstract

The structure of the title compound, 1,4-$C_6H_4$[PO($C_6H_5$)$_2$]$_2$ ($C_{30}H_{24}O_2P_2$), is the first to be reported of a phenylenebis(phosphine oxide). The molecule lies about an inversion centre and the unique P atom has a distorted tetrahedral environment; P═O 1.489 (3), average P—C 1.812 (4) Å, average C—P—C 106.9 (8) and average O—P—C 112.0 (2)°. The structure is stabilized by C—H···O intermolecular hydrogen bonds.

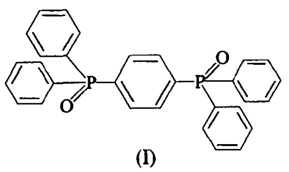
## Comment

To our knowledge, no comparable structures of phenylenebis(phosphine oxide) derivatives have been

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

reported, but the structures of di- and triphenylphosphine oxides, as well as phosphine oxides incorporating substituted benzene rings, are known. These include $(p\text{-}ClC_6H_4)PO(C_6H_5)_2$ (Dreissig & Plieth, 1971*b*), $(p\text{-}BrC_6H_4)PO(C_6H_5)_2$ (Dreissig & Plieth, 1971*a*), $(C_6H_5)_3PO$ (Spek, 1987), $(p\text{-}C_6H_4CH_3)_3PO$ (Churchill, See, Randall & Atwood, 1993) and $[2,4,6\text{-}(CH_3O)_3C_6H_3]_3PO$ (Chaloner, Harrison & Hitchcock, 1993).

The structure of the title compound, (I), comprises a central aromatic ring lying about an inversion centre and substituted at the 1 and 4 positions with diphenylphosphine oxide residues. The geometry at the unique P atom is that of a slightly distorted tetrahedron, with the angles subtended at the P atom by the C atoms [average C—P—C 106.9 (8)°] significantly less than the O—P—$C_{ipso}$ angles [average O—P—C 112.0 (2)°]. The P═O [1.489 (3) Å] and P—$C_{ipso}$ [average 1.812 (4) Å] bond distances do not differ significantly from those reported for the compounds listed above. The P═O bonds are *trans* with respect to the central aromatic ring plane and this plane makes an angle of 51.3 (3)° with the C1—P1—O1 plane (Nardelli, 1983).



(I)

The structure is stabilized by C2—H2···O1($-x$, $1-x$, $1-z$) intermolecular hydrogen bonds connecting the molecules into sheets parallel to the monoclinic *b* axis. Other possible hydrogen bonds are listed in Table 2 and give rise to an approximately pyramidal array of hydrogen bonds about the O1 atom.

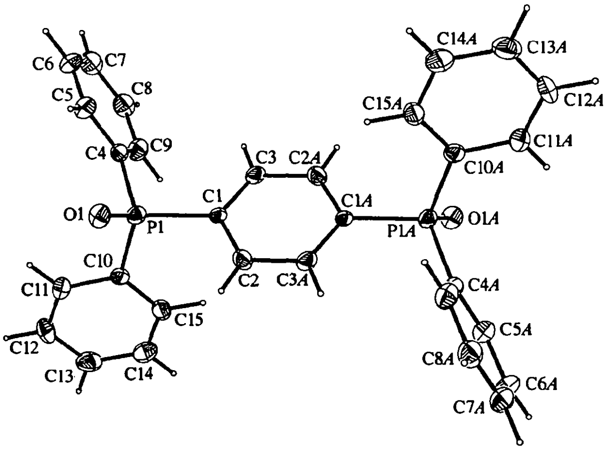


Fig. 1. Perspective drawing of the title molecule showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

## Experimental

The title compound was obtained as the ubiquitous by-product of substitution reactions of 1,4-phenylenebis(diphenylphosphine) with the cobalt–carbonyl clusters $YCCo_3(CO)_9$ (*Y* = Me, Ph) (Alexander, Robinson & Simpson, 1997) and was isolated by chromatography on silica. Pale yellow crystals were obtained from dichloromethane/hexane solution.

*Crystal data*

$C_{30}H_{24}O_2P_2$
$M_r = 478.43$
Monoclinic
$P2_1/n$
$a = 6.906\ (4)$ Å
$b = 12.009\ (7)$ Å
$c = 14.643\ (8)$ Å
$\beta = 95.88\ (4)°$
$V = 1208.0\ (12)$ Å$^3$
$Z = 2$
$D_x = 1.315$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.75–17.22°$
$\mu = 0.206$ mm$^{-1}$
$T = 293\ (2)$ K
Irregular plate
1.02 × 0.28 × 0.08 mm
Pale yellow

*Data collection*

Siemens *P*4 diffractometer
$\omega$ scans
Absorption correction: empirical $\psi$ scans (Sheldrick, 1990)
$T_{min} = 0.911$, $T_{max} = 0.984$
1981 measured reflections
1981 independent reflections

1280 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 0.99%

*Refinement*

Refinement on *F*
$R = 0.0516$
$wR = 0.0405$
$S = 1.3996$
1981 reflections
166 parameters
H atoms riding
$w = 1/[\sigma^2(F) + 0.000106F^2]$

$(\Delta/\sigma)_{max} = 0.038$
$\Delta\rho_{max} = 0.373$ e Å$^{-3}$
$\Delta\rho_{min} = -0.295$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| P1—O1 | 1.489 (3) | P1—C10 | 1.810 (4) |
| P1—C4 | 1.806 (4) | P1—C1 | 1.819 (4) |
| O1—P1—C4 | 111.9 (1) | O1—P1—C1 | 112.2 (2) |
| O1—P1—C10 | 111.8 (2) | C4—P1—C1 | 107.7 (2) |
| C4—P1—C10 | 105.6 (2) | C10—P1—C1 | 107.3 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2—H2···O1$^{i}$ | 0.91 | 2.42 | 3.179 (5) | 142 |
| C7—H7···I1$^{ii}$ | 0.98 | 2.46 | 3.342 (5) | 150 |
| C14—H14···O1$^{iii}$ | 0.98 | 2.41 | 3.307 (5) | 152 |

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The H atoms were treated using the *AFIX* routine in *SHELXTL/PC* (Sheldrick 1990).

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*.

The authors thank Professor W. T. Robinson (University of Canterbury) for the data collection. This work is supported by a grant from the Division of Sciences, University of Otago, New Zealand.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## References

Alexander, N. C., Robinson, B. H. & Simpson, J. (1997). In preparation.

Chaloner, P. A., Harrison, R. M. & Hitchcock, P. B. (1993). *Acta Cryst.* C**49**, 1072–1075.

Churchill, M. R., See, R. F., Randall, S. L. & Atwood, J. D. (1993). *Acta Cryst.* C**49**, 345–347.

Dreissig, W. & Plieth, K. (1971*a*). *Acta Cryst.* B**27**, 1141–1145.

Dreissig, W. & Plieth, K. (1971*b*). *Acta Cryst.* B**27**, 1146–1152.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL/PC. Programs for Crystal Structure Determination.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1987). *Acta Cryst.* C**43**, 1233–1235.

*Acta Cryst.* (1997). C**53**, 467–469

# 2-(Diphenylphosphinoyl)-1,3-dioxane

Wiesław R. Majzner,[a] Michał W. Wieczorek,[a] Marian Mikołajczyk[b] and Piotr P. Graczyk[b]

[a]*Institute of General Food Chemistry, Technical University of Łódź, Stefanowskiego 4/10, 90-924 Łódź, Poland, and* [b]*Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, Sienkiewicza 112, 90-363 Łódź, Poland. E-mail: wmajzner@lodz1.p.lodz.pl*

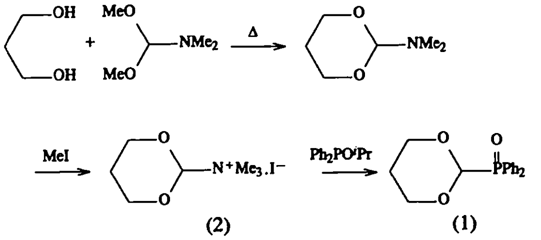
(*Received 8 January 1996; accepted 3 February 1997*)

## Abstract

The crystal and molecular structure of 2-(diphenylphosphinoyl)-1,3-dioxane, $C_{16}H_{17}O_3P$, with the phosphoryl group in the equatorial position, has been determined.

## Comment

The structure determination of the title compound, (1), forms part of our work on the nature of anomeric interactions in the structures of 1,3-dioxanes (Mikołajczyk, Graczyk, Wieczorek, Bujacz, Struchkov & Antipin, 1988; Mikołajczyk, Graczyk, Wieczorek & Bujacz, 1992), 1,3-dithianes (Mikołajczyk, Graczyk & Wieczorek, 1994; Wieczorek, Bujacz, Majzner, Graczyk & Mikołajczyk, 1995; Mikołajczyk, Graczyk, Potrzebowski, Wieczorek & Błaszczyk, 1995), 1,3-selenanes (Mikołajczyk, Mikina, Graczyk, Wieczorek & Bujacz, 1991) and 1,3-oxathianes (Mikołajczyk, Graczyk, Wieczorek & Bujacz, 1988) containing 2-phosphoryl, 2-(thiophosphoryl) or 2-(selenophosphoryl) substituents. This work presents the X-ray study of 2-(diphenylphosphinoyl)-1,3-dioxane, (1), whereas its synthesis (see scheme below) and a discussion of the anomeric effect in structures containing the O—C—P system are described in detail in our previous work (Mikołajczyk, Graczyk, Wieczorek & Bujacz, 1992).



The asymmetric part of the unit cell contains one molecule of 2-(diphenylphosphinoyl)-1,3-dioxane (Fig. 1). Analysing the geometrical data given in Table 1, we notice that the molecule of (1) is almost ideally symmetrical (mirror symmetry) in relation to the least-squares plane passing through the O8, P7, C2, H2 and C5 atoms. The corresponding bond lengths differ by no more than 0.009 Å, bond angles by no more than

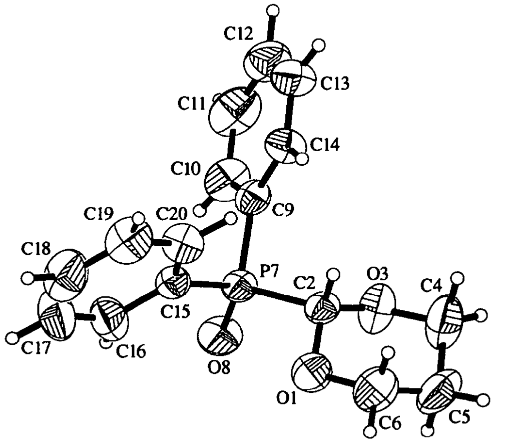


Fig. 1. The molecular structure of 2-(diphenylphosphinoyl)-1,3-dioxane showing 50% probability displacement ellipsoids.