to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*.

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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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2-(Diphenylphosphinoyl)-1,3-dioxane

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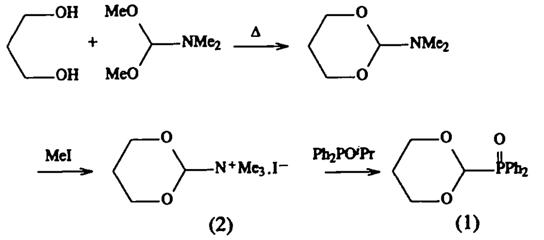
Abstract

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

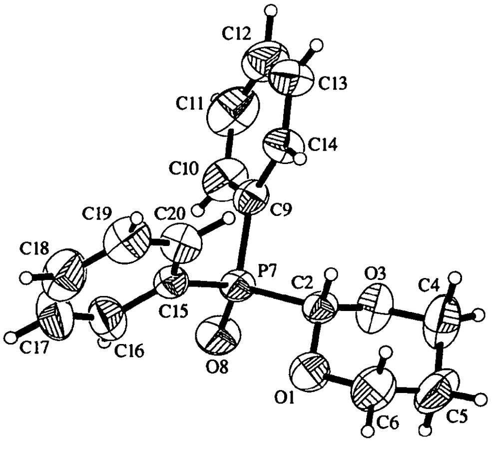


Fig. 1. The molecular structure of 2-(diphenylphosphinoyl)-1,3-dioxane showing 50% probability displacement ellipsoids.

0.8° and rotations around heterocyclic bonds by no more than 0.6°. Comparing the torsion angles O1—C2—P7—O8/C9/C15 with O3—C2—P7—O8/C15/C9 and O8/C2/C15—P7—C9—C10/C14 with O8/C2/C9—P7—C15—C16/C20 (Table 1), it can be seen that the deviation from ideal symmetry is only caused by rotation about the C2—P7 bond (~2.2°) and by a difference between the rotations about the P7—C9 and P7—C15 bonds (~4.2°).

The six-membered 1,3-dioxane ring adopts a slightly deformed chair conformation and its asymmetry parameters (Duax & Norton, 1975) are listed in Table 2. The dihedral angles between the 'basic' ring plane (least-squares plane passing through the O1, O3, C4 and C6 atoms) and the 'flattening' planes (through the O1, C2, O3 and C4, C5, C6 atoms), which describe the deviation of the six-membered heterocyclic ring from the ideal chair conformation, are different with values of 58.9 (2) and 51.1 (2)°, respectively. The diphenylphosphinoyl group at C2 occupies an equatorial position (Fig. 1); the angle between the C2—P7 bond and the 'basic' ring plane was found to be 1.3 (2)°. The P7—O8 bond is antiperiplanar with respect to C2—H2 [−176.7 (13)°]. The dihedral angles between the 'basic' ring plane (O1, O3, C4 and C6) and phenyl ring planes are 58.3 (1)° for ring C9–C14 and 62.8 (1)° for ring C15–C20. The angles between these ring planes and the C2—P7 bond are 37.76 (9) and 46.4 (1)°, respectively. The dihedral angle between the phenyl ring planes is 69.66 (9)°.

It can be seen from Fig. 2 that, in the crystal structure, there are one-dimensional chains of C2—H2···O8^{i} hydrogen-bonding contacts [symmetry code: (i) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$; Table 3] parallel to the b axis. Moreover, four inter- and two intramolecular hydrogen-bonding contacts, with a H···A distance not greater then 2.80 Å, are also observed (Table 3).

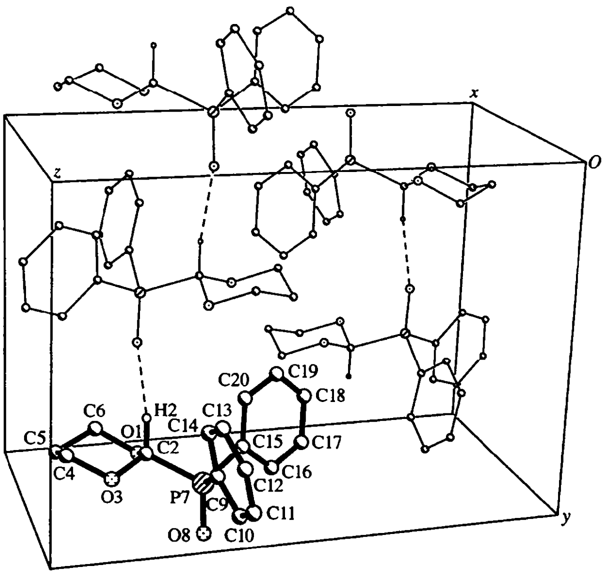


Fig. 2. Packing diagram of 2-(diphenylphosphinoyl)-1,3-dioxane showing the hydrogen-bonding system. The H atoms, except H2, have been omitted for clarity.

Experimental

A mixture of freshly prepared ammonium iodide and isopropyl diphenylphosphinite in toluene was refluxed for 3 h. The reaction mixture was then cooled, filtered and concentrated. n-Hexane was added and the mixture was left to stand overnight to give colourless crystals of (1) (Mikołajczyk, Graczyk, Wieczorek & Bujacz, 1992). Recrystallization from dichloromethane–diethyl ether afforded crystals of (1) suitable for X-ray analysis.

Crystal data

$C_{16}H_{17}O_3P$
$M_r = 288.27$
Monoclinic
$P2_1/n$
$a = 9.0191\,(9)$ Å
$b = 10.715\,(2)$ Å
$c = 15.374\,(2)$ Å
$\beta = 94.382\,(10)°$
$V = 1481.4\,(4)$ Å^3
$Z = 4$
$D_x = 1.293$ Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 19.03–26.24°$
$\mu = 1.685$ mm^{-1}
$T = 293\,(2)$ K
Monoclinic prism
0.22 × 0.14 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968; Frenz, 1986)
$T_{min} = 0.804$, $T_{max} = 0.817$
6106 measured reflections
3058 independent reflections
2146 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0884$
$\theta_{max} = 74.96°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 0$
$l = -19 \rightarrow 19$
3 standard reflections frequency: 60 min intensity decay: 0.8%

Refinement

Refinement on F^2
$R(F) = 0.0564$
$wR(F^2) = 0.1560$
$S = 1.067$
3054 reflections
250 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.411$ e Å^{-3}
$\Delta\rho_{min} = -0.485$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0027 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C2	1.386 (3)	C4—C5	1.501 (6)
O1—C6	1.447 (4)	C5—C6	1.492 (6)
C2—O3	1.388 (3)	P7—O8	1.483 (2)
C2—P7	1.838 (3)	P7—C15	1.800 (3)
O3—C4	1.445 (4)	P7—C9	1.801 (3)

C2—O1—C6	108.4 (3)	O1—C6—C5	109.5 (3)
O1—C2—O3	112.7 (2)	O8—P7—C15	112.97 (13)
O1—C2—P7	107.3 (2)	O8—P7—C9	113.20 (12)
O3—C2—P7	107.3 (2)	C15—P7—C9	106.81 (11)
C2—O3—C4	109.2 (3)	O8—P7—C2	114.42 (11)
O3—C4—C5	109.0 (3)	C15—P7—C2	104.10 (11)
C6—C5—C4	108.8 (3)	C9—P7—C2	104.49 (11)
C6—O1—C2—O3	64.5 (3)	C15—P7—C9—C14	69.0 (2)
C6—O1—C2—P7	−177.6 (3)	C2—P7—C9—C14	−40.9 (2)
O1—C2—O3—C4	−64.7 (4)	O8—P7—C9—C10	16.1 (3)
P7—C2—O3—C4	177.5 (3)	C15—P7—C9—C10	−108.8 (2)
C2—O3—C4—C5	58.5 (5)	C2—P7—C9—C10	141.2 (2)
O3—C4—C5—C6	−55.2 (5)	O8—P7—C15—C16	−6.7 (3)
C2—O1—C6—C5	−59.1 (4)	C9—P7—C15—C16	118.3 (2)
C4—C5—C6—O1	55.7 (5)	C2—P7—C15—C16	−131.5 (2)
O1—C2—P7—O8	−62.6 (2)	O8—P7—C15—C20	174.6 (2)
O3—C2—P7—O8	58.6 (2)	C9—P7—C15—C20	−60.3 (2)
O1—C2—P7—C15	61.1 (2)	C2—P7—C15—C20	49.9 (2)
O3—C2—P7—C15	−177.6 (2)	H2—C2—P7—O8	−176.7 (13)
O1—C2—P7—C9	173.0 (2)	H2—C2—P7—C9	59.0 (13)
O3—C2—P7—C9	−65.7 (2)	H2—C2—P7—C15	−52.9 (13)
O8—P7—C9—C14	−166.0 (2)		

Table 2. *Asymmetry parameters (°) (Duax & Norton, 1975) of the 1,3-dioxane ring of (1)*

$\Delta C_s(\mathrm{O1}) = \Delta C_s(\mathrm{C4})$	6.4 (8)	$\Delta C_2(\mathrm{O1–C2}) = \Delta C_2(\mathrm{C4–C5})$	4.4 (8)
$\Delta C_s(\mathrm{C2}) = \Delta C_s(\mathrm{C5})$	0.5 (8)	$\Delta C_2(\mathrm{C2–O3}) = \Delta C_2(\mathrm{C5–C6})$	5.1 (9)
$\Delta C_s(\mathrm{O3}) = \Delta C_s(\mathrm{C6})$	6.7 (8)	$\Delta C_2(\mathrm{O3–C4}) = \Delta C_2(\mathrm{C6–O1})$	9.2 (9)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O8^{i}	1.02 (2)	2.22 (2)	3.242 (3)	172 (2)
C6—H61···O8^{i}	1.00 (5)	2.79 (5)	3.609 (5)	139 (3)
C10—H10···O8	0.89 (3)	2.68 (3)	3.069 (4)	108 (3)
C14—H14···O8^{i}	0.99 (3)	2.79 (3)	3.762 (3)	168 (2)
C16—H16···O8	0.97 (4)	2.53 (4)	3.050 (4)	114 (3)
C18—H18···O3^{ii}	0.99 (4)	2.52 (4)	3.363 (4)	142 (3)
C20—H20···O8^{i}	1.02 (3)	2.75 (3)	3.705 (4)	155 (2)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$.

Anisotropic displacement parameters were applied for all non-H atoms. H atoms were found in a difference Fourier map and refined isotropically.

Data collection: *CAD*-4 *Manual* (Schagen, Straver, van Meurs & Williams, 1989). Cell refinement: *CAD*-4 *Manual*. Data reduction: *SDP* (Frenz, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXTL-Plus* and *CSU* (Vicković, 1988).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KA1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Intra- and Intermolecular Hydrogen Bonding in a Tetrahydroxycalix[4]arene

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Abstract

The title calix[4]arene, *cis*-11,17-di-*tert*-butyl-2,5,23-trimethyl-14-(4-nitrophenyl)pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(26),9,11,13(27),15,17,19(28),21,23-dodecaene-25,26,27,28-tetraol–chloroform (1/0.5), $C_{45}H_{49}NO_6.0.5CHCl_3$, substituted at two opposite methylene bridges by methyl and *p*-nitrophenyl groups, forms centrosymmetric hydrogen-bonded dimers in the solid state. This results in an eight-membered (O—H···)$_8$ ring, with O···O distances in the range 2.637 (4)–2.828 (4) Å. Pairs of calix[4]arene molecules (related by another inversion centre) each have a *p*-methyl group of one molecule fitting snugly into the cavity of the other, with shortest intermolecular C···C

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