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3-Diphenylphosphino-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-1D-*chiro*-inositol

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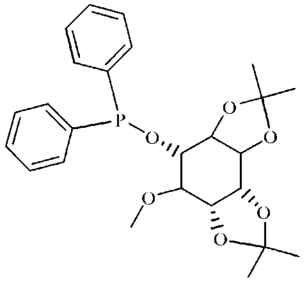
The novel title compound, $C_{25}H_{31}O_6P$, contains rigid fused rings which are shown to be similar to the precursor structures. Weak $C—H\cdots O$ intermolecular interactions produce two-dimensional sheets composed of $R_4^4(28)$ rings.

Comment

This study is part of a programme aimed at generating new hydrogenation catalyst ligands (Gainsford *et al.*, 2005). No monophosphinite ligands based on isopropylideneinositols have been reported previously.



(I)

The asymmetric unit of the title compound, (I), contains one independent 3-diphenylphosphino-1,2:5,6-di-*O*-isopropylidene-4-*O*-methyl-1D-*chiro*-inositol molecule (Fig. 1). The chemically determined absolute configuration (*S*, *R*, *R* and *S* for C2, C3, C4 and C5, respectively) was confirmed by the refinement. There are two reported di-*O*-isopropylidene-*chiro*-inositol structures [Cambridge Structural Database (CSD; Allen, 2002); another D enantiomer (CSD refcode HOFLOD; Falshaw *et al.*, 1999) and a substituted L enantiomer (refcode IPRTIN; McConnell *et al.*, 1972)]. Two other isoprolylidene-*myo*-inositol structures, *viz*. refcodes PINMII (Chung *et al.*, 1994) and NAGZOL (Sureshan *et al.*, 2004), are known, while another 1,2:5:6-di-*O*-isopropylidene-4-methyl-1D-*chiro*-inositol, hereafter (II), has also been resolved by us (Falshaw *et al.*, 2006).

The P—O bond length (Table 1) is similar to that found in two diphenylphosphinite ephedrine compounds [refcodes DERLEQ and DERKIU, with 1.666 (6) and 1.640 (2) Å, respectively; Brunet *et al.*, 1999], while the P—O—C angle is larger than that of the closest ring analogue (refcode MUKREP; Nazarov *et al.*, 2002), which has a P—O—C angle of 117.24 (10)° and a P—O distance of 1.6617 (12) Å. The torsion angles involving the Ph_2PO link [*e.g.* C14—P1—O3—C3 = −124.59 (12)°] are also similar to those of the latter compound [−129.40 (11)°]. Other dimensions are normal.

The inositol ring adopts a twist-boat conformation with Q = 0.6739 (17) Å, θ = 93.86 (15)° and φ = 340.19 (15)° (Cremer & Pople, 1975). This is quite different from the skew-boat found for the tosylated (L) derivative (refcode IPRTIN). The two isopropylidene rings have slightly different conformations; C1/O1/C7/O2/C2 is best described as an envelope on C2, while the puckered C5/O5/C10/O6/C6 ring adopts a twisted form on C10—O5 (Evans & Boeyens, 1989). Comparison with (II) and

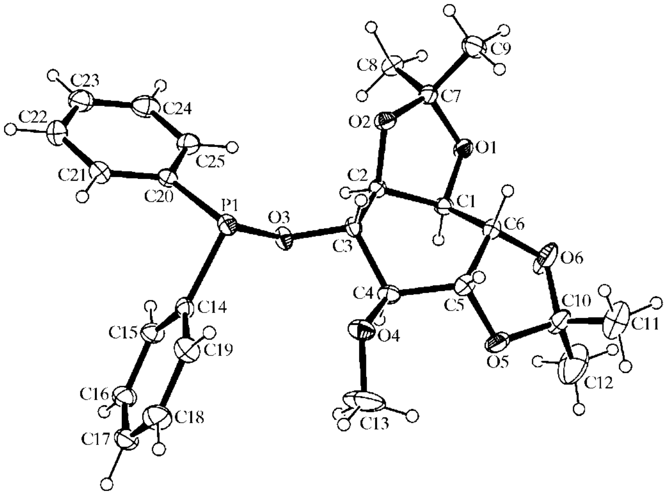


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 30% probability level.

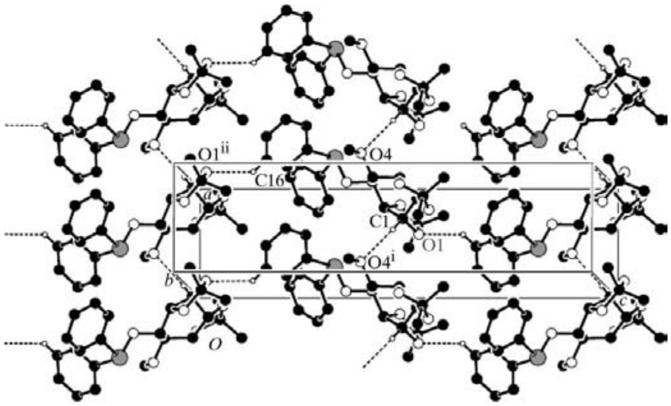


Figure 2
The main intermolecular packing interactions in (I), viewed down the *b* axis. Only H atoms and labels of one set of atoms in the $R_4^4(28)$ rings are shown (see *Comment*). Symmetry codes are as in Table 2.

HOFLOD shows that the 5,6-di-*O*-isopropylidene-*chiro*-inositol ring structure is quite rigid with only some minor changes in the interplanar angles of the average mean planes through the rings and the twist about O1—C1 (Table 3).

The packing is stabilized mainly by two weak C—H···O interactions, described according to Bernstein *et al.* (1995) (see Table 2), *viz.* entry 1, which forms a *C*(6) chain running parallel to the *a* axis, and entry 2, which forms a *C*(10) chain running parallel to the *c* axis, generated by the screw axis at ($\frac{3}{4}$, $\frac{1}{2}$, *z*). Together, these interactions form two-dimensional sheets composed of $R_4^4(28)$ rings (Fig. 2). One weak C—H···π interaction provides a possible interaction in the third dimension (entry 3 in Table 2, where *Cg*1 is the centroid of phenyl ring C20–C25). Other weaker intra- and intermolecular interactions (entries 4–6) are listed for completeness.

Experimental

A solution of Ph_2PCl (468 mg, 2.12 mmol) in tetrahydrofuran (5 ml) was added dropwise to a magnetically stirred solution of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-1D-*chiro*-inositol (582 mg, 2.12 mmol) and pyridine (0.32 g, 4 mmol) dissolved in tetrahydrofuran (10 ml) at room temperature. The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under high vacuum. Toluene (10 ml) was added and the mixture was filtered through neutral alumina. Removal of the solvents under high vacuum yielded (I) (0.84 g, 1.83 mmol, 87%) as a white solid. $[\alpha]_D$ = +12.2° (*c* 0.5, $CHCl_3$). Analysis calculated for $C_{25}H_{31}O_6P$: C 65.49, H 6.82%; found: C 66.06, H 6.78%.

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.6541 (12)	O1—C7	1.4567 (19)
P1—C14	1.8286 (17)	O3—C3	1.4372 (18)
P1—C20	1.8329 (18)	O6—C10	1.404 (2)
O3—P1—C14	100.97 (7)	C14—P1—C20	100.25 (8)
O3—P1—C20	97.85 (7)	C3—O3—P1	120.41 (10)
C14—P1—O3—C3	−124.59 (12)	P1—O3—C3—C2	−133.05 (11)
C7—O2—C2—C3	158.37 (13)	O3—C3—C4—O4	−60.63 (16)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O4^{i}	1.00	2.53	3.474 (2)	158
C16—H16···O1^{ii}	0.95	2.60	3.377 (2)	139
C9—H9*B*···*Cg*1^{iii}	0.98	2.84	3.573 (2)	133
C16—H16···O6^{ii}	0.95	2.70	3.391 (2)	131
C13—H13*C*···O5	0.98	2.59	3.215 (3)	122
C25—H25···O3	0.95	2.49	2.899 (2)	106

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

Crystal data

$C_{25}H_{31}O_6P$
M_r = 458.47
Orthorhombic, $P2_12_12_1$
a = 5.7381 (5) Å
b = 19.5148 (16) Å
c = 21.9735 (18) Å
V = 2460.5 (4) Å^3
Z = 4
D_x = 1.238 Mg m^{-3}
Mo *Kα* radiation
μ = 0.15 mm^{-1}
T = 166 (2) K
Needle, colourless
0.81 × 0.25 × 0.12 mm

Data collection

Siemens *P*4 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.743, T_{max} = 0.979
31585 measured reflections
5014 independent reflections
3486 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.059
S = 0.87
5014 reflections
294 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), 2109 Friedel pairs
Flack parameter: 0.06 (7)

All H atoms were constrained to their expected geometries (C—H = 0.95, 0.98 and 1.0 Å) and refined with U_{iso}(H) values of $1.2U_{eq}$ of the parent atom. The methyl H atoms were additionally allowed to rotate freely about the parent C—C bonds.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: RB3020). Services for accessing these data are described at the back of the journal.

Table 3
Torsion and interplanar angles (°) for related structures[a].

Source[b]	φ1	φ2	φ3	φ4	A_{12}	A_{23}	A_{13}
This work	158.37 (13)	−100.61 (15)	151.95 (15)	−128.73 (16)	14.93 (10)	32.01 (10)	46.70 (9)
(II)	158.8 (2)	−110.0 (2)	153.8 (2)	−129.3 (2)	10.06 (15)	30.85 (14)	40.90 (14)
HOFLOD^{B}	158.7 (7)	−110.7 (8)	150.9 (8)	−128.0 (8)	10.8 (5)	28.0 (5)	37.2 (5)
HOFLOD^{C}	154.3 (8)	−119.4 (8)	150.4 (7)	−136.2 (9)	9.6 (6)	30.1 (5)	39.7 (5)

Notes: (*a*) φ1: C7—O2—C2—C3; φ2: C7—O1—C1—C6; φ3: C10—O5—C5—C4; φ4: C10—O6—C6—C1; A_{nm}: angles between mean planes (*nm*) through (1) O1/C1/C2/O2/C7, (2) C6/O6/C10/O5/C5 and (3) C1–C6. (*b*) *B* and *C* signify two independent molecules.

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