organic compounds

1D-3,4-Di-*O*-(diphenylmethylphosphonio)-1,2,5,6-tetra-*O*-methyl-*c*hiro-inositol diiodide

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The title compound, 3,4,5,6-tetramethoxycyclohexane-1,2-diyldioxybis(methyldiphenylphosphonium) diiodide, $C_{36}H_{44}$-$O_6P_2^{2+} \cdot 2I^-$, was prepared from a New Zealand natural product, D-*chiro*-inositol, in order to develop new catalytic metal complexes. The inositol ring retains its usual chair conformation with only minor perturbations caused by the bound diphenylmethylphosphines. Crystal-packing forces are provided by C—H⋯I cation–anion interactions.

Comment

The use of rhodium complexes containing carbohydrate-based ligands in the catalytic hydrogenation of alkenes is well known (RajanBabu *et al.*, 1999, and references therein). High enantio-purity is often obtained and this has prompted our interest in the preparation of the title compound, (I). The preparation of suitable crystals as an iodide salt to confirm the stereochemistry of the molecule followed after unsuccessful attempts with other anions. The structure consists of 1D-3,4-di-*O*-(diphenylmethylphosphonio)-1,2,5,6-tetra-*O*-methyl-*chiro*-inositol cations (Fig. 1) and iodide anions bound together by H⋯I interactions.

(I)
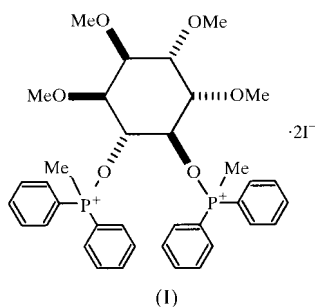
The cation has an approximate non-crystallographic twofold symmetry axis passing through the midpoint of the C1—C2 and C4—C5 bonds. This C_2 symmetry was found in L-*chiro*-inositol (Jeffrey & Yeon, 1987, hereafter FOPKOK), the enantiomer of the parent molecule, and it is only broken here by the methyl C41 and C51 atoms, as shown by the

dihedral angles C5—C4—O4—C41 and C4—C5—O5—C51 of 147.9 (3) and 91.7 (3)°, respectively. The inositol O atoms are not involved in intermolecular hydrogen bonding as in FOPKOK, but there are several intramolecular contacts which, in combination, suggest why these two methyl atoms are not symmetrically related. One attractive interaction involves one of the protons on C41 (H41*B*⋯O3 2.49 Å and C41—H41*B*⋯O3 122°), but also there are other weak interactions (H20*C*⋯O3 2.31 Å and H10*C*⋯O6 2.45 Å). The cyclohexane chair conformation is closer to a strain-free state than in FOPKOK, with an average C—C—C—C dihedral angle of 60.5° compared with 54.8° in FOPKOK; this is also confirmed by the Q, θ and φ values (Cremer & Pople, 1975) which are 0.631 (3) Å, 177.2 (3) and 221 (4)°, and 0.559 Å, 4.3 and 289° for (I) and FOPKOK, respectively. The dihedral angle involving the phosphonium-bonded O atoms (O1—C1—C2—O2) is also barely perturbed at −57.4 (2)°.

The P—O—C bonding (with C—O, P—O, and P—O—C means of 1.453, 1.577 Å, and 126.9°) is similar to that found in the few known structures containing this fragment: 1.458, 1.573 Å, and 122.5° observed in neopentyloxy(phenacyl)-diphenylphosphonium bromide (Henrick *et al.*, 1991), 1.479, 1.554 Å, and 136.0° in (heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecanyloxy)triphenylphosphonium iodide (Chow *et al.*, 1996) and 1.475, 1.568 Å, and 121.4° in neopentyloxymethyl-diphenylphosphonium bromide (Henrick *et al.*, 1980, hereafter DPHNPP). Bonding around the P atoms is normal, with mean values for P—C(phenyl) and P—C(methyl) of 1.787 and 1.783 Å compared with 1.788 and 1.779 Å in DPHNPP. The O—P—C(phenyl) angles are all less than 109.4°, except for O1—P1—C121 of 112.5 (1)°. Analysis of the intramolecular contacts suggests that minor twists at the P atoms have alleviated repulsive close contacts between the methyl- and phenyl-group atoms and the inositol fragment.

The intermolecular packing here is interesting, since it involves non-classical potentially hydrogen-bonding contacts
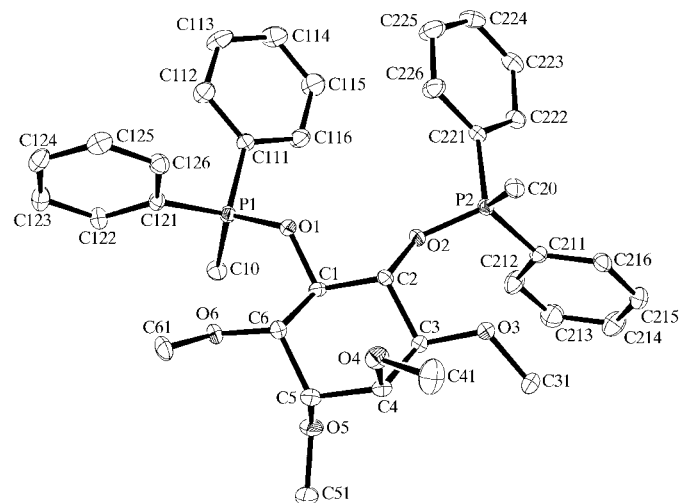

Figure 1
*ORTEP*II (Johnson, 1976; Farrugia, 1997) drawing of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms have been excluded for clarity.

between iodide anions and methyl, *ortho*- and *para*-phenyl protons attached to P atoms in this highly ordered (low R factor) crystal (see Table 2). In searching the Cambridge Structural Database (ConQuest, 2000), it became apparent that some of these interactions, where the H···I distances are less than the sum of their van der Waals radii (3.18 Å), have not always been recognized, although there are exceptions (*e.g.* Glidewell *et al.*, 1994). We restricted our searches to those compounds with tetrahedral P (phosphine) atoms and free iodide anions.

Close contacts with *para*-phenylphosphine H atoms were found 18 times, with a minimum H···I distance of 2.81 Å, C—H···I angles of 126–172°, and average H···I, C···I and C—H···I values of 3.08, 3.94 Å and 147°, respectively. Two representative examples are found in 1,3-bis(dimethylamino)-1,3-bis(triphenylphosphonio)allene diiodide (Weiss *et al.*, 1981), with H···I distances of 3.06 and 3.08 Å, and C—H···I angles of 147 and 139°, and 1,1′-ferrocenediylbis(methyltri-phenylphosphonium) diiodide dichloromethane solvate (Glidewell *et al.*, 1994, hereafter HATWAA), with an H···I distance of 3.05 Å and a C—H···I angle of 153°.

ortho-Phenylphosphine-H···I⁻ interactions have been observed more often (24 times), with a minimum H···I distance of 2.94 Å, C—H···I angles of 130–176°, and average H···I, C···I and C—H···I values of 3.05, 3.94 Å and 152°, respectively. Typical examples are found in 2,2-bis(diphenyl phosphanomethyl)(η^5-cyclopentadienylpropyl)oxomolyb-denum(IV) iodide ethanol solvate (Antelmann *et al.*, 1998), with an H···I distance of 3.06 Å and a C—H···I angle of 143°, and in HATWAA, with H···I distances of 3.01, 3.02, 3.08 and 3.16 Å, and C—H···I angles of 168, 154, 160 and 168°, respectively.

Methylphosphine-H···I⁻ interactions were found in 24 structures (59 contacts), with a minimum H···I distance of 2.81 Å, C—H···I angles of 141–174° (a noticeably higher minimum angle than for the phenyl H contacts), and average H···I, C···I and C—H···I values of 3.08, 4.01 Å and 159°, respectively. In trimethylphenylphosphonium iodides (Schodel *et al.*, 1995), the H···I distances vary from 2.99 to 3.17 Å and the C—H···I angles from 140 to 163°; in (η^5-cyclopentadienyl)(dimethylphenylphosphine)(*N*-2-pyrrolyl-methylene-1-phenylamine)cobalt iodide (Zhou *et al.*, 1993), the H···I distances are 2.95 and 3.11 Å, and the C—H···I angles are 173 and 166°, respectively, and in μ^2-hydrido-bis[(diphenylmethylphosphine)imino(diphenylphospine oxide)] iodide (Slawin *et al.*, 1996), H···I is 2.95 Å and C—H···I is 173°.

We conclude from this analysis that the H···I interactions itemized in Table 2 represent significant binding interactions in the crystal.

Experimental

Crystals of (I) were crystallized from acetonitrile. Complete details of the preparation of 1D-3,4-di-*O*-(diphenylmethylphosphino)-1,2,5,6-tetra-*O*-methyl-*chiro*-inositol diiodide and its precursor, 1D-3,4-di-*O*-(diphenylphosphino)-1,2,5,6-tetra-*O*-methyl-*chiro*-inositol, have been reported (Enright *et al.*, 2000).

Crystal data

$C_{36}H_{44}O_6P_2{}^{2+}\cdot2I^-$	Mo $K\alpha$ radiation
$M_r = 888.45$	Cell parameters from 8192
Orthorhombic, $P2_12_12_1$	reflections
$a = 10.306\,(3)$ Å	$\theta = 2.64$–$27.52°$
$b = 12.953\,(4)$ Å	$\mu = 1.758$ mm^{-1}
$c = 28.826\,(9)$ Å	$T = 163\,(2)$ K
$V = 3848\,(2)$ Å^3	Block, colourless
$Z = 4$	$0.25 \times 0.23 \times 0.16$ mm
$D_x = 1.534$ Mg m^{-3}	

Data collection

CCD area-detector diffractometer	7920 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.036$
Absorption correction: multi-scan	$\theta_{max} = 27.89°$
(Blessing, 1995)	$h = -8 \to 13$
$T_{min} = 0.647$, $T_{max} = 0.755$	$k = -16 \to 16$
51 053 measured reflections	$l = -36 \to 37$
5120 independent reflections (plus 3509 Friedel-related reflections)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0295P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.051$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.045$	$\Delta\rho_{max} = 0.80$ e Å^{-3}
8629 reflections	$\Delta\rho_{min} = -0.55$ e Å^{-3}
415 parameters	Absolute structure: Flack (1983)
H atoms constrained	Flack parameter = $-0.009\,(10)$

Table 1
Selected geometric parameters (Å, °).

P1—O1	1.573 (2)	O1—C1	1.456 (3)
P1—C121	1.784 (3)	O2—C2	1.449 (3)
P1—C111	1.788 (3)	O3—C3	1.424 (3)
P1—C10	1.788 (3)	O3—C31	1.437 (3)
P2—O2	1.5796 (18)	O4—C4	1.428 (3)
P2—C20	1.779 (3)	O4—C41	1.433 (4)
P2—C211	1.783 (3)	C1—C6	1.514 (4)
P2—C221	1.794 (3)	C1—C2	1.528 (3)
O1—P1—C121	112.52 (12)	C211—P2—C221	108.78 (13)
O1—P1—C111	102.88 (11)	C1—O1—P1	126.88 (15)
C121—P1—C111	106.18 (13)	C2—O2—P2	126.96 (16)
O1—P1—C10	112.71 (12)	C3—O3—C31	113.9 (2)
C121—P1—C10	112.16 (13)	C4—O4—C41	115.8 (2)
C111—P1—C10	109.75 (14)	C5—O5—C51	113.4 (3)
O2—P2—C20	114.85 (12)	C6—O6—C61	112.6 (2)
O2—P2—C211	108.86 (11)	O1—C1—C6	110.3 (2)
C20—P2—C211	112.92 (13)	O1—C1—C2	107.19 (19)
O2—P2—C221	104.70 (11)	C6—C1—C2	108.4 (2)
C20—P2—C221	106.23 (13)	O2—C2—C1	106.8 (2)
C121—P1—O1—C1	101.7 (2)	C6—C1—C2—C3	63.0 (3)
C111—P1—O1—C1	−144.5 (2)	C31—O3—C3—C4	80.8 (3)
C10—P1—O1—C1	−26.4 (2)	C41—O4—C4—C3	−92.0 (3)
C20—P2—O2—C2	−28.6 (2)	C41—O4—C4—C5	147.9 (3)
C211—P2—O2—C2	99.1 (2)	C51—O5—C5—C6	−148.5 (2)
C221—P2—O2—C2	−144.7 (2)	C51—O5—C5—C4	91.7 (3)
P1—O1—C1—C6	−74.6 (3)	C10—P1—C111—C116	−67.3 (3)
P1—O1—C1—C2	167.71 (17)	C20—P2—C211—C216	−17.0 (3)
P2—O2—C2—C1	174.48 (15)	C20—P2—C211—C212	163.8 (2)
P2—O2—C2—C3	−67.2 (3)	O2—P2—C221—C222	−127.0 (2)
O1—C1—C2—O2	−57.4 (2)	O2—P2—C221—C226	60.1 (3)
C6—C1—C2—O2	−176.35 (19)		

All H atoms were constrained to an isotropic displacement parameter 1.2 times that of the equivalent U of their parent atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*97

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10A⋯I2[i]	0.98	2.98	3.954 (3)	176
C212—H212⋯I2[i]	0.95	2.90	3.795 (3)	158
C216—H216⋯I1[ii]	0.95	3.02	3.799 (3)	140

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

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WINGX* (Farrugia, 1999) and *ORTEP*-3 (Farrugia, 1997) based on *ORTEP*II (Johnson, 1976).

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