

Methyl 2,6-di-*O*-benzyl-3,4-*O*-phenylphosphinediyl- β -*D*-galactopyranoside- (*P*—*B*)borane with chirality on the P atom

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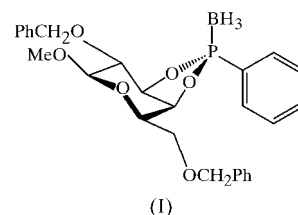
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A carbohydrate-derived optically active *P*-chiral dioxophenylphospholane–borane complex, $C_{27}H_{32}BO_6P$, was prepared from bis(diethylamino)phenylphosphine and methyl 2,6-di-*O*-benzyl- β -*D*-galactopyranoside. The phosphinite was prepared with high diastereoselectivity and in good yield. The absolute configuration (*R*) at the *P* atom was deduced from the known configuration of the sugar moiety. Weak intermolecular interactions link the molecules into a three-dimensional network.

Comment

In the drive to design and optimize ligands for asymmetric catalysis, the preparation and characterization of new optically active phosphorus compounds is essential. A great variety of phosphonites have been prepared (Jugé, Stephan, Genet *et al.*, 1990; Murillo *et al.*, 1983; Reetz & Gosberg, 1999), but only a few have been prepared as the corresponding borane complex. The use of a stabilizing complex with borane was developed by Imamoto and co-workers (Imamoto *et al.*, 1990). Borane prevents the phosphinite from oxidizing to the corresponding

phosphonate. To our knowledge, no crystal structure of a carbohydrate-derived dioxophospholane–borane complex has been reported previously.



Electron-deficient *P*-chiral ligands are rare. Jugé and co-workers have shown the great potential of such compounds, both as ligands and as chiral building blocks in the synthesis of new *P*-chiral compounds (Jugé, Stephan, Laffitte & Genet, 1990). Most likely, selective opening of the dioxophospholane borane complex with either lithium or Grignard reagents can give rise to novel carbohydrate-derived phosphonites and, ultimately, *P*-chiral phosphines. The title compound, (I), has, in addition to *P*-chirality, a chiral carbohydrate moiety. The use of a carbohydrate as a chiral auxiliary is very interesting,

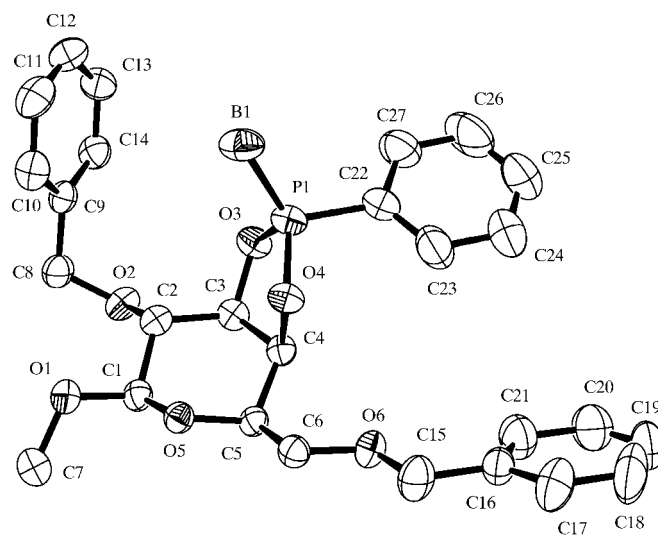


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

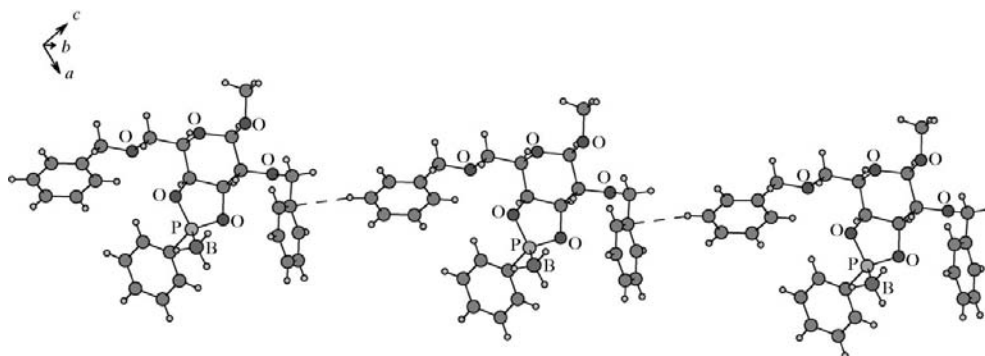


Figure 2
A view of a chain in (I), connected through $C-H \cdots \pi$ interactions (dashed lines). The $C-H \cdots \pi$ $C18 \cdots C9$ distance is 3.675 (8) Å.

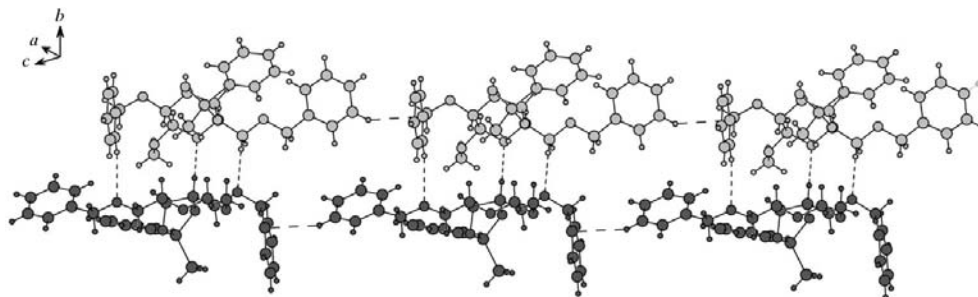


Figure 3
Two parallel chains in (I), connected through C—H···O interactions.

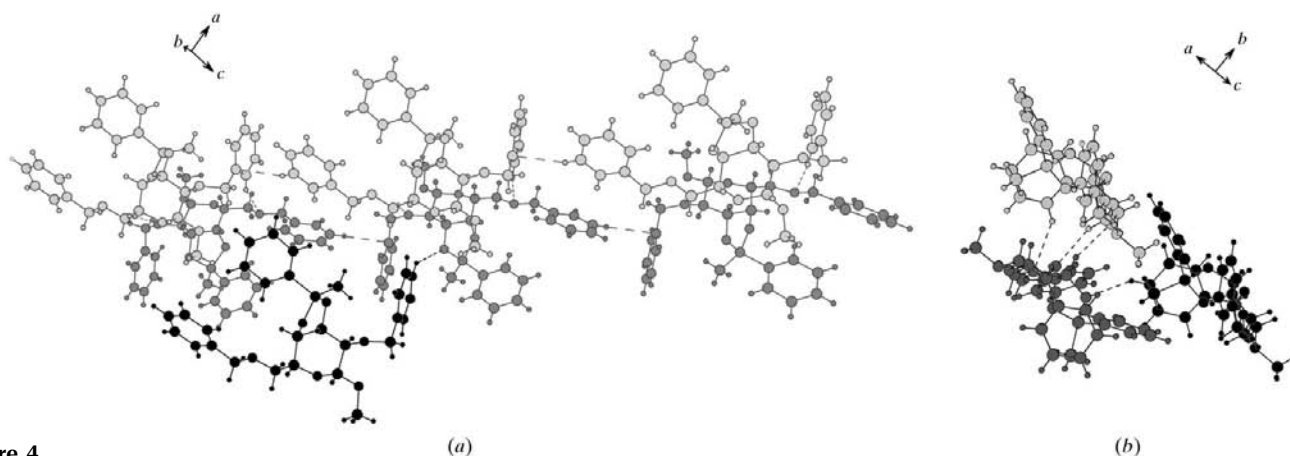


Figure 4
(a) Side and (b) front views, showing the C12—H12···O3 interaction connecting the stacked chains in (I).

and the greater peripheral chirality on the carbohydrate moiety induces a highly chiral environment. P-chirality moves a stereocentre closer to a potential metal, a feature that might prove interesting in metal-catalysed reactions. These factors will be explored further in a range of asymmetric reactions.

A view of the asymmetric unit of (I), comprising a single molecule, is shown in Fig. 1. The geometry of the five-membered dioxophospholane ring P1/O3/C3/C4/O4 and at the P atom are consistent with a previously reported similar structure (Jugé, Stephan, Genet *et al.*, 1990). The carbohydrate moiety is in a distorted chair conformation. In the dioxophenylphospholane–borane moiety, the O3—C3—C4—O4 torsion angle is 40.0 (2)°, compared with a value of 60.8 (4)° in the corresponding carbohydrate, which is only protected in the anomeric position (Banerjee *et al.*, 1994), and a similar value of 36.63 (2)° in another β -D-galactopyranoside, where a five-membered ring is assembled between the 3- and 4-position O atoms (Hoogendorp *et al.*, 1983).

The packing in (I) is governed by non-classical hydrogen-bonding interactions. These can be divided into C—H··· π and C—H···O(ether) weak interactions (Table 2). As shown in Fig. 2, the C—H··· π interaction results in chains running along the [101] direction. These chains are connected by weak C—H···O interactions (C···O \simeq 3.33 Å) between screw-axis-related molecules (Fig. 3). Finally, a C12—H12···O3 interaction forms a link between the chains, creating a three-dimensional network (Fig. 4).

Experimental

Bis(diethylamino)phenylphosphine (151.4 mg, 0.5 mmol) and methyl-2,6-di-*O*-benzyl- β -D-galactopyranoside (187.1 mg, 0.5 mmol) were dissolved in toluene (10 ml). The resulting mixture was then refluxed under an argon atmosphere until no evolution of diethylamine could be detected by the use of a pH indicator (approximately 16 h). The solution was then cooled to 273 K and BH₃·DMS (0.3 ml, 0.6 mmol) was added dropwise by syringe. After stirring for an additional 16 h at ambient temperature, the reaction mixture was concentrated under reduced pressure to yield a colourless syrup. This syrup was recrystallized from 2-propanol by slow evaporation.

Crystal data

C₂₇H₃₂BO₆P
M_r = 494.32
Monoclinic, *P*2₁
a = 10.7567 (19) Å
b = 9.800 (9) Å
c = 12.926 (4) Å
 β = 96.63 (2)°
V = 1353.6 (13) Å³
Z = 2

D_x = 1.213 Mg m⁻³
Mo *K* α radiation
Cell parameters from 19 reflections
 θ = 11.1–15.3°
 μ = 0.14 mm⁻¹
T = 293 (2) K
Rod, colourless
0.55 × 0.25 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
5762 measured reflections
3105 independent reflections
1621 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.142
 θ _{max} = 27.0°

h = -13 → 13
k = -12 → 0
l = -16 → 16
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.001$
$R(F) = 0.048$	$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.144$	$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
$S = 1.04$	Absolute structure: Flack (1983)
3105 reflections	Flack parameter = 0.0 (4)
319 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (\AA , $^\circ$).

C22–P1	1.790 (5)	O4–P1	1.600 (3)
O3–P1	1.597 (3)	P1–B1	1.851 (6)
C3–O3–P1	110.4 (2)	O4–P1–C22	105.1 (2)
C4–O4–P1	108.1 (2)	O3–P1–B1	115.2 (3)
O3–P1–O4	97.59 (14)	O4–P1–B1	115.4 (2)
O3–P1–C22	107.5 (2)	C22–P1–B1	114.3 (3)
O3–C3–C4–O4	40.0 (2)		

Approximately 8% of the collected data were removed due to bad background. The poor quality also results in an unusually high R_{int} value of 0.142. The absolute configuration could not be determined from the diffraction data because of the high uncertainty (0.4) in the Flack (1983) parameter, but was assigned by the known configuration of the carbohydrate moiety. H atoms were placed in calculated positions and refined riding on their carrier atoms at distances of 0.93, 0.96, 0.96, 0.97 and 0.98 \AA for aromatic, borane, methyl, methylene and methine H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{B})$, where $x = 1.5$ for methyl and borane H atoms, and 1.2 for all others.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Table 2

Intermolecular contact geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3–H3 \cdots O5 ⁱ	0.98	2.37	3.314 (6)	162
C6–H6A \cdots O2 ⁱⁱ	0.97	2.43	3.352 (6)	159
C18–H18 \cdots C9 ⁱⁱⁱ	0.93	2.84	3.675 (8)	150
C12–H12 \cdots O3 ^{iv}	0.93	2.71	3.510 (6)	145

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1560). Services for accessing these data are described at the back of the journal.

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