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O^1,O^2:O^3,O^5-Bis(phenylboranediyl)-α-D-glucofuranose

Scott P. Draffin,[a] Peter J. Duggan,[a,b] Gary D. Fallon[a]* and Edward M. Tyndall[c]

[a]School of Chemistry, Monash University, Victoria 3800, Australia, [b]CSIRO Molecular Science, Private Bag 10, Clayton South, Victoria 3169, Australia, and [c]Centre for Green Chemistry, Monash University, Victoria 3800, Australia

Correspondence e-mail:
gary.fallon@sci.monash.edu.au

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.070
Data-to-parameter ratio = 10.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{18}B_2O_6$, was formed by the reaction between phenylboronic acid and D-glucose. The structure is analogous to those of D-glucoboronates previously prepared and characterized by NMR. In the crystal structure, molecules are linked into one-dimensional chains along [100] *via* O—H···O hydrogen bonds [O···O = 2.8283 (17) Å].

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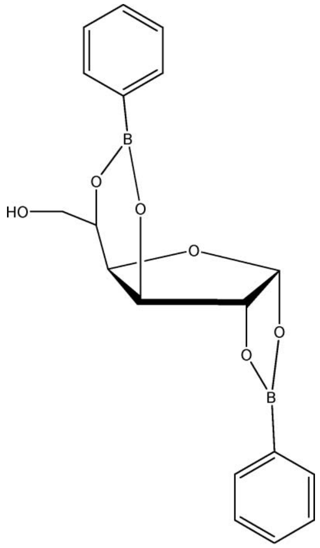
Comment

Boronic acids have received much attention as potential components of online D-glucose sensors (Fang *et al.*, 2004; James & Shinkai, 2002). Many diboronic acids designed to be selective for D-glucose have been synthesized. The selectivity of these compounds has often relied on relatively subtle structural features present in their scaffolds, in order to orient the boronic acid functional groups such that binding of D-glucose is favoured over other monosaccharides. Such investigations have used information on solution structures of D-glucose boronates, determined using NMR methods (Wood & Siddiqui, 1974; Edelev *et al.*, 1974; Norrild & Eggert, 1995) and molecular modelling studies, in order to design better D-glucose binders. However, the most accurate structural description of a diboronate ester of D-glucose, *i.e.* an X-ray crystal structure, has, until now, been missing from the literature, despite the fact that the information provided by such a structure could significantly assist the development of selective sugar sensors.



(I)

Bourne and co-workers (Bourne *et al.*, 1965, 1972) first described a crystalline diphenylboronate of D-glucose, which was formed in an alcohol solvent from D-glucose and

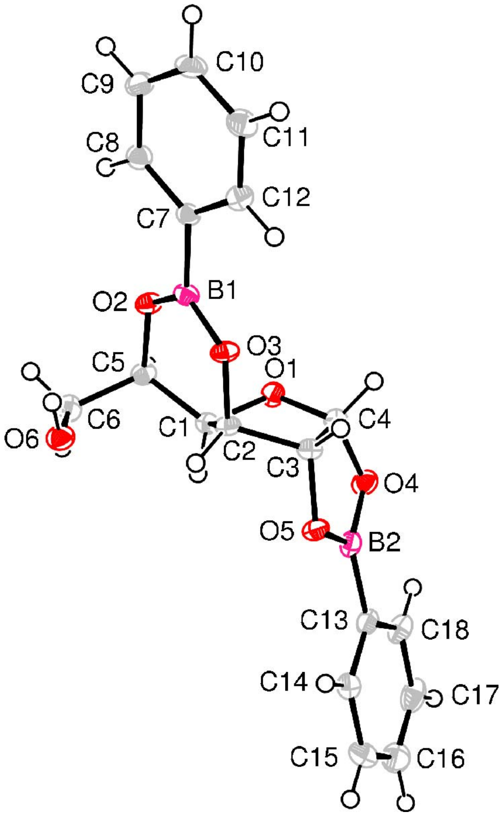


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

phenylboronic anhydride and recrystallized from toluene. These workers suggested the product was O^1,O^2:O^3,O^5-bis(phenylboranediyl)-α-D-glucofuranose, and NMR studies by three separate research groups (Wood & Siddiqui, 1974; Edelev *et al.*, 1974; Norrild & Eggert, 1995) showed that, in solution, this was the most likely structure.

Here we describe the crystal structure of the title compound, (I), a continuation of the investigation of the solid-state structures of boronates derived from monosaccarides (Draffin *et al.*, 2004).

Compound (I) was formed by heating a 2:1 mixture of phenylboronic acid and D-glucose in dioxane at reflux in a Dean–Stark apparatus. After evaporation of residual dioxane, the product was crystallized from a dichloromethane–hexane mixture (and recrystallized from dichloromethane–petroleum ether (303–313 K). The X-ray crystal structure obtained from these crystals confirmed that the compound was a diboronate of α-D-glucofuranose, with a five-membered cyclic boronate having been formed from the 1,2-diol and a six-membered cyclic boronate formed from the 3,5-diol. This structure is the same as the solution structures determined by Wood & Siddiqui (1974) and Edelev *et al.* (1974) and is analogous to the di-*p*-tolylboronate identified by Norrild & Eggert (1995) in solutions of D-glucose and *p*-tolylboronic acid in $(CD_3)_2SO$.

The crystal structure consists of discrete molecules of (I), stabilized by a strong intermolecular hydrogen bond (Table 1). The B centres show very little deviation from planarity.

Experimental

The title glucose diphenylboronate was prepared in a similar way to that described for the corresponding fructose derivative (Draffin *et al.*, 2004). Thus, D-glucose (2.30 g, 12.7 mmol), phenylboronic acid (3.00 g, 24.6 mmol) and dioxane (32 ml) were combined in a Dean–Stark apparatus and heated at reflux with azeotropic removal of water for *ca* 6 h. A total of *ca* 21 ml of distillate was collected. Once cooled, the reaction mixture became murky and was filtered prior to the removal of the solvent. The residue thus obtained was a colourless sticky foam (4.5 g) which was crystallized from dichloromethane–hexane (50:50) to give a white crystalline solid (3.01 g, 70%). A sample of this material was recrystallized from dichloromethane–petroleum ether (303–313 K) (50:50) to give prismatic crystals of (I) suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.89 (4H, *m*, m-ArH), 7.35–7.56 (6H, *m o*,*p*-ArH), 6.22 (1H, *d*, *J* = 4 Hz, H1), 5.03 (1H, *d*, *J* = 4 Hz, H2), 4.74 (1H, *d*, *J* = 2 Hz, H3), 4.50 (1H, *t*, *J* = 4 Hz, H5), 4.32 (1H, *d*, *J* = 3 Hz, H4), 3.90 (1H, *br d*, *J* = 12 Hz, H6′), 3.74 (1H, *br d*, *J* = 12 Hz, H6), 1.90 (1H, *br s*, –OH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 64.1, 70.8, 74.2, 75.0, 86.4, 104.5, 127.7, 128.0, 131.2, 132.3, 134.0, 135.2; m.p. 428–431 K [literature value (Wood & Siddiqui, 1974) 432–435 K].

Crystal data

$C_{18}H_{18}B_2O_6$
$M_r = 351.94$
Orthorhombic, $P2_12_12_1$
$a = 10.2706$ (1) Å
$b = 12.5577$ (2) Å
$c = 13.3708$ (2) Å
$V = 1724.50$ (4) Å^3
$Z = 4$
$D_x = 1.356$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 24 578 reflections
$\theta = 3.6–28.2°$
$\mu = 0.10$ mm^{-1}
$T = 123$ (2) K
Prism, colourless
0.31 × 0.27 × 0.24 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Thick-slice φ and ω scans
24 578 measured reflections
2400 independent reflections
2188 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.039$
$\theta_{\rm max} = 28.2°$
$h = -12 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.07$
$S = 1.07$
2400 reflections
236 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.427P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O1$^{\rm i}$	0.84	2.00	2.8283 (17)	168

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

In the absence of significant anomalous scattering effects, 1816 Friedel pairs were merged and the absolute configuration assigned by reference to D-glucose. All H atoms were placed in calculated positions, with C—H distances in the range 0.95–1.00 Å and with an O—H distance of 0.84 Å. They were included in the refinement in a riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ (1.5$U_{\rm eq}$ for methyl and hydroxyl H atoms) of the carrier atom.

o1734 Draffin *et al.* • $C_{18}H_{18}B_2O_6$ *Acta Cryst.* (2005). E**61**, o1733–o1735

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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