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1,6-Dibenzoyloxy-2:4,3:5-O^2:O^4,O^3:O^5-bis(phenylboronoyloxy)-D-mannitol

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.005 Å
R factor = 0.060
wR factor = 0.097
Data-to-parameter ratio = 10.4

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

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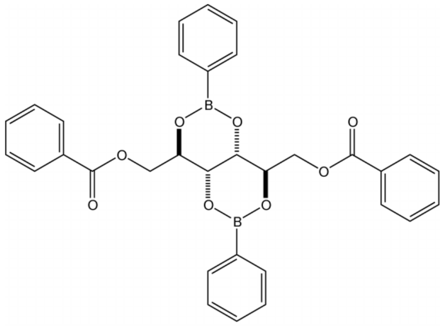
The title compound, $C_{32}H_{28}B_2O_8$, was obtained by the condensation of 1,6-dibenzoyloxy-D-mannitol with two equivalents of phenylboronic acid. The crystal structure confirms that the phenylboronate moieties exist as six-membered rings in the solid state.

Comment

The application of boronic acids as labile protective agents in the selective functionalization of polyols is currently a focus area of our research (Duggan & Tyndall, 2002; Bhaskar *et al.*, 2001, 2003). The title compound, (I), was first obtained as an intermediate in the terminally selective acylation of D-mannitol, performed with benzoyl chloride in a mixture of hot benzene, pyridine and phenylboronic acid (Bhaskar *et al.*, 2001). Compound (I) is of interest because it showed an unusually high hydrolytic stability compared with other alkylation or acylation products (Bhaskar *et al.*, 2001). Since the initial study, two analogous D-mannitol 1,6-disilyl bis(phenylboronate) esters have been synthesized which possess similar hydrolytic stabilities to (I). Their solid-state crystal structures are also similar to that of (I) (Bhaskar *et al.*, 2003).



(I)

Compound (I) crystallized as large white needles after slow evaporation of an acetonitrile solution. The asymmetric unit comprises a single molecule of (I) (Fig. 1). Two six-membered dioxaborolane rings are fused to a mannitol backbone, with benzoyl ester substituents at the terminal positions. The borate rings have a sofa conformation, with atoms C3 and C4 deviating from planes *A* (B1/O1/O2/C2/C4) and *A*′ (B2/O3/O4/C3/C5) by 41.7 (2) and 45.1 (2)°, respectively. The dihedral angle between the phenylboronate aromatic rings, *B* (C7–C12) and *B*′ (C13–C18), is 88.1 (1)°. These aromatic rings are coplanar with their corresponding borate systems [dihedral angles between planes *A*/*B* and *A*′/*B*′ are 7.1 (2) and 3.5 (2)°, respectively], which indicates that electron density is shared between the aromatic systems and the electron-deficient B atoms. These observations are consistent with those for similar

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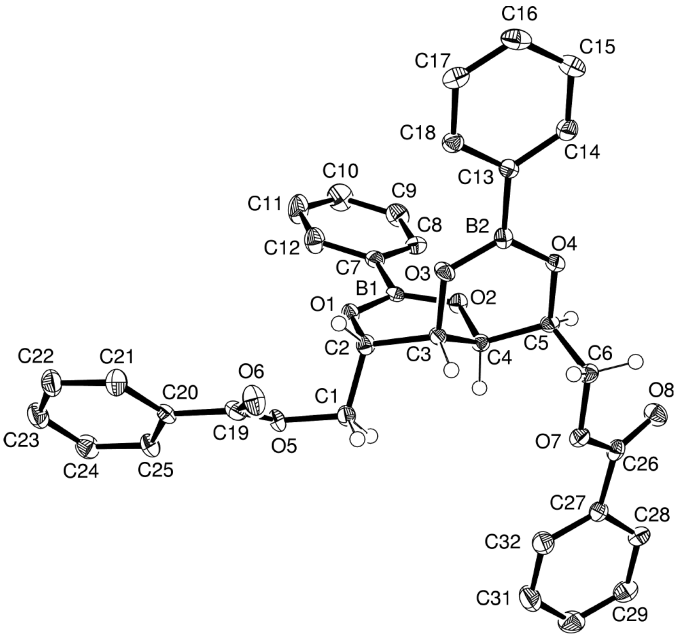

Figure 1
View of (I), with ellipsoids at the 50% probability level. Aromatic H atoms have been omitted for clarity.

boronate structures (Bhaskar *et al.*, 2003; Salazar-Pereda *et al.*, 1994; Ishi-i *et al.*, 1998). It is noteworthy that (I) crystallizes exclusively as the six-membered bis(phenylboronate) rather than the five-membered analogue.

Experimental

1,6-Dibenzoyloxy-D-mannitol (50 mg, 0.13 mmol) and phenylboronic acid (31 mg, 0.26 mmol) were ground together with a mortar and pestle and heated gently with a heat gun for 5 min, after which time the mixture became a colourless viscous liquid. Upon cooling, the diboronate ester crystallized as a white solid (73 mg, quantitative); m.p. 430–431 K. This product was recrystallized as white needles by slow evaporation of an acetonitrile solution of the compound.

Crystal data

$C_{32}H_{28}B_2O_8$
$M_r = 562.16$
Orthorhombic, $P2_12_12_1$
$a = 5.9646\ (1)$ Å
$b = 18.0749\ (3)$ Å
$c = 25.8911\ (6)$ Å
$V = 2791.31\ (9)$ Å^3
$Z = 4$
$D_x = 1.338$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 33 223 reflections
$\theta = 2.4$–28.4
$\mu = 0.09$ mm^{-1}
$T = 123\ (2)$ K
Plate, colourless
0.25 × 0.15 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
33 146 measured reflections
3926 independent reflections
2524 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.128$

$\theta_{\rm max} = 28.4°$
$h = -7 \rightarrow 7$
$k = -24 \rightarrow 24$
$l = -34 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.097$
$S = 1.05$
3926 reflections
379 parameters
H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 1.1628P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7—B1	1.550 (5)	B1—O1	1.371 (4)
C13—B2	1.555 (5)	B2—O4	1.365 (4)
B1—O2	1.368 (4)	B2—O3	1.374 (4)
O2—B1—O1	122.7 (3)	O4—B2—C13	120.8 (3)
O2—B1—C7	118.2 (3)	O3—B2—C13	116.8 (3)
O1—B1—C7	119.1 (3)	B2—O4—C5	121.1 (3)

As the absolute configuration could not be determined reliably for this light-atom study, all data, including Friedel pairs, were merged. The relatively high value of $R_{\rm int}$ reflects the less than optimal quality of the crystal chosen for X-ray analysis. The H atoms were included in the riding-model approximation.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Bhaskar, V. K., D'Elia, A., Duggan, P. J., Humphrey, D. G., Krippner, G. Y., Nhan, T. T. & Tyndall, E. M. (2003). *Aust. J. Chem.*. Submitted.

Bhaskar, V. K., Duggan, P. J., Humphrey, D. G., Krippner, G. Y., McCarl, V. & Offermann, D. A. (2001). *J. Chem. Soc. Perkin Trans.* 1, pp. 1098–1102.

Duggan, P. J. & Tyndall, E. M. (2002). *J. Chem. Soc. Perkin Trans.* 1, pp. 1325–1339.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Ishi-i, T., Nakashima, K., Shinkai, S. & Araki, K. (1998). *Tetrahedron*, **54**, 8679–8686.

Nonius (1997–2002). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Salazar-Pereda, V., Martinez-Martinez, L., Flores-Parra, A., Rosales-Hoz, M. d. J., Arisa-Castolo, A. & Contreras, R. (1994). *Heteroatom Chem.* **5**, 139–143.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.