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Pentaerythrityl tetrakis(4-bromobenzyl ether)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.055
wR factor = 0.165
Data-to-parameter ratio = 15.0

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

The title compound {alternatively called tetrakis[(4-bromobenzyloxy)methyl]methane}, $C_{33}H_{32}Br_4O_4$, was crystallized from ethyl acetate. The molecule has crystallographic twofold rotation symmetry. Key features of the structure include intramolecular edge-to-face aromatic interactions, intermolecular Br$\cdots\pi$ interactions and intermolecular Br$\cdots$O contacts.

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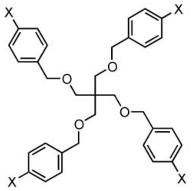
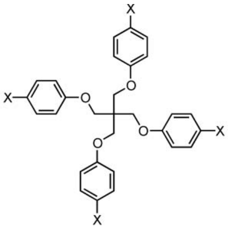
Comment

An emerging strategy in crystal engineering relies on the use of special molecules called tectons (Simard *et al.*, 1991). Tectons have structurally well defined cores attached to multiple 'sticky' functional groups which govern intermolecular association according to reliable patterns, thereby causing neighboring tectons to be placed in predetermined positions. Much initial research in molecular tectonics has been aimed at identifying effective cores and sticky sites. Rigid cores derived from tetraphenylmethane, spirobifluorene and related molecules are particularly attractive because they orient peripheral sticky sites in predictable ways. In addition, however, significantly less rigid cores, such as those derived from pentaerythrityl tetrakis(phenyl ether) (Laliberté *et al.*, 2004; Laliberté, Maris & Wuest, 2003) and dipentaerythrityl hexakis(phenyl ether) (Laliberté, Maris *et al.*, 2003), are proving to be valuable in molecular tectonics. As part of a systematic investigation of potential cores, we have turned our attention to derivatives of pentaerythrityl tetrakis(benzyl ether). Such compounds are similar to the corresponding tetrakis(phenyl ethers) studied previously, but they include four extra CH_2 groups, which introduce additional elements of flexibility and further separate the central quaternary C atom from the peripheral sticky sites. In recent work, carbohydrates have been attached to the pentaerythrityl tetrakis(benzyl ether) core to produce multivalent glycoconjugates designed to interact strongly with proteins (Liu & Roy, 2001). In order to learn more about the preferred conformation and geometry of pentaerythrityl tetrakis(benzyl ethers), we have synthesized the title compound, (I), crystallized it from ethyl acetate and determined its structure.

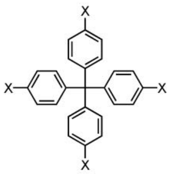


(X = Br)

(I)



(II)



(III)

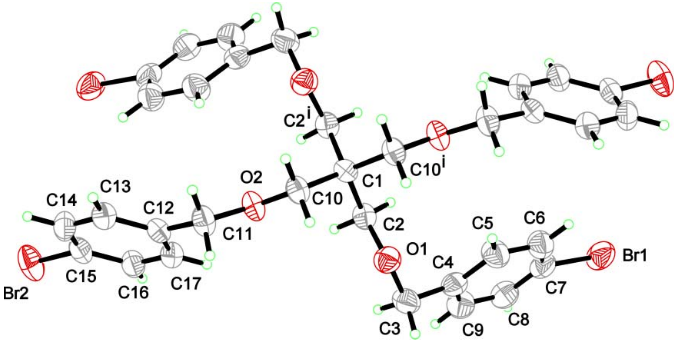


Figure 1
View of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.]

Compound (I) (Fig. 1), with crystallographic twofold rotation symmetry, incorporates four benzene rings attached to a nominally tetrahedral quaternary C atom by $–CH_2OCH_2–$ arms. It is instructive to compare its structure with those of pentaerythrityl tetrakis(phenyl ethers), (II), in which the connecting arms are $–CH_2O–$, and tetraphenylmethanes, (III), in which the phenyl groups are connected directly to the central C atom without spacers. In (I), the observed torsion angles show that the individual $–CH_2OCH_2–$ arms are all nearly fully extended [C1—C2—O1—C3 = 178.1 (4)° and C1—C10—O2—C11 = 175.2 (4)°]. Furthermore, the extension continues across the central C atom to create two nearly fully extended $–CH_2OCH_2CCH_2OCH_2–$ chains [$C2^{i}$—C1—C2—O1 = −174.9 (4)° and $C10^{i}$—C1—C10—O2 = −178.5 (5)°; symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$]. In contrast, extension in the individual $–CH_2O–$ arms of pentaerythrityl tetrakis(phenyl ether), (II) (with X = H), does not continue across the central C atom and the structure is more compact (Laliberté, Maris & Wuest, 2003). In (I), full extension of two of the $–CH_2OCH_2–$ arms also continues further and includes the attached benzene rings [C12—C11—O2—C10 = −173.7 (5)°]. However, the remaining two attached benzene rings [C4—C3—O1—C2 = −70.5 (6)°] are oriented in a way that permits intramolecular edge-to-face aromatic interactions with the other two benzene rings. In these contacts, the shortest H⋯C distance ($H6^{i}$⋯C13) is 3.04 (1) Å, with $C6^{i}$—$H6^{i}$⋯C13 = 138.7 (1)°.

In compounds (I), (II) and (III), the C—C—C angles at the core are close to the ideal tetrahedral value, but the peripheral benzene rings diverge from the core in distinctly different ways. These differences are best assessed by comparing the $C_p \cdots C_{core} \cdots C_p$ angles defined by the central C atom (C_{core}) and the *para* positions of the benzene rings (C_p). In tetraphenylmethane, (III) (with X = H), these angles are close to the tetrahedral ideal [110.85 (8)° (× 4) and 106.74 (15)° (× 2); Claborn *et al.*, 2002]. In pentaerythrityl tetrakis(phenyl ether), (II) (with X = H), the two independent $C_p \cdots C_{core} \cdots C_p$ angles have the values 87.77 (5)° and 121.30 (3)°, showing that the overall molecule deviates significantly from tetrahedral geometry (Laliberté, Maris & Wuest, 2003). In (I), the orientation of the benzene rings is far from tetrahedral, and the $C_p \cdots C_{core} \cdots C_p$ angles range from 42.3 (1)° to 154.2 (1)°. As a result, tectons derived from pentaerythrityl tetrakis(benzyl ether) are expected to produce networks with architectures completely different from those built from related derivatives of pentaerythrityl tetrakis(phenyl ether) and tetraphenylmethane.

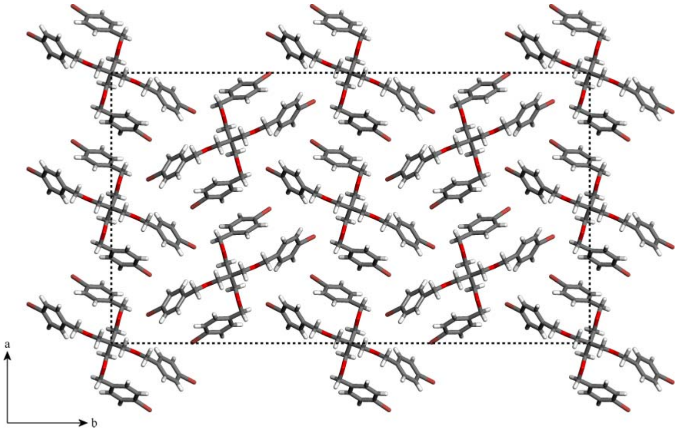


Figure 2
A projection, along the c axis, of the unit-cell contents of (I).

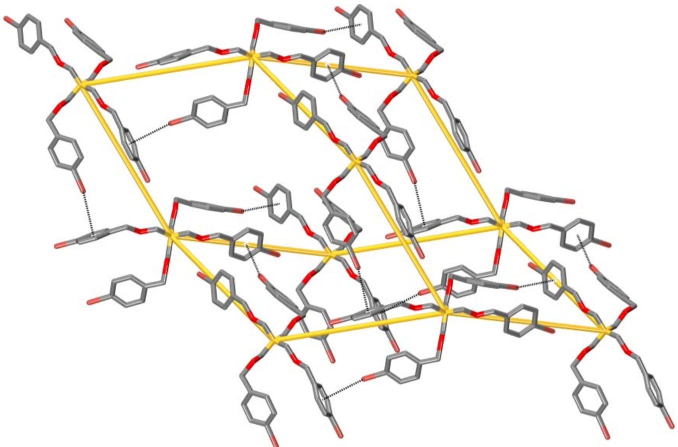


Figure 3
A view of one diamondoid network resulting from molecular association *via* Br⋯π interactions, shown by broken lines.

Intermolecular cohesion in the crystal structure of (I) results in part from van der Waals contacts and multiple Br⋯π interactions (Fig. 2). Specifically, atom Br1 is in close contact [3.587 (2) Å] with the centroid ($Cg2$) of the benzene ring composed of atoms C12–C17, and the C7—Br1⋯$Cg2$ angle is 164.81 (18)°. These Br⋯π interactions link each molecule to four neighbors and thereby define a threefold interpenetrated diamondoid network (Figs. 3 and 4). The individual networks are in van der Waals contact. No Br⋯Br contacts are present, in contrast with the structure of tetrakis(4-bromophenyl)methane, (III) (with X = Br), which features characteristic Br_4 clusters (Reddy *et al.*, 1996). However, the diamondoid networks of (I) are reinforced by related Br2⋯O1 interactions [3.304 (4) Å, C15—Br2⋯O1 = 163.80 (17)°] (Legon, 1999).

Together, these observations confirm that derivatives of pentaerythrityl tetrakis(benzyl ether) may prove to be useful

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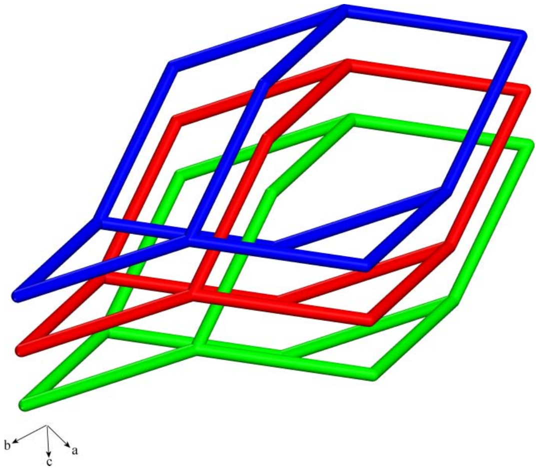

Figure 4
A view of the threefold interpenetration of diamondoid networks resuting from Br···π interactions (see Fig. 3).

in molecular tectonics, that networks constructed from these compounds are unlikely to resemble those built from analogous derivatives of pentaerythrityl tetrakis(phenyl ether) or tetraphenylmethane, and that interactions such as Br···Br and Br···π are not expected to be sufficiently strong and directional to control crystallization of flexible molecules such as pentaerythrityl tetrakis(benzyl ethers) or pentaerythrityl tetrakis(phenyl ethers) in predictable ways.

Experimental

The title compound, (I), was prepared by Williamson etherification of pentaerythritol by 4-bromobenzyl bromide according to standard procedures (Liu & Roy, 2001).

Crystal data

$C_{33}H_{32}Br_4O_4$
$M_r = 812.23$
Orthorhombic, *Fdd*2
$a = 25.342$ (5) Å
$b = 44.671$ (5) Å
$c = 5.7889$ (9) Å
$V = 6553.3$ (18) Å^3
$Z = 8$
$D_x = 1.646$ Mg m^{-3}
Cu *Kα* radiation
Cell parameters from 9698 reflections
$\theta = 4.0$–$68.1°$
$\mu = 6.28$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.25 × 0.05 × 0.05 mm

Data collection

Bruker SMART6000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.620$, $T_{\max} = 0.730$
16 557 measured reflections
2814 independent reflections
2559 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 68.4°$
$h = -30 \rightarrow 29$
$k = -53 \rightarrow 53$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.165$
$S = 1.08$
2814 reflections
187 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1152P)^2 + 3.049P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.035$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), with 1156 Friedel Pairs
Flack parameter: 0.11 (4)

Table 1
Selected geometric parameters (Å, °).

Br1—C7	1.899 (6)	C2—O1	1.414 (7)
Br2—C15	1.885 (5)	C3—O1	1.426 (7)
C1—C10	1.534 (6)	C3—C4	1.516 (8)
C1—C10	1.534 (6)	C10—O2	1.405 (6)
C1—C2	1.536 (6)	C11—O2	1.421 (6)
C1—C2	1.536 (6)	C11—C12	1.503 (8)
C10—C1—C10	106.0 (6)	O1—C2—C1	108.9 (4)
C10—C1—C2	111.0 (3)	O1—C3—C4	113.2 (4)
C10—C1—C2	111.6 (3)	O2—C10—C1	108.9 (4)
C10—C1—C2	111.6 (3)	O2—C11—C12	109.4 (5)
C10—C1—C2	111.0 (3)	C2—O1—C3	112.2 (5)
C2—C1—C2	105.8 (6)	C10—O2—C11	111.9 (4)
C10—C1—C2—O1	64.2 (5)	C2—C1—C10—O2	60.5 (5)
C10—C1—C2—O1	−53.7 (5)	O2—C11—C12—C13	143.4 (5)
C2—C1—C2—O1	−174.9 (4)	O2—C11—C12—C17	−37.1 (7)
O1—C3—C4—C9	150.4 (6)	C1—C2—O1—C3	178.1 (4)
O1—C3—C4—C5	−37.9 (9)	C4—C3—O1—C2	−70.5 (6)
C10—C1—C10—O2	−178.5 (5)	C1—C10—O2—C11	175.2 (4)
C2—C1—C10—O2	−57.2 (5)	C12—C11—O2—C10	−173.7 (5)

H atoms were placed in idealized positions, with C—H distances in the range 0.93–0.97 Å and refined using a riding model, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (2000). *SHELXTL*. Bruker AXS Inc., Madison, USA.
Bruker (2001). *SMART*. Bruker AXS Inc., Madison, USA.
Bruker (2003). *SAINT*. Bruker AXS Inc., Madison, USA.
Claborn, K., Kahr, B. & Kaminsky, W. (2002). *CrystEngComm*, **4**, 252–256.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Laliberté, D., Maris, T., Sirois, A. & Wuest, J. D. (2003). *Org. Lett.* **5**, 4787–4790.
Laliberté, D., Maris, T. & Wuest, J. D. (2003). *Acta Cryst.* E**59**, o799–o801.
Laliberté, D., Maris, T. & Wuest, J. D. (2004). *J. Org. Chem.* **69**, 1776–1787.
Legon, A. C. (1999). *Angew. Chem. Int. Ed.* **38**, 2686–2714.
Liu, B. & Roy, R. (2001). *Tetrahedron*, **57**, 6909–6913.
Reddy, D. S., Craig, D. C. & Desiraju, G. R. (1996). *J. Am. Chem. Soc.* **118**, 4090–4093.
Sheldrick, G. M. (2001). *SADABS*. Bruker AXS Inc., Madison, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Simard, M., Su, D. & Wuest, J. D. (1991). *J. Am. Chem. Soc.* **113**, 4696–4698.

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