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Tetrakis(dimethoxyboryl)methane

Sumeng Liu and Gregory S. Girolami*

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600, South Mathews Avenue, Urbana, IL 61801, USA. *Correspondence e-mail: girolami@scs.illinois.edu

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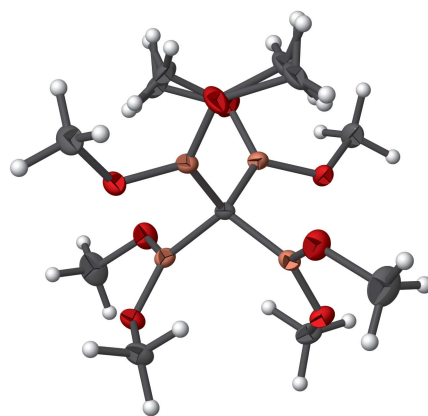
Keywords: crystal structure; tetrakis(dimethoxyboryl)methane; methane derivative.

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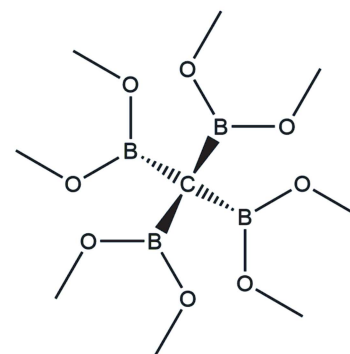
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, tetrakis(dimethoxyboryl)methane (systematic name: octamethyl methanetetrayltetraboronate), $C_9H_{24}B_4O_8$ or $C[B(OMe)_2]_4$, is a useful synthetic intermediate. Crystals of this compound at 102 K conform to the orthorhombic space group $Pbcn$. The molecules, which reside on sites of crystallographic twofold symmetry, have idealized $\bar{4}$ point symmetry like most other CX_4 molecules in which each X group bears two non-H substituents at the 1-position. The central C atom has a slightly distorted tetrahedral coordination geometry, with C—B bond lengths of 1.5876 (16) and 1.5905 (16) Å. One of the methoxy groups is disordered over two sets of sites; the major component has an occupancy factor of 0.676 (8).

3D view



Chemical scheme



Structure description

Tetrakis(dimethoxyboryl)methane (systematic name: octamethyl methanetetrayltetraboronate), which was first reported in 1969 (Castle *et al.*, 1969), is a useful synthetic intermediate (Matteson, 1975; Scherbaum *et al.*, 1988). For example, treatment with ethanol-free lithium ethoxide generates the tris(dimethoxyboryl)methide anion, $\{C[B(OMe)_2]_3\}^-$, whereas treatment with mercuric salts generates $C(HgX)_4$ derivatives (Matteson, 1975). Several crystal structures of tetrasubstituted methanes are known in which the central C atom forms four C—N bonds; these include tetrakis(pyrazolyl)methane, $C(N_2C_3H_3)_4$ (Claramunt *et al.*, 1989), tetrakis(4,5,6,7,8,9-hexahydro-1H-cycloocta[*d*][1,2,3]triazol-1-yl)methane, $C(N_3C_8H_{12})_4$ (Banert *et al.*, 2007), tetrakis(pyrryl)methane, $C(NC_4H_4)_4$ (Müller *et al.*, 2001), and tetrakis(3,5-dimethyl-1H-pyrazol-1-yl)methane, $C(N_2C_3HMe_2)_4$ (Benisvy *et al.*, 2009). All of these molecules adopt idealized $\bar{4}$ geometries and each substituent is planar, as we see for $C[B(OMe)_2]_4$. In all of these CX_4 molecules, each planar X group bears two non-H substituents at the 1-position. Secondary interactions between the substituents (such as between a C—H bond and an aromatic ring) may be relevant to the formation of this geometry (Banert *et al.*, 2007). In fact, as mentioned above, the present molecule features 2.5 Å $B \cdots H-C$ interactions between each B atom and a methyl H atom on another $B(OMe)_2$ substituent. Some other

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₉ H ₂₄ B ₄ O ₈
<i>M_r</i>	303.52
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	102
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5362 (2), 15.1084 (4), 14.5384 (4)
<i>V</i> (Å ³)	1655.34 (8)
<i>Z</i>	4
Radiation type	Cu Kα
<i>μ</i> (mm ⁻¹)	0.83
Crystal size (mm)	0.41 × 0.31 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Integration (<i>SADABS</i> ; Bruker, 2005)
<i>T_{min}</i> , <i>T_{max}</i>	0.800, 0.921
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18589, 1515, 1407
<i>R_{int}</i>	0.113
(sin θ/λ) _{max} (Å ⁻¹)	0.602
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.100, 1.07
No. of reflections	1515
No. of parameters	106
No. of restraints	2
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.30, -0.19

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *pubCIF* (Westrip, 2010).

CX₄ compounds adopt idealized $\bar{4}2m$ geometries (Columbus & Biali, 1994; Heard *et al.*, 2000; Kozhushkov *et al.*, 2001; Narasimhamurthy *et al.*, 1990). This point group is seen, for example, when *X* is an alkoxy, thiolate, or a primary or secondary alkyl group. In these CX₄ molecules, there are no

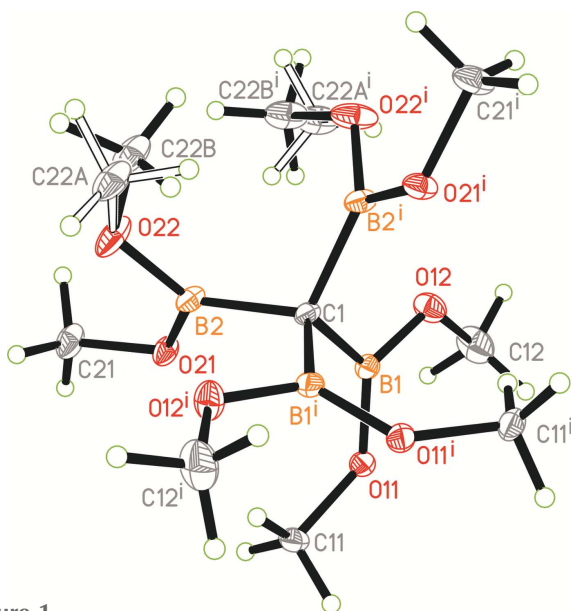


Figure 1
The molecular structure of the title compound, shown with 35% probability displacement ellipsoids. The H atoms are depicted with arbitrary radii. [Symmetry code: (i) $-x, y, \frac{3}{2} - z$.]

weak inter-ligand bonding interactions, and typically (although not invariably) the *X* group bears one non-H substituent at the 1-position. For borates with boron attached to a Csp³ atom, the C–B bond length is typically 1.575 Å (Wadepohl *et al.*, 2000; Al-Masri *et al.*, 2005; Harlow *et al.*, 2013), but is slightly longer, 1.603 (2) Å, in the sterically crowded molecule (*E*)-2-(1,1-dicyclohexyl-3-phenyl-3-allyl)-5,5-dimethyl-1,3,2-dioxaborinane (El-Hiti *et al.*, 2013). The C–B bond length in C[B(OMe)₂]₄ lies within this range.

The structure of the title compound (Fig. 1) is the first of a nonpolyhedral compound in which a single C atom is connected to four B atoms. Molecules of C[B(OMe)₂]₄ reside on crystallographic twofold axes, but adopt idealized $\bar{4}$ geometries. The central C atom has a slightly distorted tetrahedral coordination geometry, with C–B bond distances of 1.5876 (16) and 1.5905 (16) Å. The B atoms have trigonal planar geometries owing to π donation from the methoxy groups. Each B atom also forms a long intramolecular contact of 2.5 Å to a methyl H atom on another B(OMe)₂ substituent, consistent with the presence of a weak B···H–C interaction. One of the methyl groups is disordered over two sites.

Synthesis and crystallization

The title compound was synthesized according to a literature procedure (Castle *et al.*, 1969), but on a reduced scale. The product was sublimed at 348 K (10 mTorr) to give colorless crystals [m.p. 350–351 K; literature 349–351 K (Castle *et al.*, 1969)]. ¹H NMR (400 MHz, CCl₄): δ 3.62 (s); literature: δ 3.45 (Castle *et al.*, 1969). ¹¹B NMR (400 MHz, CCl₄): δ 30.6 (s), referenced to BF₃·Et₂O. The crystal used for the X-ray analysis was grown by slow sublimation in a vacuum.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. One of the methoxy groups is disordered over two sets of sites; the major component has an occupancy factor of 0.676 (8). The disordered O–C bond lengths were restrained to be 1.43 (1) Å, and the anisotropic displacement parameters of the disordered partial C atoms were restrained to be equal. H atoms were placed in idealized positions, with C–H = 0.98 Å; the methyl groups were allowed to rotate about the C–O axis to find the best least-squares positions. The displacement parameters for the methyl H atoms were set at 1.5 times *U*_{eq}(C). An isotropic extinction parameter was refined to a final value of $x = 2.708 \times 10^{-6}$, where *F*_c is multiplied by the factor $k [1 + F_c^2 \times \lambda^3 / \sin(2\theta)]^{-1/4}$, with *k* being the overall scale factor.

Acknowledgements

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References

- Al-Masri, H. T., Sieler, J., Junk, P. C., Domasevitch, K. V. & Hey-Hawkins, E. (2005). *J. Organomet. Chem.* **690**, 469–476.
- Banert, K., Joo, Y.-H., Rüffer, T., Walfort, B. & Lang, H. (2007). *Angew. Chem. Int. Ed.* **46**, 1168–1171.
- Benisvy, L., Wanke, R., Kuznetsov, M. L., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2009). *Tetrahedron*, **65**, 9218–9223.
- Bruker (2005). *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Castle, R. B. & Matteson, D. S. (1969). *J. Organomet. Chem.* **20**, 19–28.
- Claramunt, R. M., Elguero, J., Fabre, M. J., Foces-Foces, C., Cano, F. H., Fuentes, I. H., Jaime, C. & López, C. (1989). *Tetrahedron*, **45**, 7805–7816.
- Columbus, I. & Biali, S. E. (1994). *J. Org. Chem.* **59**, 8132–8138.
- El-Hiti, G. A., Smith, K., Elliott, M. C., Jones, D. H. & Kariuki, B. M. (2013). *Acta Cryst.* E**69**, o1403.
- Harlow, G. P., Zakharov, L. N., Wu, G. & Liu, S.-Y. (2013). *Organometallics*, **32**, 6650–6653.
- Heard, G. L., Gillespie, R. J. & Rankin, D. W. H. (2000). *J. Mol. Struct.* **520**, 237–248.
- Kozhushkov, S. I., Kostikov, R. R., Molchanov, A. P., Boese, R., Benet-Buchholz, J., Schreiner, P. R., Rinderspacher, C., Ghiviriga, I. & de Meijere, A. (2001). *Angew. Chem. Int. Ed.* **40**, 180–183.
- Matteson, D. S. (1975). *Synthesis*, **7**, 147–158.
- Müller, M., Lork, E. & Mews, R. (2001). *Angew. Chem. Int. Ed.* **40**, 1247–1249.
- Narasimhamurthy, N., Manohar, H., Samuelson, A. G. & Chandrasekhar, J. (1990). *J. Am. Chem. Soc.* **112**, 2937–2941.
- Scherbaum, F., Grohmann, A., Huber, B., Krüger, C. & Schmidbaur, H. (1988). *Angew. Chem. Int. Ed.* **27**, 1544–1546.
- Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.
- Wadepohl, H., Arnold, U., Kohl, U., Pritzkow, H. & Wolf, A. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3554–3565.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2016). **1**, x161264 [doi:10.1107/S2414314616012645]

Tetrakis(dimethoxyboryl)methane

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Octamethyl methanetetrayltetraboronate

Crystal data

$C_9H_{24}B_4O_8$

$M_r = 303.52$

Orthorhombic, *Pbcn*

$a = 7.5362$ (2) Å

$b = 15.1084$ (4) Å

$c = 14.5384$ (4) Å

$V = 1655.34$ (8) Å³

$Z = 4$

$F(000) = 648$

$D_x = 1.218$ Mg m⁻³

Melting point: 350 K

Cu *K*α radiation, $\lambda = 1.54178$ Å

Cell parameters from 9956 reflections

$\theta = 5.9$ – 68.2°

$\mu = 0.83$ mm⁻¹

$T = 102$ K

Prism, colourless

$0.41 \times 0.31 \times 0.15$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

Absorption correction: integration
(SADABS; Bruker, 2005)

$T_{\min} = 0.800$, $T_{\max} = 0.921$

18589 measured reflections

1515 independent reflections

1407 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.113$

$\theta_{\max} = 68.2^\circ$, $\theta_{\min} = 5.9^\circ$

$h = -9 \rightarrow 9$

$k = -18 \rightarrow 16$

$l = -15 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.100$

$S = 1.07$

1515 reflections

106 parameters

2 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.7225P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.19$ e Å⁻³

Extinction correction: *SHELXL2014* (Sheldrick,
2015), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0027 (5)

Special details

Experimental. One distinct cell was identified using APEX2 (Bruker, 2010). Frame series were integrated and filtered for statistical outliers using SAINT (Bruker, 2005) then corrected for absorption by integration using SHELXTL/XPREP V2005/2 (Bruker, 2005) before using SADABS (Bruker, 2005) to sort, merge, and scale the combined data. No decay correction was applied.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.0000	0.90014 (10)	0.7500	0.0155 (4)	
B1	0.12770 (19)	0.95880 (9)	0.81186 (9)	0.0169 (3)	
O11	0.08349 (11)	1.03111 (5)	0.86281 (6)	0.0192 (3)	
C11	-0.09245 (17)	1.06218 (9)	0.87896 (9)	0.0227 (3)	
H11A	-0.1752	1.0308	0.8384	0.034*	
H11B	-0.0982	1.1258	0.8663	0.034*	
H11C	-0.1249	1.0512	0.9432	0.034*	
O12	0.30328 (12)	0.93573 (6)	0.81320 (7)	0.0254 (3)	
C12	0.42669 (19)	0.98075 (12)	0.87109 (11)	0.0369 (4)	
H12A	0.3794	0.9837	0.9338	0.055*	
H12B	0.4459	1.0408	0.8477	0.055*	
H12C	0.5396	0.9486	0.8715	0.055*	
B2	-0.11652 (19)	0.84032 (9)	0.81675 (9)	0.0193 (3)	
O21	-0.11510 (12)	0.86140 (6)	0.90809 (6)	0.0208 (3)	
C21	-0.2149 (2)	0.81036 (9)	0.97275 (9)	0.0286 (4)	
H21A	-0.1618	0.7514	0.9787	0.043*	
H21B	-0.3375	0.8047	0.9512	0.043*	
H21C	-0.2136	0.8400	1.0327	0.043*	
O22	-0.21478 (16)	0.76806 (6)	0.79387 (6)	0.0334 (3)	
C22A	-0.2612 (10)	0.7418 (4)	0.7017 (3)	0.0324 (11)	0.677 (14)
H22A	-0.2640	0.6771	0.6978	0.049*	0.677 (14)
H22B	-0.1728	0.7649	0.6584	0.049*	0.677 (14)
H22C	-0.3784	0.7657	0.6860	0.049*	0.677 (14)
C22B	-0.2050 (18)	0.7274 (8)	0.7041 (6)	0.0324 (11)	0.323 (14)
H22D	-0.2996	0.6833	0.6980	0.049*	0.323 (14)
H22E	-0.0895	0.6985	0.6967	0.049*	0.323 (14)
H22F	-0.2193	0.7729	0.6566	0.049*	0.323 (14)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0213 (8)	0.0111 (7)	0.0141 (8)	0.000	0.0014 (6)	0.000
B1	0.0188 (7)	0.0150 (6)	0.0168 (6)	-0.0001 (5)	0.0010 (5)	0.0023 (5)
O11	0.0176 (5)	0.0168 (5)	0.0233 (5)	-0.0019 (3)	0.0011 (3)	-0.0041 (3)
C11	0.0220 (7)	0.0186 (6)	0.0277 (7)	0.0026 (5)	0.0022 (5)	-0.0058 (5)
O12	0.0186 (5)	0.0303 (5)	0.0273 (5)	0.0039 (4)	-0.0027 (4)	-0.0042 (4)
C12	0.0192 (7)	0.0502 (10)	0.0413 (9)	0.0013 (6)	-0.0075 (6)	-0.0095 (7)
B2	0.0273 (7)	0.0132 (6)	0.0172 (7)	-0.0029 (5)	-0.0005 (6)	0.0003 (5)
O21	0.0288 (5)	0.0187 (5)	0.0149 (5)	-0.0073 (4)	0.0024 (4)	-0.0001 (3)
C21	0.0404 (8)	0.0275 (7)	0.0178 (7)	-0.0126 (6)	0.0055 (6)	0.0019 (5)

O22	0.0583 (7)	0.0247 (5)	0.0173 (5)	-0.0221 (5)	0.0004 (4)	-0.0021 (4)
C22A	0.052 (3)	0.025 (2)	0.0204 (8)	-0.0169 (19)	-0.0027 (15)	-0.0053 (10)
C22B	0.052 (3)	0.025 (2)	0.0204 (8)	-0.0169 (19)	-0.0027 (15)	-0.0053 (10)

Geometric parameters (Å, °)

C1—B1 ⁱ	1.5876 (16)	B2—O22	1.3604 (17)
C1—B1	1.5876 (16)	B2—O21	1.3656 (16)
C1—B2 ⁱ	1.5905 (16)	O21—C21	1.4295 (15)
C1—B2	1.5905 (16)	C21—H21A	0.9800
B1—O11	1.3613 (16)	C21—H21B	0.9800
B1—O12	1.3685 (17)	C21—H21C	0.9800
O11—C11	1.4260 (15)	O22—C22A	1.441 (4)
C11—H11A	0.9800	O22—C22B	1.444 (8)
C11—H11B	0.9800	C22A—H22A	0.9800
C11—H11C	0.9800	C22A—H22B	0.9800
O12—C12	1.4268 (18)	C22A—H22C	0.9800
C12—H12A	0.9800	C22B—H22D	0.9800
C12—H12B	0.9800	C22B—H22E	0.9800
C12—H12C	0.9800	C22B—H22F	0.9800
B1 ⁱ —C1—B1	112.12 (13)	O22—B2—C1	127.39 (11)
B1 ⁱ —C1—B2 ⁱ	107.83 (7)	O21—B2—C1	117.16 (10)
B1—C1—B2 ⁱ	109.16 (7)	B2—O21—C21	120.63 (10)
B1 ⁱ —C1—B2	109.16 (7)	O21—C21—H21A	109.5
B1—C1—B2	107.83 (7)	O21—C21—H21B	109.5
B2 ⁱ —C1—B2	110.74 (14)	H21A—C21—H21B	109.5
O11—B1—O12	115.68 (11)	O21—C21—H21C	109.5
O11—B1—C1	127.44 (11)	H21A—C21—H21C	109.5
O12—B1—C1	116.87 (10)	H21B—C21—H21C	109.5
B1—O11—C11	125.54 (10)	B2—O22—C22A	125.5 (2)
O11—C11—H11A	109.5	B2—O22—C22B	122.3 (5)
O11—C11—H11B	109.5	O22—C22A—H22A	109.5
H11A—C11—H11B	109.5	O22—C22A—H22B	109.5
O11—C11—H11C	109.5	H22A—C22A—H22B	109.5
H11A—C11—H11C	109.5	O22—C22A—H22C	109.5
H11B—C11—H11C	109.5	H22A—C22A—H22C	109.5
B1—O12—C12	121.15 (11)	H22B—C22A—H22C	109.5
O12—C12—H12A	109.5	O22—C22B—H22D	109.5
O12—C12—H12B	109.5	O22—C22B—H22E	109.5
H12A—C12—H12B	109.5	H22D—C22B—H22E	109.5
O12—C12—H12C	109.5	O22—C22B—H22F	109.5
H12A—C12—H12C	109.5	H22D—C22B—H22F	109.5
H12B—C12—H12C	109.5	H22E—C22B—H22F	109.5
O22—B2—O21	115.42 (11)		

Symmetry code: (i) $-x, y, -z+3/2$.