Data collection

Siemens *R*3*m*/*V* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (Sheldrick, 1990)
$T_{\min} = 0.82$, $T_{\max} = 0.93$
1354 measured reflections
1354 independent reflections
831 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 65°$
$h = 0 \rightarrow 6$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 33$
3 standard reflections every 97 reflections intensity decay: 7.0%

Refinement

Refinement on F^2
$R(F) = 0.0451$
$wR(F^2) = 0.1094$
$S = 1.029$
1354 reflections
183 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.159$ e Å^{-3}
$\Delta\rho_{\min} = -0.158$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0023 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 1.5 (8)

Table 1. *Selected bond lengths (Å)*

O1—C1	1.228 (4)	C1—C2	1.492 (6)
O2—C4	1.223 (4)	C2—C3	1.358 (4)
N1—C2	1.387 (4)	C3—C4	1.479 (5)
N1—C7	1.455 (6)	C3—C11	1.490 (5)
N1—C8	1.456 (5)	C4—C5	1.495 (6)
N2—C5	1.394 (4)	C5—C6	1.332 (5)
N2—C9	1.442 (5)	C8—C7	1.467 (6)
N2—C10	1.454 (6)	C9—C10	1.462 (6)
C1—C6	1.443 (5)		

Table 2. *Contact distances (Å)*

C8···O2^{i}	3.570 (4)	C10···N2^{v}	3.427 (5)
C8···O1^{ii}	3.542 (4)	C10···O1^{vi}	3.376 (4)
C9···O2^{iii}	3.528 (4)	C15···O2^{vii}	3.355 (4)
C9···O1^{iv}	3.631 (5)		

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y, z$; (iii) $1+x, y, z$; (iv) $x, 1+y, z$; (v) $\frac{1}{2}+x, \frac{5}{2}-y, -z$; (vi) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (vii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically and H atoms were generated with ideal geometries (C—H = 0.96 Å) and refined as riding groups with a single group displacement parameter [$U_H = 0.086(4)$ Å^2].

Data collection: *P*3 *Software* (Siemens, 1989). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

Financial support from the Cancer Research Campaign (to SPM) and the Medical Research Council of the United Kingdom (to RHJH) is gratefully acknowledged.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1183). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 751–753

Benzyltrimethylammonium Tetramethoxoborate

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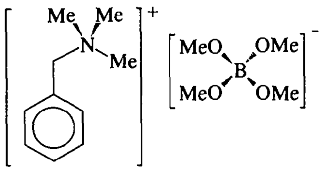
(*Received 16 January 1997; accepted 3 March 1997*)

Abstract

In the title compound, $C_{10}H_{16}N^+.C_4H_{12}BO_4^-$ or $[PhCH_2NMe_3][B(OMe)_4]$, the anion has essentially $\bar{4}2m$ (D_{2d}) symmetry, with a tetragonal elongation to give two opposite O—B—O angles markedly smaller than the other four. Comparison with the structures of other salts indicates that this is an intrinsic property of the anion rather than the result of specific interionic or intermolecular interactions.

Comment

In the course of our investigations into non-aqueous polyborate chemistry, we have synthesized an organic salt of tetramethoxoborate, $[B(OMe)_4]^-$, as a soluble building block. The benzyltrimethylammonium salt, (I), is readily prepared from $B(OMe)_3$ and $[PhCH_2NMe_3]$-$[OMe]$ in methanol.



(I)

The crystal structure consists of discrete benzyltrimethylammonium cations and tetramethoxoborate $[B(OMe)_4]^-$ anions (Fig. 1). These are held together by normal electrostatic and van der Waals interactions. Four previously determined structures of salts of $[B(OMe)_4]^-$ are in the most recent release of the Cambridge Structural Database (Allen & Kennard, 1993). One of them has the anions linked *via* lanthanum(III) cations into polymeric chains (Matthews, Kahwa, Johnson, Mague & McPherson, 1993) and one has strong interactions of two of the methoxo ligands with a lithium cation (Al-Juaid *et al.*, 1989). The third has sodium cations and both water and methanol molecules of crystallization (Heller & Horbat, 1977) and the fourth is the piperidinium salt (Alcock, Hagger, Harrison & Wallbridge, 1982), so both of these salts have potential for hydrogen bonding or other directional cation–anion interactions, which may influence the geometry of the anion. The title compound, without any such interactions, thus provides a reference structure for the anion against which the geometrical effects of specific interactions can be assessed.

It is notable, therefore, that in every one of the structures (and with two crystallographically independent anions in the solvated sodium salt), the coordination of boron by four methoxo groups shows a marked tetragonal elongation, such that two opposite O—B—O angles are reduced from the ideal tetrahedral angle of 109.5° [103.0 (2) and 101.2 (2)° in the title compound, and within the range 98.4–103.6° for the other structures] and the other four angles are increased [112.4 (2)–113.9 (2)° in the title compound and 112.2–115.4° for the others]. In the lithium and lanthanum compounds, the smallest angles are associated with the pairs of bridging ligands, as is expected. The B—O and O—C bond lengths, and B—O—C angles are also similar in all the structures (1.451–1.482, 1.391–1.443 Å and 114.7–119.3°, respectively, for the other structures) and in each case, the anion, considered in isolation, has approximate $\bar{4}2m$ (D_{2d}) symmetry, with four O—B—O—C torsion angles close to 180°. This appears, then, to be the intrinsically preferred geometry of the anion, which is subject to only minor perturbation from interactions of the O atoms with cations or with solvent molecules capable of hydrogen bonding.

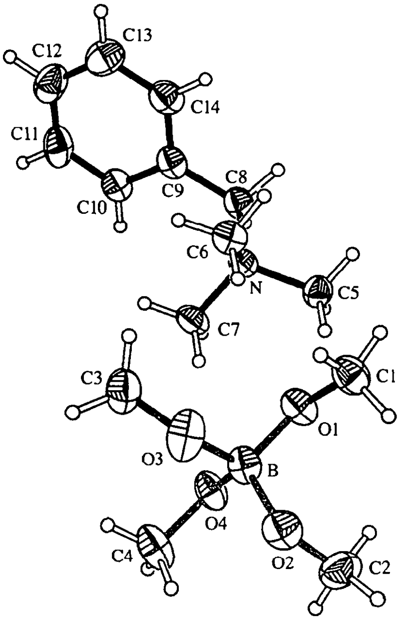


Fig. 1. The structure of the title salt with atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

$B(OMe)_3$ (0.72 g, 6.93 mmol) was added to a methanol solution of $[PhCH_2NMe_3][OMe]$ (40%, 1.26 g, 6.93 mmol) and the mixture was stirred for 20 min. After removal of the volatiles *in vacuo* to give a white powder, colourless needles were obtained by recrystallization from hot acetonitrile. ^{1}H NMR (200 MHz, CD_3CN solution): δ 7.55 (*m*, 5H, C_6H_5), 4.68 (*s*, 2H, CH_2), 3.10 (*s*, 9H, NMe_3), 3.06 (*q*, J_{BH} = 2.5 Hz, 12H, OMe); ^{11}B NMR (96.3 MHz, CH_3CN solution, $BF_3.OEt_2$ reference): δ −14.9.

Crystal data

$C_{10}H_{16}N^+.C_4H_{12}BO_4^-$
M_r = 285.18
Tetragonal
$P4_2/n$
a = 16.178 (2) Å
c = 12.462 (3) Å
V = 3261.7 (10) Å^3
Z = 8
D_x = 1.162 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 32 reflections
θ = 10.32–12.48°
μ = 0.082 mm^{-1}
T = 160 (2) K
Block
0.50 × 0.35 × 0.32 mm
Colourless

Data collection

Stoe–Siemens diffractometer with Cryostream cooler (Cosier & Glazer, 1986)
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: none
7551 measured reflections
2870 independent reflections

1938 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0657
$\theta_{\rm max}$ = 25.04°
h = −19 → 19
k = −19 → 19
l = −14 → 14
5 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0496$
$wR(F^2) = 0.1423$
$S = 1.033$
2870 reflections
189 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 2.508P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.018$
$\Delta\rho_{\max} = 0.285$ e Å^{-3}
$\Delta\rho_{\min} = -0.229$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0043 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

B—O1	1.461 (3)	O1—C1	1.410 (3)
B—O2	1.471 (3)	O2—C2	1.403 (3)
B—O3	1.473 (3)	O3—C3	1.394 (3)
B—O4	1.464 (3)	O4—C4	1.417 (3)
O1—B—O2	112.4 (2)	O3—B—O4	113.6 (2)
O1—B—O3	113.9 (2)	C1—O1—B	115.40 (18)
O1—B—O4	102.95 (18)	C2—O2—B	115.73 (19)
O2—B—O3	101.24 (19)	C3—O3—B	119.9 (2)
O2—B—O4	113.2 (2)	C4—O4—B	114.41 (18)
O4—B—O1—C1	−172.7 (2)	O2—B—O3—C3	−161.0 (2)
O3—B—O2—C2	179.3 (2)	O1—B—O4—C4	−179.6 (2)

H atoms were placed geometrically and refined with a riding model (including free rotation about *X*—Me bonds) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank EPSRC and Borax Research for financial support.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1461). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 753–755

(2*R*,3*R*,4*S*)-3-(*tert*-Butyldiphenylsiloxy)-4-hydroxy-3-methylhex-5-ene-1,2-diyl Diacetate

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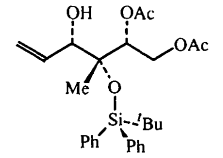
(*Received 9 October 1996; accepted 13 January 1997*)

Abstract

The crystal structure and absolute configuration of the title compound, $C_{27}H_{36}O_6Si$, have been determined. The molecules are linked through hydrogen bonds between the hydroxy and acetoxy groups. The dihedral angle between the planes of the phenyl rings is 55.4 (1)°.

Comment

The diphenyl-*tert*-butylsilyl substituent was found to be an effective steric directing group for the substrate-controlled diastereoselective synthesis of allenylcarbinols from chiral allenals (Marshall & Tang, 1993). This methodology was applied to synthesize the title compound, (I), as part of a study on enantioselective synthesis of carbohydrate precursors (Marshall & Tang, 1994). The crystal structure was determined in order to establish the stereochemistry of the reaction product.



(I)

The least-squares planes of the phenyl rings are inclined by 13.3 (1) and 47.6 (1)° with respect to the Si, C21, C31 plane. Bond lengths and angles within both rings show distortion patterns from perfect hexagons, similar to the distortion already reported in other Si compounds (Karle, Karle & Nielsen, 1986; Tomlins, Lydon, Akrigg & Sheldrick, 1985). Both Si—C bond lengths are longer than 1.87 (2) Å, the average value observed in 51 other *tert*-butyldiphenylsilyloxy groups found in the April 1996 edition of the Cambridge Structural Database (Allen & Kennard, 1993). Also, the Si—C bond to the *tert*-butyl group of 1.900 (2) Å is longer than average. The torsion angle C4—O2—Si—C41 of 156.2 (2)° differs from an ideal *trans* conformation to a greater extent than observed in the majority of structures containing the *tert*-butyldiphenylsilyloxy group.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997