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Structure of 4,4,6-Trimethyl-2-(triphenylsiloxy)-1,3,2-dioxaborinane

By George Ferguson* and Alan J. Lough
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

and James P. Sheehan and Trevor R. Spalding†
Chemistry Department, University College, Cork, Ireland

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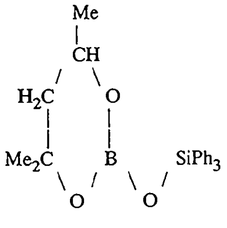
Abstract. $C_{24}H_{27}BO_3Si$, $M_r = 402{\cdot}4$, orthorhombic, *Pcab*, $a = 10{\cdot}737\,(2)$, $b = 19{\cdot}403\,(4)$, $c = 21{\cdot}974\,(5)$ Å, $V = 4578\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}17$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}2$ cm^{-1}, $F(000) = 1712$, $T = 294$ K, $R = 0{\cdot}046$ for 2017 observed reflections. The trigonal-planar BO_3 unit is joined to the tetrahedral Ph_3SiO group by a B—O—Si linkage [B—O 1·363 (5), Si—O 1·634 (2) Å, B—O—Si 133·1 (2)°]. The six-membered C_3O_2B ring has a conformation intermediate between a half-chair and a sofa, with B—O 1·347 (5) and 1·361 (5), C—O 1·435 (5) and 1·449 (5) Å.

Introduction. Although many compounds containing B—O—B or Si—O—Si linkages have been structurally characterized, there appears to be a lack of data where B—O—Si binding is concerned. We have prepared the triphenylsiloxy derivative of 4,4,6-trimethyl-1,3,2-dioxaborinan-2-ol by the condensation reaction between the latter and Ph_3SiOH in refluxing toluene (1:1 mole ratio; 27 h; 89·3% yield). This compound, like the precursor 2-borinanol, was notably stable to air at ambient temperature and only began to show signs of decomposition after exposure for 24 h. Recrystallization from CH_2Cl_2/heptane produced single crystals of the title compound (I) which were subjected to X-ray analysis.



(I)

Experimental. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $11 < \theta < 18°$. Crystal dimensions $0{\cdot}60 \times 0{\cdot}50 \times 0{\cdot}40$ mm; intensities of reflections with indices h 0 to 13, k 0 to 24, l 0 to 28, with $2 < 2\theta < 54°$ measured; ω–2θ scans, ω-scan width $(0{\cdot}6 + 0{\cdot}35\tan\theta)°$; graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 5085 reflections measured, 4985 unique, 2017 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz and polarization effects. Space group *Pcab* was determined uniquely by the systematic absences ($0kl$ absent if $l = 2n + 1$; $h0l$ absent if $h = 2n + 1$; $hk0$ absent if $k = 2n + 1$). The structure was solved with the aid of *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. A difference map showed maxima in positions consistent with the expected locations of the H atoms. In the final rounds of calculations, the H atoms were positioned on geometrical grounds (C—H, 0·95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 7·0 Å^2. the final cycle of refinement included 262 variable parameters, $R = 0{\cdot}046$, $wR = 0{\cdot}065$, goodness-of-fit 1·76, $w = 1/[\sigma^2(F_o) + 0{\cdot}04(F_o)^2]$, $w(\Delta F)^2$ minimized. Max. shift/e.s.d. in final refinement cycle $< 0{\cdot}005$; density in final difference map $\pm 0{\cdot}23$ e Å^{-3}; there were no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (Frenz, 1983). Atomic coordinates‡ and

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* E-mail address: CHMFERG@VM.UOGUELPH.CA
† E-mail address: STCH8006@IRUCCVAX

‡ Lists of structure factors, anisotropic thermal parameters, calculated hydrogen coordinates, mean plane data, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52656 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional and equivalent isotropic thermal parameters with their e.s.d.'s*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$B_{eq} = (4/3)(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}).$$

	x	y	z	B_{eq} (Å^2)
Si	0·45784 (9)	0·43342 (5)	0·35937 (4)	3·70 (2)
O1	0·4615 (2)	0·41375 (12)	0·28711 (9)	4·47 (5)
O2	0·6612 (2)	0·36889 (13)	0·27250 (10)	5·18 (6)
O3	0·5021 (2)	0·35374 (15)	0·19777 (10)	5·62 (6)
C4	0·5836 (4)	0·3155 (2)	0·1586 (2)	6·1 (1)
C5	0·5428 (5)	0·3277 (2)	0·0949 (2)	7·1 (1)
C6	0·7130 (4)	0·3284 (2)	0·1733 (2)	6·6 (1)
C7	0·7475 (4)	0·3262 (2)	0·2386 (2)	5·50 (9)
C8	0·7399 (5)	0·2552 (3)	0·2661 (2)	9·3 (1)
C9	0·8742 (5)	0·3572 (3)	0·2487 (3)	11·1 (2)
C11	0·5396 (3)	0·5167 (2)	0·3724 (2)	4·07 (8)
C12	0·4946 (4)	0·5661 (2)	0·4122 (2)	4·90 (9)
C13	0·5605 (4)	0·6264 (2)	0·4233 (2)	5·8 (1)
C14	0·6724 (4)	0·6375 (2)	0·3958 (2)	6·2 (1)
C15	0·7196 (4)	0·5894 (2)	0·3556 (2)	6·6 (1)
C16	0·6548 (4)	0·5293 (2)	0·3447 (2)	5·6 (1)
C21	0·2899 (3)	0·4418 (2)	0·3797 (2)	3·88 (7)
C22	0·2490 (4)	0·4394 (2)	0·4394 (2)	5·43 (9)
C23	0·1249 (4)	0·4483 (2)	0·4530 (2)	6·9 (1)
C24	0·0404 (4)	0·4598 (2)	0·4101 (2)	7·7 (1)
C25	0·0762 (4)	0·4630 (3)	0·3495 (2)	7·4 (1)
C26	0·2014 (4)	0·4537 (2)	0·3348 (2)	5·7 (1)
C31	0·5345 (3)	0·3640 (2)	0·4047 (1)	4·04 (8)
C32	0·6444 (4)	0·3746 (2)	0·4351 (2)	6·0 (1)
C33	0·7057 (5)	0·3209 (3)	0·4621 (2)	8·7 (1)
C34	0·6586 (5)	0·2554 (3)	0·4600 (2)	8·3 (1)
C35	0·5510 (5)	0·2439 (2)	0·4316 (2)	7·5 (1)
C36	0·4881 (4)	0·2975 (2)	0·4046 (2)	6·0 (1)
B	0·5441 (4)	0·3781 (2)	0·2521 (2)	4·12 (9)

details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *ORTEP*II (Johnson, 1976).

Table 2. *Molecular dimensions*

(*a*) Bond lengths (Å)

Si	O1	1·634 (2)	C12	C13	1·389 (5)
Si	C11	1·861 (3)	C13	C14	1·362 (6)
Si	C21	1·864 (4)	C14	C15	1·381 (6)
Si	C31	1·866 (3)	C15	C16	1·379 (6)
O1	B	1·363 (5)	C21	C22	1·384 (5)
O2	C7	1·449 (5)	C21	C26	1·389 (5)
O2	B	1·347 (5)	C22	C23	1·377 (6)
O3	C4	1·435 (5)	C23	C24	1·327 (6)
O3	B	1·361 (5)	C24	C25	1·387 (7)
C4	C5	1·486 (6)	C25	C26	1·395 (6)
C4	C6	1·448 (6)	C31	C32	1·372 (5)
C6	C7	1·484 (6)	C31	C36	1·383 (5)
C7	C8	1·507 (6)	C32	C33	1·368 (7)
C7	C9	1·503 (7)	C33	C34	1·368 (7)
C11	C12	1·385 (5)	C34	C35	1·332 (7)
C11	C16	1·400 (5)	C35	C36	1·374 (6)

(*b*) Bond angles (°)

O1	Si	C11	110·0 (1)	C12	C13	C14	120·3 (4)
O1	Si	C21	106·0 (1)	C13	C14	C15	120·0 (4)
O1	Si	C31	109·8 (1)	C14	C15	C16	119·9 (4)
C11	Si	C21	110·1 (2)	C11	C16	C15	121·2 (4)
C11	Si	C31	109·7 (2)	Si	C21	C22	122·1 (3)
C21	Si	C31	111·2 (2)	Si	C21	C26	120·4 (3)
Si	O1	B	133·1 (2)	C22	C21	C26	117·5 (3)
C7	O2	B	120·1 (3)	C21	C22	C23	120·6 (4)
C4	O3	B	120·2 (3)	C22	C23	C24	121·9 (4)
O3	C4	C5	107·6 (3)	C23	C24	C25	120·0 (4)
O3	C4	C6	111·2 (3)	C24	C25	C26	118·9 (4)
C5	C4	C6	117·7 (4)	C21	C26	C25	121·1 (4)
C4	C6	C7	116·8 (4)	Si	C31	C32	122·1 (3)
O2	C7	C6	108·7 (3)	Si	C31	C36	120·9 (3)
O2	C7	C8	106·4 (3)	C32	C31	C36	116·7 (4)
O2	C7	C9	105·9 (4)	C31	C32	C33	120·8 (4)
C6	C7	C8	113·6 (4)	C32	C33	C34	121·0 (4)
C6	C7	C9	110·9 (4)	C33	C34	C35	119·5 (5)
C8	C7	C9	110·9 (4)	C34	C35	C36	120·1 (4)
Si	C11	C12	122·3 (3)	C31	C36	C35	122·0 (4)
Si	C11	C16	120·1 (3)	O1	B	O2	119·2 (3)
C12	C11	C16	117·5 (3)	O1	B	O3	117·1 (3)
C11	C12	C13	121·1 (4)	O2	B	O3	123·8 (3)

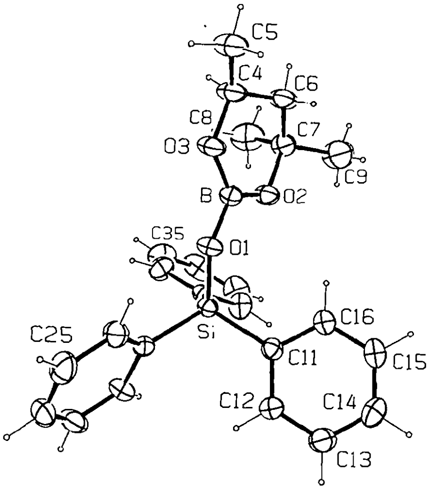

Fig. 1. A view of the molecule with the numbering scheme.

Discussion. The molecule contains a trigonal-planar BO_3 unit bonded to a tetrahedral Ph_3SiO group. The conformation of the six-membered C_3BO_2 ring is intermediate between a half-chair and a sofa; four atoms define a plane (B,O2,O3,C4, maximum deviation 0·001 Å) with C6 0·0460 (4) Å and C7 −0·111 (4) Å from this plane. The Si atom is −0·389 (1) Å from the BO_3 plane corresponding to a rotation of the O—Si bond through 19·1° out of the plane of the BO_3 unit. The B—O—Si angle of 133·1 (2)° suggests that the hybridization used by the bridging O atom is close to sp^2. This in turn could lead to significant π bonding between the O atom and the B or Si atom. Compounds containing three-coordinate boron in B—O—B linkages have been reported to show a range of B—O—B angles from 120·6° in the $(O_2B—O—BO_2)^{4-}$ ion (Konig, Hoppe & Jansen, 1979) to 144·4° in $Me_2B—O—BMe_2$ (Gundersen & Vahrenkamp, 1976). Likewise a range of Si—O—Si angles from 144·1 (9)° in $(H_3Si)_2O$ (Almenningen, Bastiansen, Ewing, Hedberg & Trætteberg, 1963) to 176·8 (7)° in $(Ph_3Si)_2O$ (Glidewell & Liles, 1977) has been reported. The B—O bond lengths are equal (within 3σ) and the average value of 1·357 Å is typical for three-coordinate BO_3 units and close to the values in boric acid, 1·361 Å (Zachariasen, 1954) and 4,6-dimethyl-

1,3,2-dioxaborinan-2-ol, average 1·363 Å (Kuribayashi, 1973). The Si—O bond length, 1·634 (2) Å, is exactly the same as that in $(H_3Si)_2O$ (Almenningen *et al.*, 1963) but slightly longer than the value of 1·616 (1) Å observed in $(Ph_3Si)_2O$ (Glidewell & Liles, 1977). Other $(X_3Si)_2O$ compounds (X = F, Cl) have *d*(Si—O) values of 1·580 (25) Å (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970) and 1·592 (10) Å (Airey, Glidewell, Robiette & Sheldrick, 1971), respectively. Although there has been extensive discussion in the literature about the role of π bonding in Si—O bonds, it is generally agreed that there is no simple correlation between *d*(Si—O) and Si—O—Si angles and the amount of π bonding. A similar situation appears to pertain in boron–oxygen chemistry if we compare the data from the present work on the (triphenylsiloxy)-dioxaborinane derivative and the data from the 4,6-dimethyl-1,3,2-dioxaborinan-2-ol (Kuribayashi, 1973). In these compounds the heterocyclic BO_2C_3 entities are virtually identical as are the exocyclic B—O bond lengths [B—OSi 1·363 (5) and B—OH 1·365 (7) Å respectively]. However, in the first compound a 'π-bonding' $SiPh_3$ group is present whereas in the second the H atom clearly cannot participate in π bonding. Therefore other steric and/or electronic effects must be operating to equalize the observed B—O bond lengths. The C—C and C—O bond lengths are all normal. The Ph_3Si group has an irregular propeller conformation (angles between the phenyl ring planes and the relevant O—Si—C planes are 43·0, 19·7 and 64·4°); there are no untoward intermolecular contacts.

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Functionalized Hydrocarbons with Condensed Ring Skeletons. V. Substituted 1,2-Dimethyltricyclo[8.4.0.$0^{2,7}$]tetradec-8-ene

BY ANDRÉ G. MICHEL,*† PIERRE GIGUERE,‡ PIERRE DESLONGCHAMPS‡ AND NADINE MICHEL-DEWEZ†

Laboratoire de chimie structurale and Laboratoire de synthèse organique, Université de Sherbrooke, Sherbrooke (Québec), Canada J1K 2R1

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Abstract. Tetramethyl 1,2-*trans*-1,10-*cis*-2,7-*cis*-1,2-dimethyltricyclo[8.4.0.0.^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate, $C_{24}H_{34}O_8$, $M_r = 450·53$, monoclinic, $A2/n$, $a = 25·8320$ (10), $b = 6·8873$ (3), $c = 26·4287$ (8) Å, $\beta = 99·620$ (3)°, $V = 4635·88$ Å^3, $D_x = 1·291$ Mg m^{-3}, $Z = 8$, λ(Cu $K\bar{\alpha}$) = 1·54056 Å, $\mu = 0·66$ mm^{-1}, $F(000) = 1935·79$, room temperature, final $R = 0·044$ for 3692 observed reflections. The tricyclic compound has the opposite configuration at C(10), from the triterpene saponins. The relative stereochemistry is *cis* for the *AB* ring junction, *anti* between C(1) methyl and C(2) methyl and *cis* for the *BC* ring junction (abbreviated to *CAC*).

Introduction. We have reported a general strategy for the synthesis of polycyclic compounds *via* the trans-

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* Laboratoire de chimie structurale.

† To whom correspondence should be addressed.

‡ Laboratoire de synthèse organique.

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