

4-BROMOPHENYLBORONATE DERIVATIVES OF RING AND CAGE BOROSILICATES

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Dedicated to Professor Jaromír Plešek to mark the occasion of his 75th birthday and in recognition of his many outstanding contributions to boron chemistry.

The reactions between equimolecular amounts of 4-bromophenylboronic acid and di-*tert*-butylsilanediol or *tert*-butylsilanetriol in toluene solutions at reflux temperatures afforded the borosilicate ring compound [(4-BrC₆H₄B)O₂Si(*t*-Bu)₂]₂ (**1**), and the cube-based species [(*t*-BuSi)₄(4-BrC₆H₄B)₄O₁₀] (**2**), in medium (62%) and low (13%) yields, respectively. These compounds were characterised by microanalysis, IR and NMR (¹H, ¹¹B, ¹³C and ²⁹Si) spectroscopy and single crystal X-ray crystallography. During the work-up of **2**, a sample of the boroxine, [(4-BrC₆H₄BO)₃] (**3**), was isolated and was characterised by single crystal diffraction.

Keywords: Borosilicate; Boroxine; Crystal structures; Inorganic rings; Inorganic cages.

It is a long-term intention of our work to synthesise inorganic-organic hybrid materials which contain two-dimensional and three-dimensional structure-forming borosilicate species. To this end, we have studied the synthesis of 4-bromophenylboronate containing borosilicate compounds which are based on the two-dimensional Si₂B₂O₄ ring structure (Diagram 1) and

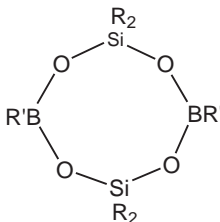


DIAGRAM 1

three-dimensional cube-based $\text{Si}_4\text{B}_4\text{O}_{10}$ and sphere-based $\text{Si}_2\text{B}_3\text{O}_6$ structures (Diagrams 2 and 3, respectively). The bromine atom of the 4-bromophenyl group offers many possibilities as a site with potential for coupling reactions *via*, for example, Heck reactions¹.

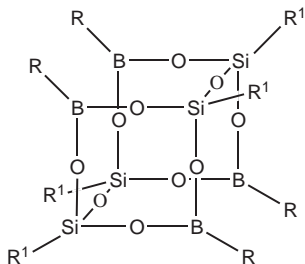


DIAGRAM 2

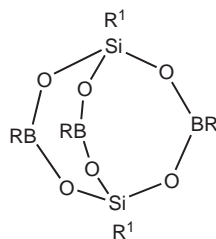


DIAGRAM 3

It is anticipated that the combination of the above borosilicates with suitable organic reagents will permit the synthesis of novel chain, sheet and three-dimensional inorganic-organic hybrid materials. We report here the syntheses and single crystal X-ray studies of $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{Si}(t\text{-Bu})_2]_2$ (**1**), and $[(t\text{-BuSi})_4(4\text{-BrC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ (**2**). During the present work, crystals of the boroxine, $(4\text{-BrC}_6\text{H}_4\text{BO})_3$, (**3**), were isolated in low yield and the structure of this compound was determined by X-ray crystallographic techniques.

Previously published work on compounds related to **1–3** has reported details of the synthesis and structures of the ring borosilicates $[\text{PhBO}_2\text{Si}(t\text{-Bu})_2]_2$, (**4**)², and $[\text{PhBO}_2\text{SiPh}_2]_2$ (**5**)^{3,4}, the 4-vinylphenyl cube-based compound $[(t\text{-BuSi})_4(4\text{-H}_2\text{C}=\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ (**6**)⁵, the 4-bromophenylboronate derivatives of **5**, *i.e.* $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{SiPh}_2]_2$ (**7**)⁶, and the sphere-based compound $[(t\text{-BuSi})_2\{\text{O}(4\text{-BrC}_6\text{H}_4\text{B})\}_3]$ (**8**)^{7,8}.

EXPERIMENTAL

All reactions were carried out under an inert atmosphere. Solvents were dried according to literature methods and distilled prior to use. The following reagents were supplied by Aldrich Chemical Co., and used as supplied: *tert*-butyltrichlorosilane, di-*tert*-butyldichlorosilane and 4-bromophenylboronic acid. The silanols, $t\text{-Bu}_2\text{Si}(\text{OH})_2$ and $t\text{-BuSi}(\text{OH})_3$, were prepared by literature methods from the corresponding chlorides^{8–10}. Infrared spectra (wavenumbers in cm^{-1}) were recorded on a Perkin Elmer Paragon 1000 Fourier transform spectrometer. Samples were prepared as KBr discs. All ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer and all ¹¹B and ²⁹Si NMR spectra were recorded on a Bruker 500 MHz spectrometer. Tetramethylsilane and boron trifluoride etherate were used as standards and deuterated chloroform as the solvent. All NMR spectra were recorded at ambient temperature. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hz. Melting points were recorded on an Electrothermal IA 9000 Series digital melting

point apparatus. Elemental (C/H) analyses were carried out on an Exeter Analytical Inc., CE 440 Elemental Analyser at the Microanalytical Laboratory, University College, Cork.

Synthesis of [(4-BrC₆H₄B)O₂Si(*t*-Bu)₂]₂ (1)

To a solution of *t*-Bu₂Si(OH)₂ (0.20 g, 1.47 mmol) in toluene (100 cm³), was added 4-BrC₆H₄B(OH)₂ (0.25 g, 1.23 mmol) and the mixture heated at reflux in a Dean-Stark apparatus for 3.5 h. The reaction mixture was transferred to a rotary film evaporator and the toluene was removed under reduced pressure. The resulting solid was crystallised from 1,2-dichloroethane to give colourless crystals of [(4-BrC₆H₄B)O₂Si(*t*-Bu)₂]₂ (1), yield 0.24 g (62%), m.p. 312–314 °C. For C₂₈H₄₄B₂Br₂O₄Si₂ calculated: 49.3% C, 6.5% H; found: 48.5% C, 6.4% H. IR (KBr disc, only very strong or strong vibrations are reported): 2 962, 2 956, 2 861, 1 473, 1 441, 1 376, 1 343, 1 303, 1 280, 1 148, 831, 696, 666, 568. ¹H NMR: 1.12 (s, 18 H); 7.39–7.95 (d, 4 H); 7.89–7.94 (d, 4 H). ¹³C NMR: 20.34 C(CH₃)₃; 27.32 C(CH₃)₃; 126.88, 130.78, 131.22 and 135.15 all 4-BrC₆H₄. ¹¹B NMR: 43.3. ²⁹Si NMR: –23.57.

Synthesis of [(*t*-BuSi)₄(4-BrC₆H₄B)₄O₁₀] (2)

To a solution of *t*-BuSi(OH)₃ (0.40 g, 2.94 mmol) in toluene (40 cm³), was added 4-BrC₆H₄B(OH)₂ (0.59 g, 2.94 mmol) and the mixture heated at reflux in a Dean-Stark apparatus for 10 h. The reaction mixture was cooled and stirred overnight at room temperature. The toluene was removed by rotary film evaporation and the resultant powder was dissolved in hexane and filtered. Evaporation of the hexane afforded colourless crystals of [(*t*-BuSi)₄(4-BrC₆H₄B)₄O₁₀] (2), yield 0.11 g (12.7%), m.p. 294–295 °C. For C₄₀H₅₂B₄Br₄O₁₀Si₄ calculated: 41.1% C, 4.5% H, 2.6% B; found: 40.9% C, 4.3% H, 2.5% B. IR (KBr disc, only very strong or strong vibrations are reported): 2 955, 2 937, 2 863, 1 587, 1 470, 1 415, 1 398, 1 377, 1 348, 1 310, 1 150, 1 131, 1 085, 1 101, 865, 822, 724, 704, 640, 605, 593. ¹H NMR: 1.34 (s, 18 H), C(CH₃)₃; 7.52 (d, 6 H, *J*_{H-H} = 1.5), C₆H₄Br; 7.73 (d, 6 H, *J*_{H-H} = 1.5), 4-BrC₆H₄. ¹³C NMR: 16.95 C(CH₃)₃; 25.74 C(CH₃)₃; 126.76, 131.13, 130.68 and 136.52 all 4-BrC₆H₄. ¹¹B NMR: 44.5. ²⁹Si NMR: –65.96. Prior to the isolation of 2, colourless needle-shaped crystals of the boroxine [(4-BrC₆H₄BO)₃] (3), were filtered from the reaction mixture, 0.04 g, m.p. 282–283 °C. For C₁₈H₁₂B₃Br₃O₃ calculated: 39.4% C, 2.2% H; found 39.7% C, 2.1% H. This compound was identified by X-ray crystallographic methods.

Crystal Structure Analysis for Compounds 1–3

Crystal of 1, 0.40 × 0.40 × 0.25 mm, is monoclinic, space group *P2*₁/*c*, formula C₂₈H₄₄B₂Br₂O₄Si₂, *M* = 682.25, *a* = 9.6973(10) Å, *b* = 15.589(2) Å, *c* = 11.2725(14) Å, β = 101.309(10)°, *U* = 1 671.0(3) Å³, μ = 2.527 mm⁻¹, *Z* = 2, *T* = 173 K, *S* = 1.06, *R*(*F*_o) = 0.051, for 2 244 observed reflections with *I* > 2σ(*I*), *wR*₂(*F*²) = 0.171 for all 3 096 unique reflections, *T*_{min} = 0.806, *T*_{max} = 0.953, Δρ_{max} = 0.58 e Å⁻³, Δρ_{min} = –0.87 e Å⁻³.

Crystal of 2, 0.30 × 0.30 × 0.12 mm, is monoclinic, space group *P2*₁/*c*, formula C₄₀H₅₂B₄Br₄O₁₀Si₄, *M* = 1168.06, *a* = 13.440(3) Å, *b* = 16.192(3) Å, *c* = 13.375(2) Å, β = 116.167(14)°, *U* = 2 612.4(8) Å³, μ = 3.222 mm⁻¹, *Z* = 2, *T* = 173 K, *S* = 1.03, *R*(*F*_o) = 0.053, for 2 947 observed reflections with *I* > 2σ(*I*), *wR*₂(*F*²) = 0.124 for all 4 838 unique reflections, *T*_{min} = 0.662, *T*_{max} = 0.968, Δρ_{max} = 0.60 e Å⁻³, Δρ_{min} = –0.67 e Å⁻³.

A very weakly diffracting crystal of 3, 0.25 × 0.20 × 0.18 mm, was used for the analysis. Crystals of 3 are orthorhombic, space group *Pnma*, formula C₁₈H₁₂B₃Br₃O₃, *M* = 548.44, *a* =

18.746(3) Å, $b = 21.818(3)$ Å, $c = 4.8462(8)$ Å, $U = 1\,982.1(5)$ Å³, $\mu = 6.121$ mm⁻¹, $Z = 4$, $T = 173$ K, $S = 1.09$, $R(F_o) = 0.091$, for 713 observed reflections with $I > 2\sigma(I)$, $wR_2(F^2) = 0.281$ for all 1 884 unique reflections, $T_{\min} = 0.743$, $T_{\max} = 1.000$, $\Delta\rho_{\max} = 0.95$ e Å⁻³, $\Delta\rho_{\min} = -1.05$ e Å⁻³.

All data were collected on a Nonius MACH-3 diffractometer using MoK α graphite monochromated radiation, $\lambda = 0.7107$ Å, and corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares on all F^2 data using SHELXL97¹¹. The hydrogen atoms were placed in calculated positions and allowed to ride on the parent atom. CCDC 182475 for **1**, CCDC 182473 for **2** and CCDC 182474 for **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction between equimolar amounts of $t\text{-Bu}_2\text{Si}(\text{OH})_2$ and $4\text{-BrC}_6\text{H}_4\text{B}(\text{OH})_2$ in toluene solution at reflux afforded $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{Si}(t\text{-Bu})_2]_2$ (**1**), in good yield (62%). Similar reactions between phenylboronic⁴ or 4-bromophenylboronic⁶ acid and diphenylsilandiol have been reported as alternative routes to eight-membered borosilicate ring compounds from phenylboron dichloride and di-*tert*-butylsilandiol², or phenylboronic acid and $(\text{EtO})_2\text{SiRR}'$ where $\text{R} = \text{R}' = \text{Et}$ and $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$ ¹².

Reaction between equimolar amounts of $t\text{-BuSi}(\text{OH})_3$ and $4\text{-BrC}_6\text{H}_4\text{B}(\text{OH})_2$ afforded the cage compound $[(t\text{-BuSi})_4(4\text{-BrC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ (**2**), in low yield (13%). A small amount of the boroxine $[(4\text{-BrC}_6\text{H}_4\text{BO})_3]$ (**3**), was also isolated. The formation of compound **2** may possibly proceed by the initial synthesis of the eight-membered $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{Si}(t\text{-Bu})\text{OH}]_2$ ring. However, compound **2** can only be formed by the combination of two such rings when they contain the Si–OH groups aligned with the two OH entities in *cis* configurations across each ring as in Diagram 4.

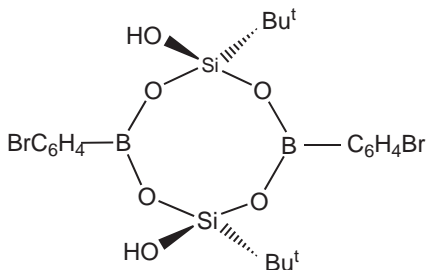


DIAGRAM 4

Subsequent elimination of two water molecules from two $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{Si}(t\text{-Bu})\text{OH}]_2$ molecules would form the Si–O–Si bonds ob-

served in **2**. At this stage in our work the mode of formation of the boroxine $[(4\text{-BrC}_6\text{H}_4\text{BO})_3]$ (**3**), is unclear and further studies are being undertaken to elucidate this aspect of the reaction between $t\text{-BuSi(OH)}_3$ and $4\text{-BrC}_6\text{H}_4\text{B(OH)}_2$. Compound **2** is only the second example of an incomplete cuboid cage containing four boron and four silicon atoms. Previously, $[(t\text{-BuSi})_4(4\text{-H}_2\text{C}=\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$, the 4-vinylphenylboronate analogue of **2**, was synthesised by the reaction between $t\text{-BuSiCl}_3$, $4\text{-CH}_2=\text{CHC}_6\text{H}_4\text{B(OH)}_2$ and aqueous aniline⁵.

Structural Studies of Compounds **1**, **2** and **3**

Compound $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{Si}(t\text{-Bu})_2]_2$ (**1**) is a cyclic silylborate with a central eight-membered ring containing four B–O–Si linkages (Fig. 1 and Table I) and a centre of symmetry at the centre of the $\text{B}_2\text{O}_4\text{Si}_2$ ring. Each boron atom subtends a 4-bromophenyl group and each silicon has two *tert*-butyl groups attached. A notable feature of the central ring system in **1** is its apparent planarity with atoms B(3) and O(4) showing most deviation from the calculated mean plane at $+0.040(3)$ and $-0.036(3)$ Å, respectively. A second notable feature of the structure of **1** is the apparent coplanarity of the borosilicate ring and the phenyl rings attached to the boron atoms. The interplanar angle between the calculated mean plane of the $\text{B}_2\text{O}_4\text{Si}_2$ borosilicate

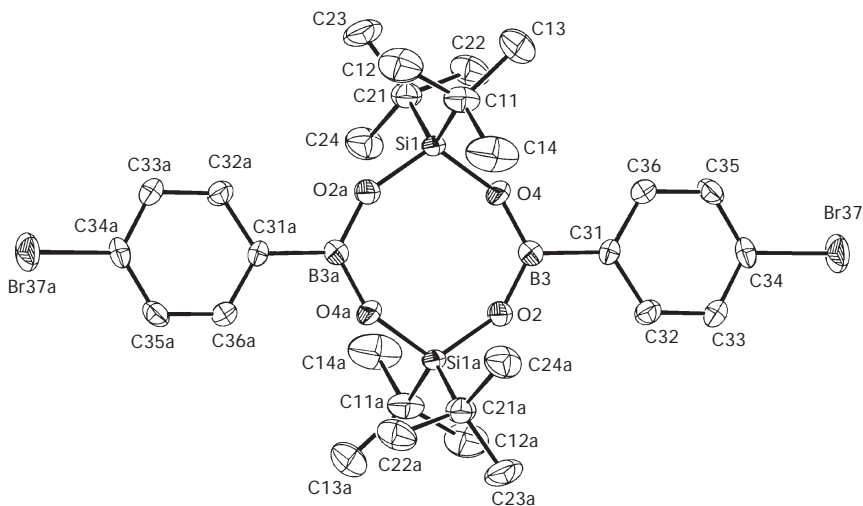


FIG. 1

A view of **1** showing the numbering scheme. Anisotropic displacement parameters are drawn at the 30% probability level

silicate ring and the calculated mean plane of a phenyl ring is $7.9(2)^\circ$ and the torsion angle O(2a)–B(3)–C(31)–C(32) is $-6.7(7)^\circ$. This latter datum may be compared with that for the analogous angle in $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{SiPh}_2]_2$ (**7**), of $1.3(6)^\circ$ ⁶. The silicon to oxygen distances in **1** are almost identical at 1.629(3) and 1.631(3) Å. The boron to oxygen are less similar at 1.338(6) and 1.352(6) Å. The two B–O–Si angles B(3)–O(4)–Si(1) and B(3a)–O(2)–Si(1) are significantly different at $150.7(3)$ and $153.0(3)^\circ$. In the non-brominated analogue of **1**, *i.e.* $[\text{PhBO}_2\text{Si}(t\text{-Bu})_2]_2$ (**4**)², the B–O–Si angles are very similar at $149.1(3)$ and $149.9(2)^\circ$ whereas in the related Si–Ph containing derivatives $[\text{PhBO}_2\text{SiPh}_2]_2$ (**5**)⁴, and $[(4\text{-BrC}_6\text{H}_4\text{B})\text{O}_2\text{SiPh}_2]_2$ (**7**)⁶, the B–O–Si angles are $145.3(3)$ and $160.9(3)$ and $144.7(3)$ and $150.7(3)^\circ$, respectively. The large range of B–O–Si angles in borosilicates is not surprising since, as has been shown previously by structural and theoretical studies¹³, the deformation of these angles requires relatively small amounts of energy. The structure of compound **1** is typical of borosilicates containing organoboron groups with the O–B–O angle greater than 120° at $123.4(4)^\circ$ whilst the O–B–C angles are less than 120° at $118.3(4)^\circ$. The O–Si–O angle in compound **1** is greater at $112.05(17)^\circ$ than the tetrahedral angle whilst the

TABLE I
Selected bond lengths (in Å) and angles (in $^\circ$) for **1**

Bond lengths			
Si1–O4	1.629(3)	Si1–O2	1.631(3)
Si1–C21	1.875(5)	Si1–C11	1.891(5)
O2–B3A	1.338(6)	B3–O2A	1.338(6)
B3–O4	1.352(6)	B3–C31	1.575(6)
Bond angles			
O4–Si1–O2	112.05(17)	O4–Si1–C21	106.2(2)
O2–Si1–C21	107.0(2)	O4–Si1–C11	107.0(2)
O2–Si1–C11	105.3(2)	C21–Si1–C11	119.5(2)
B3A–O2–Si1	150.7(3)	O2A–B3–O4	123.4(4)
O2A–B3–C31	118.4(4)	O4–B3–C31	118.2(4)
B3–O4–Si1	153.0(3)		

Symmetry transformations used to generate equivalent atoms: $-x, -y + 2, -z + 1$.

O–Si–C angles are less than 109° with mean value of $106.4(2)^\circ$. All other bond distances and angles are unremarkable.

Compound **2** (Fig. 2 and Table II) contains a borosilicate framework which may be described as an incomplete B_4Si_4 cube with eight B–O–Si and two Si–O–Si edges. Alternatively, it may be described as consisting of two $B_2O_4Si_2$ rings, as in compound **1**, joined confacially *via* two Si–O–Si bridges. Unlike the $B_2O_4Si_2$ rings in compound **1**, however, those of **2** are distinctly non-planar with atoms B(3) and O(4) deviating from the calculated mean plane containing O(2), Si(1), O(8), B(7), O(6), and Si(5) by 0.696(7) and 0.812(4) Å, respectively. This is also in marked contrast to the equivalent $B_2O_4Si_2$ sections of the 4-vinylphenyl analogue of **2**, *i.e.*, $[(t\text{-BuSi})_4(4\text{-H}_2\text{C}=\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$, compound **6**⁵. Here all the atoms except one silicon atom in each $B_2O_4Si_2$ ring lie in a plane with root-mean-square deviation of 0.053 Å. The silicon atom's deviation from the mean plane was 0.705(2) Å compared with deviations in the range $-0.062(1)$ to $0.081(2)$ Å for all other atoms in the $B_2O_4Si_2$ ring. Other notable differences between compounds **2** and **6** concern the benzene rings in each compound. In **6**, the benzene rings attached to boron atoms in the confacially joined $B_2O_4Si_2$ rings were essentially parallel whereas in compound **2** they are clearly not (Fig. 2). The interplanar angle between the mean planes containing the C(11) to C(16) atoms attached to B(3) and the C(21) to C(26) atoms attached to B(7a) is $46.4(2)^\circ$. Hence any stabilisation of the structure of $[(t\text{-BuSi})_4(4\text{-H}_2\text{C}=\text{CHC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ (**6**), due to π – π interactions between adjacent benzene rings (and vinyl groups in compound **6**) has been removed in the case of $[(t\text{-BuSi})_4(4\text{-BrC}_6\text{H}_4\text{B})_4\text{O}_{10}]$ (**2**).

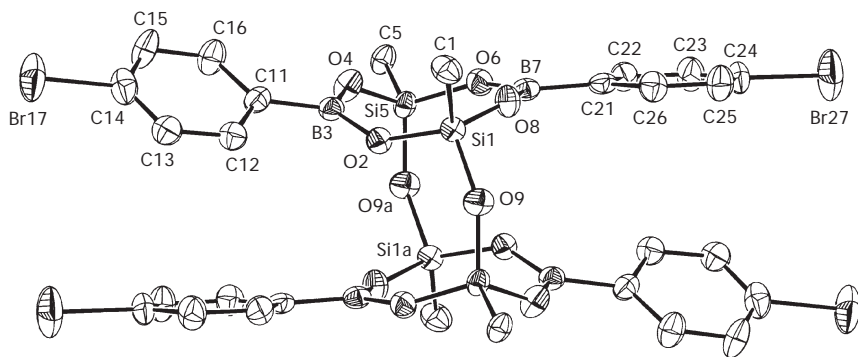


FIG. 2

A view of **2** showing the numbering scheme. Anisotropic displacement parameters are drawn at the 30% probability level. Methyl groups are omitted for clarity

The Si–O–Si angles in **2** and **6** are 147.5(2) and 154.14(14)°, respectively. Like B–O–Si angles, there are large variations in reported Si–O–Si angles with values from 89.4 to 180°¹⁴. The ranges of B–O–Si angles in **2** and **6** are 135.8(3) to 149.8(4)° and 137.5(2) to 154.4(2)°, respectively. The mean values are 142.7 and 144.8°, respectively.

Mean bond distances in [(*t*-BuSi)₄(4-BrC₆H₄B)₄O₁₀] (**2**) were 1.361(7) and 1.628(4) Å for the B–O and Si–O bonds, respectively. These may be compared with 1.366(3) and 1.616(4) Å for the equivalent bonds in [(*t*-BuSi)₄(4-H₂C=CHC₆H₄B)₄O₁₀] (**6**)⁵.

TABLE II
Selected bond lengths (in Å) and angles (in °) for **2**

Bond lengths			
Si1–O9	1.614(4)	Si1–O8	1.626(4)
Si1–O2	1.634(3)	Si1–C1	1.850(6)
O2–B3	1.377(6)	B3–O4	1.352(7)
B3–C11	1.557(7)	O4–Si5	1.634(4)
Si5–O9A	1.615(4)	Si5–O6	1.619(4)
Si5–C5	1.846(5)	O6–B7	1.364(6)
B7–O8	1.350(7)	B7–C21	1.557(7)
Bond angles			
O9–Si1–O8	107.7(2)	O9–Si1–O2	106.90(19)
O8–Si1–O2	111.36(17)	O9–Si1–C1	110.8(2)
O8–Si1–C1	109.3(2)	O2–Si1–C1	110.8(2)
B3–O2–Si1	142.1(3)	O4–B3–O2	120.3(5)
O4–B3–C11	119.2(4)	O2–B3–C11	120.5(5)
B3–O4–Si5	135.8(3)	O9A–Si5–O6	108.39(19)
O9A–Si5–O4	108.8(2)	O6–Si5–O4	111.2(2)
O9A–Si5–C5	111.3(2)	O6–Si5–C5	109.0(2)
O4–Si5–C5	108.2(2)	B7–O6–Si5	143.1(3)
O8–B7–O6	122.4(5)	O8–B7–C21	119.7(4)
O6–B7–C21	117.9(5)	B7–O8–Si1	149.8(4)
Si1–O9–Si5A	147.5(2)		

Symmetry transformations used to generate equivalent atoms: $-x, -y + 1, -z$.

The crystal of compound **3**, $[(4\text{-BrC}_6\text{H}_4\text{BO})_3]$ (Fig. 3 and Table III), used for X-ray measurements, was not of a very high standard and consequently, the solution of the crystal structure afforded distance and angle values with relatively high standard uncertainties. However, the structure solution did

TABLE III
Selected bond lengths (in Å) and angles (in °) for **3**

Bond lengths			
O1-B1	1.40(2)	O1-B1A	1.40(2)
O2-B1	1.37(3)	O2-B2	1.399(19)
Bond angles			
B1-O1-B1A	123(2)	B1-O2-B2	121.4(17)
O2-B1-O1	117.5(18)	O2-B1-C11	121.5(17)
O1-B1-C11	120.9(18)	O2A-B2-O2	119(2)
O2-B2-C21	120.5(12)		

Symmetry transformations used to generate equivalent atoms: $x, -y + 1/2, z$.

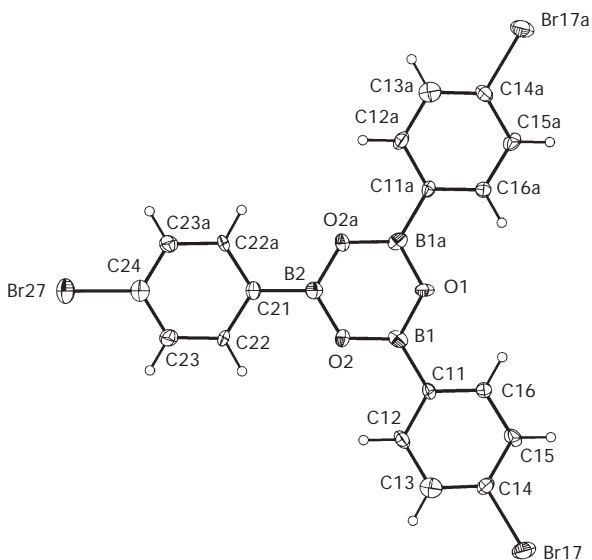


FIG. 3

A view of **3** showing the numbering scheme. Anisotropic displacement parameters are drawn at the 30% probability level

establish that, like previously reported boroxine compounds, the molecule contained a B_3O_3 ring with each boron atom attached to a $4-BrC_6H_4$ group. The mean value for the B–O distance was 1.39 Å, and the mean values for the O–B–O and B–O–B angles were 118 and 122°, respectively. Comparable mean B–O distances are 1.386 Å in $(PhBO)_3$ ¹⁵ and 1.384 Å in $[(4-MeC_6H_4BO)_3]$ ¹⁶, respectively.

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