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Synthesis and structural characterization of cycloborasiloxanes: the X-ray crystal structures of *cyclo*-1,3,3,5,5-pentaphenyl-1-bora-3,5-disiloxane and *cyclo*-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane

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Abstract

Cycloborasiloxanes $[PhB(OSiPh_2)O]_2$ (**1**) and $RB[(OSiPh_2)_2O]$ [R = Ph (**2**); 2,4,6-$Me_3C_6H_2$ (**3**)] containing eight- and six-membered rings, respectively, have been synthesized by the reaction of $RB(OH)_2$ with 1,1,3,3-tetraphenyl-1-3-dihydroxy-1,3-disiloxane or diphenylsilanediol. The structures of **1** and **2** have been determined, and both contain essentially planar Si–O–B rings, although the Si–O and B–O bonds are shorter in the larger ring. The factors affecting the structural parameters of related heterocyclic ring systems are reviewed.

Introduction

Although heterosiloxanes have been known for over 30 years [1], structural characterization of such species is relatively recent. The largely intractable nature of high molecular weight polymers has focussed attention on small molecule model systems, of which the siloxides are the most common. The recent report of the preparation and structure of $Cu[OSi(O^tBu)_3]_2(py)_2$ (py = pyridine) typifies attempts to isolate and characterize silicon analogues of alkoxides [2]. Cyclic, oligomeric systems represent further Si–O–M aggregation, and the structures of several cyclic and spirocyclic metallasiloxanes containing MSi_nO_{2n+2} (M = Ti, n = 3 [3]; M = Ti, Co, Cu, n = 4 [4–6]) have now been published. Among the group 13 and 14 element compounds, both Me_3Al and Tl(OEt) react with poly(organosiloxanes), $(R_2SiO)_n$, to yield $[Me_2Al(OSiMeR_2)]_2$ [7] and $\{[Tl_2(OSiMe_2)_2O]_2\}_n$ [8], respectively. The latter contains TlOSiOSiOTl fragments linked into rings by $O\colon \rightarrow Tl$ interactions; further $O\colon \rightarrow Tl$ coordination links the rings into a polymeric array, centred on Tl_4O_4 cubes. Non-planar eight-membered Si–O–Ge rings are present in $[R_2Ge(OSiPh_2)O]_2$ (R = Me, Ph), and these rings are more puckered

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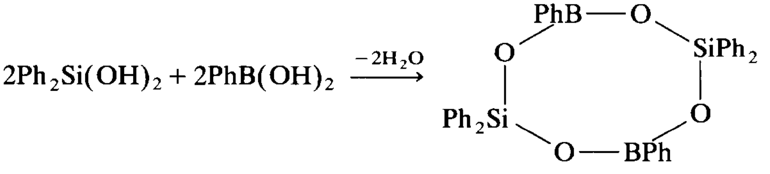
than those of cyclotetrasiloxanes [9]. Finally, the vertex-deficient cuboids $R_7Si_7O_9(OH)_3$ ($R = c\text{-}C_5H_9$, $c\text{-}C_6H_{11}$, $c\text{-}C_7H_{13}$) [10] can be capped by a range of both transition [11] and main group [12] element fragments to provide model structures for silica-supported metal catalysts.

Our interest in this area stems from the use of suitably functionalized siloxanes as carriers for various cationic, inorganic or organic species [13], and as control release media for bio-active materials. As part of this study we have synthesised model cycloborosiloxanes in order to obtain structural information on a class of Si–O–B-containing materials, as, to our knowledge, only two examples of B–O–Si based heterocycles have previously been structurally characterized. Thus, *cyclo*-$FB[O({}^tBu_2SiOSiMe_2OSi{}^tBu_2O)]$ contains an eight-membered slightly non-planar ring system [14], and a preliminary report on the structure of the strained six-membered heterocycle $PhBO(SiPh_2O)_2$ (**2**) appeared during the course of the preparation of this paper [15]. Inorganic heterocycles are also of current interest from the viewpoint of their electronic structures and their potential quasi-aromatic character [16]. In principle, rings of general formula $B_nSi_mO_{n+m}$ will have $2(n+m)$ π-electrons available for delocalization from the oxygen lone pairs. If $n+m=3$, the Hückel criterion of 6 π-electrons is met, whereas if $n+m=4$, an anti-aromatic 8 π-electron count results.

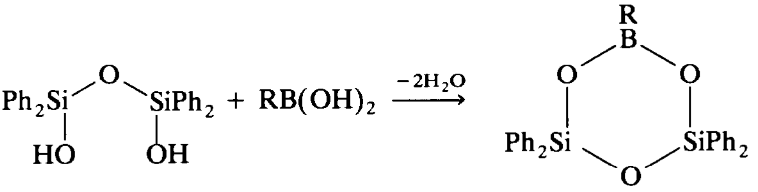
We now present the structures of two compounds representative of each of these classes, containing the BSi_2O_3 and $B_2Si_2O_4$ ring systems, respectively. The structure recently reported for **2** differs only marginally in terms of geometric data from our own findings, although the monoclinic unit cell data differ in both c and β. The structural data from our study of **2** are included in this report along with the data from ref. 15 for direct comparison with that for **1**, although tabular data relating to our structure determination of **2** (positional parameters, atomic displacements, etc.) have been omitted. These latter tables of data are, however, available in supplementary form.

Results and discussion

Condensation of phenylboronic acid with diphenylsilane diol leads to high yields of the eight-membered heterocycle $[PhB(OSiPh_2)O]_2$ (**1**). The six-membered heterocycles $RB[(OSiPh_2)_2O]$ [R = Ph (**2**), 2,4,6-$Me_3C_6H_2$ (**3**)] are formed in high yields on reaction of the appropriate arylboronic acid with 1,3-dihydroxy-1,1,3,3-tetraphenyldisiloxane, provided water is continuously removed.



(**1**)



R = Ph (**2**)
R = 2,4,6-$Me_3C_6H_2$ (**3**)

Compound **2** has been prepared previously by the reaction of $PhB(OH)_2$ with 1,3-dichlorotetraphenyldisiloxane in a diethyl ether/triethylamine mixture [15], and related compounds, differing only in the organic substituents on boron and silicon, have been reported previously although not structurally characterized. The six-membered B_2SiO_3 and ten-membered BSi_4O_5 systems are also known [1].

The structures of **1** and **2** are shown in Figs. 1 and 2, respectively. Structural data for **2** are similar to those recently reported [15], although the *c* axis is significantly different in length in the two determinations [17.099(6) and 17.733(4) Å]. The somewhat smaller value obtained in our study is confirmed by measurement of the oscillation photograph, which yields $c = 17.11$ Å. Moreover, the calculated layer spacing for the literature structure, based on Fe-K_α radiation used in this part of the work and the fourth layer line, is 27.8 mm, unequivocally different to the spacing of 29.2 mm we observe. There is no obvious reason for the

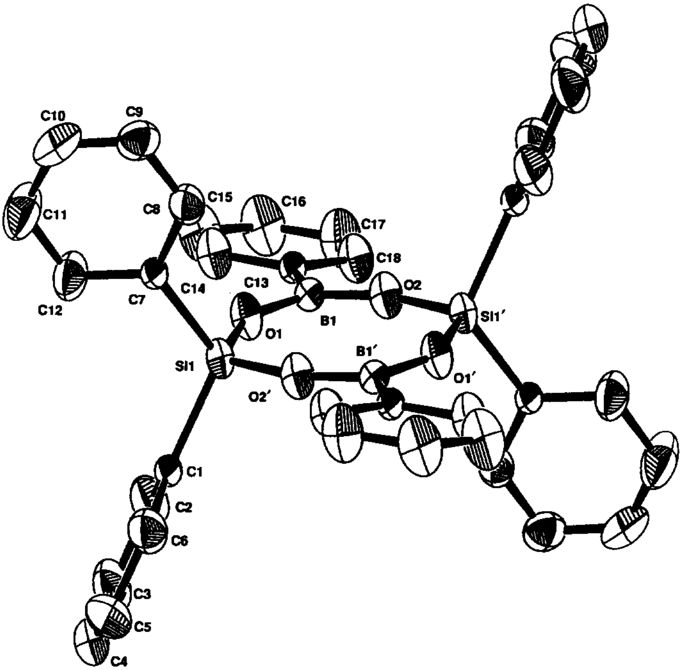


Fig. 1. The molecular structure of **1** showing the labelling scheme used in the text. Primed atoms are related to the unprimed atoms of the asymmetric unit by $0.5 - x$, $0.5 - y$, $1 - z$. Thermal ellipsoids are at the 30% probability level.

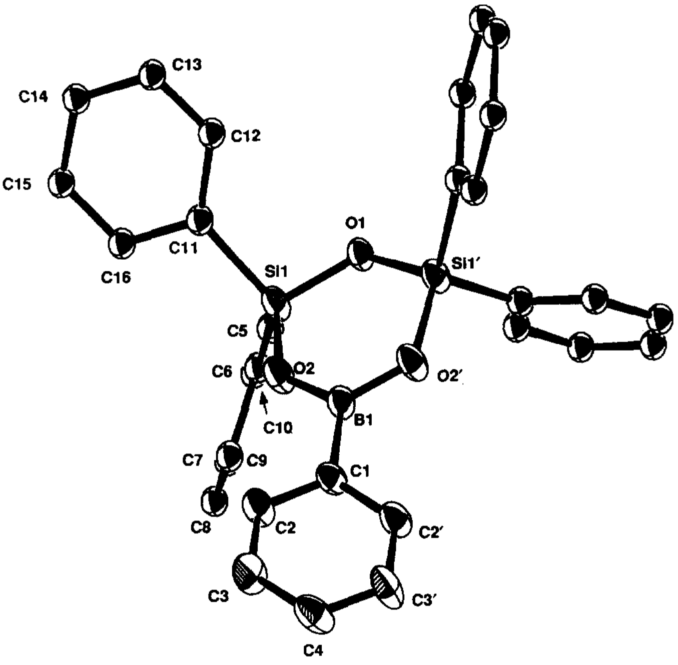


Fig. 2. The molecular structure of **2** showing the labelling scheme used in the text. Primed atoms are related to the unprimed atoms of the asymmetric unit by $-x$, y, $0.5-z$. Thermal ellipsoids are at the 30% probability level.

different axial lengths observed, except possibly that different crystal packing accrues from the differing recrystallization solvents employed in the two cases (diethyl ether/petrol *versus* dichloromethane/hexane). Interestingly, the β angle of the monoclinic cell also differs [114.58(2) and 119.14(2)°], resulting in virtually identical cell volumes (2665, 2641 Å^3) [15]. Comparison of the structures of the eight- and six-membered Si–O–B systems given below is based on the data for **2** determined at Bath, although for completeness, the data from ref. 15 are also included in Table 3.

In both compounds the central heterocyclic ring is essentially planar, the maximum deviations from the least squares planes through all the ring atoms of each heterocycle being 0.137 (O2), −0.025 (B1) for **1**, and 0.041 (Si1), −0.051 Å (O1) for **2**. In contrast, the O–B–O moiety in *cyclo*-FB[O(^{t}Bu$_2$SiOSiOMe$_2$O-Si^{t}Bu$_2$O)] lies 15.8° out of the plane of the Si_3O_2 portion of the eight-membered ring, due to weak, orthogonal F...B interactions [14]. In addition, the phenyl rings attached to boron in both structures also approach co-planarity with the B–O–Si ring (see Figs. 1 and 2), the dihedral angles O1–B1–C13–C14 (in **1**) and O2–B1–C1–C2 (in **2**) being 8.6° and −13.5°, respectively. However, in both structures the B–C bond [1.555(6) (**1**), 1.543(15) Å (**2**)] is essentially the same as in PhB(OH)$_2$ [1.562(3) Å] [17], and *cyclo*-$Ph_3B_3O_3$ [1.540(3) Å] [18] in which the three phenyl rings approach co-planarity with the boroxane. Comparison can be made with *cyclo*-$Et_3B_3O_3$ [B–C = 1.565(1) Å] [19], in which stacking of B_3O_3 rings suggests intermolecular B...O interactions rather than any π(B–C) overlap, and with the sum of the respective covalent radii (1.59 Å) [20]. Any appreciable π-delocalization

Table 1

Fractional atomic coordinates and isotropic thermal parameters (Å) for **1**

Atom	x	y	z	U_{iso} or U_{eq} *
Si1	0.15157(7)	0.13125(15)	0.45090(5)	0.0508(7) *
O1	0.1704(2)	0.1465(4)	0.5256(1)	0.062(2) *
O2	0.2171(2)	0.2144(4)	0.4248(1)	0.064(2) *
B1	0.2174(3)	0.2110(6)	0.5768(2)	0.048(3) *
C1	0.0566(3)	0.2255(5)	0.4176(2)	0.059(1)
C2	0.0107(3)	0.2775(7)	0.4538(3)	0.089(4) *
C3	−0.0598(3)	0.3513(9)	0.4288(4)	0.116(5) *
C4	−0.0860(4)	0.3722(8)	0.3682(4)	0.108(5) *
C5	−0.0433(4)	0.3236(8)	0.3302(3)	0.104(5) *
C6	0.0284(3)	0.2510(7)	0.3551(2)	0.083(4) *
C7	0.1511(2)	−0.0738(5)	0.4294(2)	0.052(1)
C8	0.2187(3)	−0.1470(6)	0.4262(2)	0.067(3) *
C9	0.2192(4)	−0.3006(7)	0.4105(2)	0.082(4) *
C10	0.1527(4)	−0.3814(7)	0.3980(3)	0.097(5) *
C11	0.0849(4)	−0.3144(7)	0.4001(3)	0.118(6) *
C12	0.0838(3)	−0.1606(6)	0.4157(3)	0.091(4) *
C13	0.1957(2)	0.1981(5)	0.6389(2)	0.050(1)
C14	0.2358(3)	0.2817(6)	0.6904(2)	0.071(3) *
C15	0.2142(3)	0.2755(8)	0.7450(2)	0.094(4) *
C16	0.1538(3)	0.1839(8)	0.7493(2)	0.101(5) *
C17	0.1142(3)	0.0980(8)	0.7001(2)	0.102(4) *
C18	0.1344(3)	0.1049(6)	0.6446(2)	0.074(3) *

from the aromatic ring onto boron (and hence the other heteroatoms) can thus be discounted.

Geometric data for the two B–O–Si rings are compared in Table 3 with those of related structures. The Si–O bond lengths in both structures are similar to those of Si–O bonds in other structures, primarily the near-planar *cyclo*-FB[O(^{t}Bu$_2$SiO-SiMe$_2$OSi^{t}Bu$_2$O)] [14] and non-planar [R$_2$Ge(OSiPh$_2$)O]$_2$ [9], all of which lie in the range 1.60–1.66 Å, although the bond lengths in the six-membered ring of **2**

Table 2

Selected bond distances (Å) and angles (degrees) for **1** and **2**, with estimated standard deviations in parentheses

1		**2**	
Si1–O1	1.627(3)	Si1–O1	1.644(2)
Si1–O2	1.615(3)	Si1–O2	1.655(5)
B1–O1	1.348(5)	B1–O2	1.374(7)
B1–O2	1.345(5)		
Si1–C1	1.844(5)	Si1–C5	1.849(7)
Si1–C7	1.847(5)	Si1–C11	1.838(7)
B1–C13	1.555(6)	B1–C1	1.543(15)
O1–Si1–O2′	112.0(2)	O1–Si–O2	106.3(3)
O1–B1–O2	121.2(3)	O2–B1–O2′	120.2(9)
B1–O1–Si1	145.3(3)	B1–O2–Si1	129.3(5)
B1–O2–Si1′	160.9(3)	Si1–O1–Si1′	127.3(4)

Table 3

Comparison of geometric data (Å, degrees) for **1** and **2** with those of related structures

	B–O	Si–O (B)	Si–O (Si)	< O–B–O	< O–Si–O	< B–O–Si	< Si–O–Si	Ref.
M_3O_3								
$Ph_6Si_3O_3$			1.64 (1)		107.7 (8)		131.8 (8)	29
$Ph_6Si_2BO_3$	1.374 (7)	1.655 (5)	1.644 (2)	120.2 (9)	106.3 (3)	129.3 (5)	127.3 (4)	This work
	1.370 (2)	1.639 (1)	1.6363 (9)	120.8 (2)	106.55 (8)	128.9 (1)	127.1 (1)	15
$Ph_3B_3O_3$	1.386 (2)			121.7 (2)		118.0 (4) [a]		18
M_4O_4								
$Ph_6Si_4O_4$			1.615 [b]		109.7 [c]		152.3 (2), 152.6 (2), 167.4 (2), 166.9 (2)	30
$FBR_2R'_4Si_3O_4$ [d]	1.313 (2), 1.320 (3)	1.626 (1), 1.635 (2)	1.612 (1), 1.621 (2)	126.3 (2)	109.1 (1) 110.1 (1)	146.6 (1), 159.8 (2)	151.3 (1) 163.6 (1)	14
$Ph_8Si_2B_2O_4$	1.348 (5), 1.345 (5)	1.615 (3), 1.627 (3)		121.2 (3)	112.0 (2)	145.3 (3), 160.9 (3)		This work.
$Me_2Ph_6Si_2Ge_2O_4$		1.615 (3), 1.590 (7) [e]		104.5 (3) [f]	113.0 (3)	135.8 (3), 138.0 (3) [g]		9
B_2O_3 [h]	1.20 (3), 1.36 (2)							[i]
BO_3^{3-}	1.20 (3), 1.36 (2)							[j]
$PhB(OH)_2$	1.369 (2), 1.359 (2)			116.3 (2) 116.2 (2)				17
$[Ph_2(OH)SiOSiPh_2(OH)]_3$ [k]			1.601 (4) [l], 1.632 (9) [m], 1.647 (8) [n]					31

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[a] < B–O–B. [b] Mean value; range = 1.609 (3)–1.621 (4) Å. [c] Mean value; range = 109.0(2)–110.8(2)°. [d] R = Me, R′ = ᵗBu. [e] Si–O(Ge). [f] < O–Ge–O. [g] < Si–O–Ge. [h] Gas phase. [i] P.A. Akishin and V.P. Spiridonov, *Dokl. Akad. Nauk. SSSR*, 131 (1960) 557. [j] J.B. Farmer, *Adv. Inorg. Chem. Radiochem.*, 25 (1982) 187. [k] Adduct with two molecules $C_4H_4N_2$. [l] < Si–O–Si = 180°. [m] Si–OH. [n] < Si–O–Si = 144.5°.

[1.644(2), 1.655(5) Å] are longer than in the eight-membered ring contained in **1** [1.615(3), 1.627(3) Å]. In all these structures, the Si–O bond is considerably shorter than the sum of the relevant covalent radii (1.88 Å) [20], suggestive of $O(p) \rightarrow Si$ π-donation. From the data collected in Table 3, it is apparent that ring planarity is not required for π-bonding, a rationale which has also been invoked to explain the similarity in the P–N bonds of both planar and non-planar *cyclo*-phosphazenes [21]. Similarly, the B–O bonds in both structures are typical of other boroxanes (Table 3) and are also shorter than the sum of the covalent radii of the atoms (1.52 Å) [20], suggesting significant $O(p) \rightarrow B(p)$ π-electron transfer. However, as with the pattern of Si–O bond lengths, the shorter B–O bonds are observed in the eight-membered ring (**1**). Indeed, the bonding pattern for the two heterocycles parallels the situation in $(NPF_2)_3$ and $(NPF_2)_4$, both of which have planar heterocyclic rings, and for which the P–N bonds are shorter in the eight- (1.51 Å) than the six-membered system (1.56 Å) [22].

Since the eight-membered ring is not expected to show any evidence of π-electron delocalization (8 π-electrons), we can conclude that no such effects are apparent in the six-membered ring either. Previous discussions of the potential aromaticity in B–O containing heterocycles have led to the conclusion that the large electronegativity difference between the two elements (*i.e.* mismatch in valence orbital energies) would only lead to localized π-interactions [23]. Indeed, the energy difference in valence $2p$ orbitals for B and O (7.6 eV) is similar to that for Al and N (7.1 eV for $3p$ and $2p$ orbitals, respectively) [24], for which neglible π-delocalization has been calculated for the hypothetical alumazene $Al_3N_3H_6$ [25,26]. Thus, an alternative explanation for the pattern of M–O bond lengths must be sought.

Both ^{11}B and ^{29}Si NMR data are sensitive to the structural and electronic environments of the respective atoms, and the relevant data for all three compounds described here have been recorded (see Experimental Section). ^{11}B chemical shifts vary very little for the three species (28.4–26.1 ppm) and are typical of those found for other trigonal RBO_2 species [27]. Chemical shifts for ^{29}Si show a greater dependence upon ring size, with deshielding of approx. 15 ppm being apparent in the six-membered (-31.0, -31.4 ppm) compared to the eight-membered ring (-44.6 ppm). Cyclic siloxanes $(Ph_2SiO)_n$ ($n = 3,4$) show a similar trend [28], but have rather different chemical shifts (approx. -21 and -30 ppm, respectively) in comparison with **1** and **2**. In view of the different electronic contributions of the constituent non-oxygen atoms of this group of borosiloxanes and siloxanes, further comparison in geometric terms alone is not warranted. However careful analysis of the ring geometries of the two structures presented is revealing, and sheds some light on the variations in bond lengths referred to above. In both **1** and **2**, the valence angles at tetrahedral silicon [**1**, 112.0(2); **2**, 106.3(3)°] and trigonal boron [**1**, 121.2(3); **2**, 120.2(9)°] are accommodated at the expense of distortions of the angles about oxygen. The final sum of the internal angles of the heterocycle is, however, close to ideal in both the six-membered M_3O_3 series ($\Sigma = 720°$) and the eight-membered M_4O_4 series ($\Sigma = 1080°$) for planar compounds spanning the spectrum of B, Si combinations, *i.e.* $Ph_6Si_3O_3$, $\Sigma = 718.5$ [29]; **2**, 718.7; $Ph_3B_3O_3$, 718.8 [18]; $Ph_8Si_4O_4$, 1078.0 [30]; ${}^tBu_4Me_2FBSi_3O_4$, 1076.9 [14]; **1**, 1078.8° (Table 3). In the case of **2**, the internal angles of an idealized hexagon (120°) are not much perturbed by the slightly smaller tetrahedral angle at

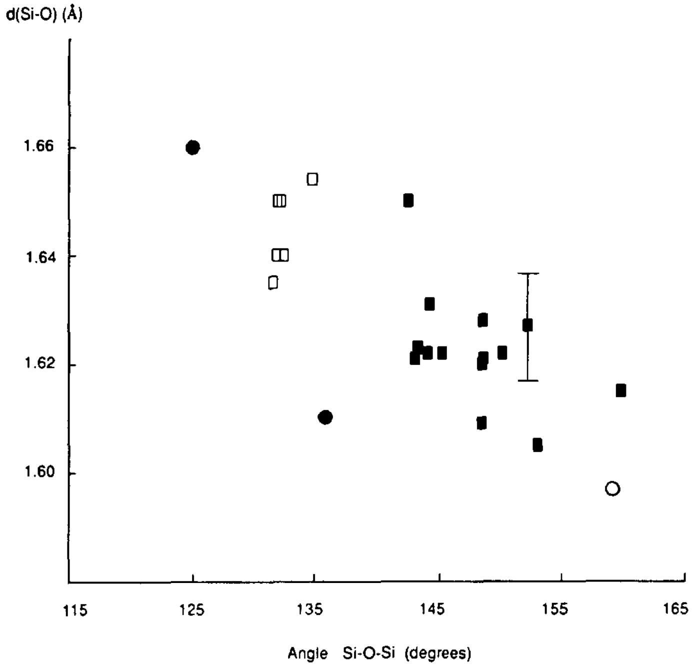

Fig. 3. Plot of *d*(Si–O) (Å) against < Si–O–Si (degrees) for Si_3O_3 (□) and Si_4O_4 (■) rings. Data are taken from ref. 33. Approximately 90% of the data are within the typical error bar shown (many of the M_4O_4 data having much smaller errors); data with larger errors are indicated by (●) or (○) for Si_3O_3 and Si_4O_4 rings, respectively.

silicon, and the angles at oxygen increase only slightly [127.3(4), 129.3(5)°]. In the case of **1**, however, the internal angles of an idealized octagon (135°) are significantly different to the valence angles at both silicon and boron, and the strain induced in the polygon in accommodating these differences results in marked opening of the angles at oxygen [145.3(3), 160.9(3)°]. In fact, even including the non-planar germanium compound $Me_2Ph_6Si_2Ge_2O_4$, the internal ring angles at B, Si or Ge are never more than $\pm 7°$ of their ideal value (most are within $\pm 5°$). Angular distortions about oxygen are common in siloxane chemistry, and Si–O–Si angles varying from approx. 90° to 180° are known [31,32]. In both structures **1** and **2** the effective hybridization at oxygen in the M–O bonds (M = Si, B) changes from sp^3 towards *sp*, but to a far greater extent in the case of **1**. The increasing *s* content of the M–O bonds will result in the shorter bonds found in **1**, and indeed other similar M_4O_4 systems (Table 3). Direct comparison can be made with the two dissimilar Si–O–Si units in $[(OH)Ph_2SiOSiPh_2(OH)]_3 \cdot (C_4H_4N_2)_2$, in which the perfectly linear entity incorporates shorter Si–O bonds [1.601(4) Å] than the fragment bent through 144.5° at oxygen [1.647(8) Å] [31]. Only in the case of non-planar $Me_2Ph_6Si_2Ge_2O_4$ (Σ(internal angles) = 982.6°) does an unusually short Si–O bond [1.590(7) Å] accrue from relatively unstrained angles about oxygen [135.8(3), 138.0(3)°] [9]. Despite the simplicity of this analysis, it holds remarkably well across a wide range of Si_3O_3 and Si_4O_4 structures, both planar and non-planar (Fig. 3) [33].

The pattern of bond angles about oxygen across the range of planar eight-membered M_4O_4 species (Table 3) is remarkably uniform, with two distinct angles differing by about 15° being the norm. Only in tricyclic $Me_{12}Si_8O_{10}$ containing two Si_3O_3 rings fused to opposite points of a near planar Si_4O_4 unit [Σ(internal angles) = 1072.4°] is equality of the O–Si–O angles observed [159.1(9)°] [33]. While the M_3O_3 rings are almost invariably planar, this is not the case for the M_4O_4 systems where planarity is relatively rare. The non-planar rings, typified by the $Si_2Ge_2O_4$ system (Table 3) [9], incorporate uniform angles about all oxygen atoms in contrast to the planar species. It would appear that in the planar species, the majority of the ring strain is concentrated at a limited number of sites, rather than being evenly distributed. Interestingly, the strain induced in the eight-membered Si_4O_4 by substitution of two boron atoms, **1**, appears to be more pronounced than the single substitution on going from $Ph_6Si_3O_3$ to **2**, as reflected in the changes in angle at the oxygen atoms (those at silicon and boron are minimal with respect to the analogous all-silicon or all-boron species; Table 3). Thus, the maximum angular change at oxygen on going from $Ph_6Si_3O_3$ to **2** is 4.5°, while the analogous angles change by over 6° (max 7.3°) from $Ph_8Si_4O_4$ to **1**. The implications for facile ring-opening polymerization of such oligomers brought on by internal angular strain has been noted by others for the M_3O_3 class of compounds [15], and is now shown to be equally applicable to the M_4O_4 analogues.

Experimental

Spectra were recorded on the following instruments: VG 70-70E (mass spectra), JEOL GX270 (^1H, ^{13}C NMR), JEOL GX400 (^{11}B, ^{29}Si NMR), Perkin–Elmer 599B (IR). NMR spectra were recorded as saturated $CDCl_3$ solutions. Zero chemical shifts are $(CH_3)_4Si$ (^1H, ^{13}C, and ^{29}Si) and $BF_3 \cdot Et_2O$ (^{11}B). Diphenylsilane diol and phenylboronic acid were purchased from Aldrich and used without further purification. 1,1,3,3-Tetraphenyl-1,3-dihydroxy-1,3-disiloxane [34] and mesitylboronic acid were prepared by literature methods [35].

Synthesis of cyclo-*1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane (1)*

A mixture of diphenylsilanediol (2.16 g, 10 mmol) and phenylboronic acid (1.22 g, 10 mmol) and sodium-dried benzene (20 ml) was refluxed for 4 h, with continuous removal of water by use of a Dean and Stark apparatus. The mixture was allowed to cool and any solid residues removed by filtration. The solvent was distilled under reduced pressure, and the solid residue recrystallized from diethyl ether/60–80°C petroleum ether (1:3) to yield **1** (2.64 g, 87%; m.p. 161–162°C). Anal. Found: C, 71.60; H, 4.97. $C_{36}H_{30}B_2Si_2O_4$ calc.: C, 71.54; H, 5.00%. ^1H NMR: 7.47–7.67 (m, 18H, m,p-C_6H_5); 7.93–7.97 (m, 8H, o-C_6H_5Si); 8.27–8.31 (m, 4H, o-C_6H_5B). ^{13}C NMR: 128.2, 128.4, 131.0, 132.1, 134.2, 135.7 (o,m,p-C_6H_5Si, C_6H_5B). ^{11}B NMR: 27.1. ^{29}Si NMR: −44.6 ppm. Mass spectrum (70 eV EI): m/z 604 (M^+), 527 (M − Ph), 423 (M − Ph–PhBO). IR: ν(B–O–Si) 1320s cm^{-1}.

Synthesis of cyclo-*1,3,3,5,5-pentaphenyl-1-bora-3,5-disiloxane (2)*

Prepared by the method described above for **1** but starting from 1,1,3,3-tetraphenyl-1,3-dihydroxy-1,3-disiloxane (2.00 g, 4.8 mmol) and phenylboronic acid (0.59

g, 4.8 mmol). Recrystallization, as above, yielded **2** (2.29 g, 95%; m.p. 152–153°C). Anal. Found: C, 71.90; H, 4.94. $C_{30}H_{25}BSi_2O_3$ calc.: C, 72.00; H, 5.03%. ^{1}H NMR: 7.26–7.64 (m, 15H, m,p-C_6H_5); 7.85–7.88 (m, 8H, o-C_6H_5Si); 8.21–8.24 (m, 2H, o-C_6H_5B). ^{13}C NMR: 127.7, 128.0, 129.9, 130.8, 131.6, 132.9, 134.4, 135.4 (i,o,m,p-C_6H_5Si, C_6H_5B). ^{11}B NMR: 26.1. ^{29}Si NMR: -31.0 ppm. Mass spectrum (70 eV EI): m/z) 500 (M^+), 423 ($M-$Ph), 345 ($M-$2Ph), 319 ($M-$Ph-PhBO). IR: ν(B–O–Si) 1320s, 980s; ν(Si–O–Si) 1110s cm^{-1}.

Synthesis of cyclo-*1-mesityl-3,3,7,7-tetraphenyl-1-bora-3,5-disiloxane (3)*

Prepared as described for **1** from 1,1,3,3-tetraphenyl-1,3-dihydroxy-1,3-disiloxane (2.00 g, 4.8 mmol) and mesitylboronic acid (0.79 g, 4.8 mmol). Recrystallization from petroleum ether yielded **3** (2.24 g, 86%; m.p. 121–123°C). Anal. Found: C, 73.02; H, 5.88. $C_{33}H_{31}BSi_2O_3$ calc.: C, 73.05; H, 5.76%. ^{1}H NMR: 2.42 (s, 3H, p-CH_3); 2.54 (s, 6H, o-CH_3); 6.98 (s, 2H, m-$C_6H_2Me_3$B); 7.48–7.62 (m, 12H, m,p-C_6H_5Si); 7.87–7.90 (m, 8H, o-C_6H_5Si). ^{13}C NMR: 22.7 (o-CH_3); 21.2 (p-CH_3); 127.6, 128.0, 130.8, 134.3, 138.6, 141.1 (o,m,p-C_6H_5Si, C_6H_5B). ^{11}B NMR: 28.4. ^{29}Si NMR: -31.4 ppm. Mass spectrum (70 eV EI): m/z 542 (M^+), 465 ($M-$ Ph), 386 ($M-$ 2Ph). IR: ν(B–O–Si) 1300s, 980s; ν(Si–O–Si) 1120s cm^{-1}.

X-Ray crystal structure of cyclo-*1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane (1)*

A crystal of approximate dimensions 0.33 × 0.33 × 0.3 mm^3 was used for data collection.

Crystal data: $C_{36}H_{30}O_4B_2Si_2$, $M = 604.4$, monoclinic, $a = 17.827(2)$, $b = 8.693(2)$, $c = 22.523(5)$ Å, $\beta = 105.95(1)$°, $U = 3356.0$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 1.20$ g cm^{-3}, μ(Mo-K_α) = 1.06 cm^{-1}, $F(000) = 1264$. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 \leq \theta \leq 22$°. 2311 reflections were collected of which 1535 were unique with $I \geq 3\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined using the SHELX [36,37] suite of programs. The asymmetric unit was found to contain only half of the molecule, the remaining portion being generated by inversion through a centre of symmetry implicit in the space group. In the final least squares cycles, all atoms except for C1, C7 and C13 were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions. Final residuals after 11 cycles of least squares were $R = 0.0530$, for unit weights. Maximum final shift/e.s.d. was 0.006. The max and min residual densities were 0.075 and -0.11 e Å^{-3}, respectively. Final fractional atomic coordinates and isotropic thermal parameters, selected bond distances and angles are given in Tables 1 and 2, respectively. The molecular structure is shown in Fig. 1, along with the labelling scheme used.

X-Ray crystal structure of cyclo-*1,3,3,5,5-pentaphenyl-1-bora-3,5-disiloxane (2)*

A crystal of approximate dimensions 0.3 × 0.25 × 0.25 mm^3 was used for data collection.

Crystal data: $C_{30}H_{25}O_3BSi_2$, $M = 500.5$,monoclinic, $a = 15.736(4)$, $b = 10.892(3)$, $c = 17.099(6)$ Å, $\beta = 114.58(2)$°, $U = 2665.0$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 1.25$ g cm^{-3}, μ(Mo-K_α) = 1.24 cm^{-1}, $F(000) = 1048$. The c axial length was confirmed from an oscillation photograph, and is 0.634 Å longer than in a recently reported structure determination [15]. Data were measured at room temperature on a Hilger and Watts Y290 four-circle diffractometer in the range $2 \leq \theta \leq 22°$. 2238 reflections were collected of which 1314 were unique with $I \geq 3\sigma(I)$. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined using the SHELX [36,37] suite of programs. The asymmetric unit was found to contain only half of the molecule, the remaining portion being generated by rotation about a two-fold axis of symmetry passing through O1, B1, C1 and C4 (see Fig. 2). These latter four atoms were assigned half occupancy sites, the remaining atoms single occupancy. In the final least squares cycles the silicon, boron and oxygen atoms along with C(1)–C(4) were treated anisotropically. All other atoms were treated isotropically. Hydrogen atoms were included at calculated positions. Final residuals after 10 cycles of least squares were $R = 0.0876$, for unit weights. Maximum final shift/e.s.d. was 0.004. The max and min residual densities were 0.19 and -0.16 e Å^{-3}, respectively. Selected bond distances and angles are given in Table 2. The molecular structure is shown in Fig. 2, along with the labelling scheme used.

Tables of atomic coordinates for **2**, anisotropic temperature factors and hydrogen atom positions for both **1** and **2** will be deposited with the Cambridge Crystallographic Data Centre.

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