

Synthesis and Crystal Structure of the Novel Borosilicate Cage Compound [B(OSiPh₂OSiPh₂O)₃B]

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The novel borosilicate cage compound [B(OSiPh₂OSiPh₂O)₃B], **1**, synthesised from the reaction between boric acid and tetraphenyldisiloxanediol in toluene, was structurally characterised using X-ray crystallography.

Polymeric borosiloxanes are common products from reactions between boric acid and difunctional diorganosilanes, R₂SiX₂ (X = OR', halide etc.).¹ Several of these compounds exhibit both unusually high elasticity under suddenly applied stress and unusually high plasticity when the stress is applied slowly.¹ Largely because of their polymeric nature, detailed structural data on these compounds are lacking. Hence, if an analysis of structure-related properties of borosilicate compounds is to be effected, it is necessary to synthesise lower molecular mass crystalline compounds. We have begun a systematic study of such compounds and reported the structures of monomeric B–O–Si compounds with one, two or three B–OSiPh₃ groups.² These compounds were prepared by the dehydration reaction between B–OH and HO–Si containing species. An extension of this work has afforded the first example of a novel borosilicate cage, [B(OSiPh₂OSiPh₂O)₃B] **1**.[†]

Molecule **1**† has twofold crystallographic symmetry and contains two planar BO₃ units, which have their planes almost parallel [interplanar angle 4.3(1)°], and these BO₃ units are bridged by three –SiPh₂–O–SiPh₂– groups (Fig. 1). When viewed along the axis passing through the boron atoms, the BO₃ units are in a staggered configuration. The B–O bond lengths [1.349(3), 1.358(3) and 1.360(3) Å] and Si–O_B lengths [1.626(2), 1.632(2) and 1.634(2) Å] are within the reported ranges of similar bonds [1.313(2)³ to 1.374(7)⁴ Å and 1.615(3)⁴ to 1.655(4)⁴ Å respectively]. Likewise the Si–O_{Si} distances [1.610(2) and 1.624(2) Å] in **1** are not unusual and are close to the value of 1.616(1) Å in (Ph₃Si)₂O.⁵ The O–B–O and O–Si–O angles approach the expected trigonal and tetrahedral values, but the B–O–Si angles vary from 137.89(18) to 140.03(18)° and the Si–O–Si angles are 156.65(14) and 167.17(19)° (see Fig. 1 legend). In general, both B–O–Si².

and Si–O–Si² angles are remarkably flexible. The B–O–Si angles in **1** are within the reported range of 128.89(14)⁷ to 160.9(3)⁸ and the Si–O–Si angles are within the range of values found in, for example, the ten-membered ring system of [Ti(OSiPh₂OSiPh₂OSiPh₂OSiPh₂O)₂] (143.8 to 172.5°).⁸

Both the 'parallel' and 'staggered' features associated with the BO₃ units are also found in the recently reported dimeric boron derivative of silasesquioxane {[cyclo-C₆H₁₁Si₇O₁₂B]₂}, **2**.⁹ However, the relatively high *R* factor for the structure of molecule **2** prevented a full discussion of the bond distances and angles in that case.

The structure of **1** has some similarities with the barium complexes [Ba₃(OSiPh₂OSiPh₂O)₃(L)] [L = (tetraglyme)₂ or (hmpa)₅(H₂O) (hmpa = hexamethylphosphoric triamide)] which contain two barium ions in similar positions to the boron atoms in **1** (but coordinated further to tetraglyme, hmpa or water ligands) and the third barium ion located centrally between the other two and bonded to seven of the nine oxygen atoms in the three bridging OSiPh₂OSiPh₂O groups.¹⁰

The mechanism of the formation of **1** is of obvious interest and it is noteworthy that compounds with the same empirical formula as **1** which are formed from boric acid and diorganodialkoxysilanes with Me₂Si, MeV_ySi (V_y = vinyl), Et₂Si or MePhSi units instead of Ph₂Si are reported to be non-crystalline polymers.¹ The structure of B(OSiPh₃)₃ affords

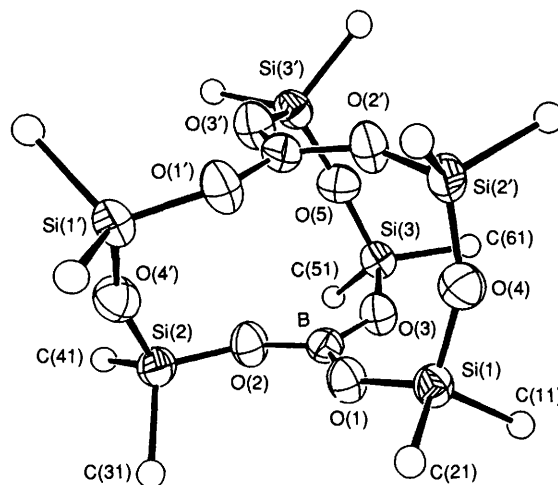


Fig. 1 A view of the central borosilicate cage section of [B(OSiPh₂OSiPh₂O)₃B] **1**, with numbering scheme. The crystallographic twofold symmetry axis passes through O(5). For clarity, the carbon atoms of phenyl groups attached to Si atoms are shown as spheres of an arbitrary size: all other phenyl C and H atoms are omitted. The silicon, oxygen and boron atoms are depicted with their thermal ellipsoids at the 50% level. Selected bond lengths (Å) and angles (°): B–O(1) 1.349(3), B–O(2) 1.360(3), B–O(3) 1.358(3), Si(1)–O(1) 1.634(2), Si(2)–O(2) 1.626(2), Si(3)–O(3) 1.632(2), Si(1)–O(4) 1.624(2), Si(3)–O(5) 1.610(2), Si(2)–O(4') 1.610(2), B...B' 3.479(4); O(1)–B–O(2) 120.61(25), O(1)–B–O(3) 120.64(25), O(2)–B–O(3) 118.75(24), B–O(1)–Si(1) 137.95(18), B–O(2)–Si(2) 140.03(18), B–O(3)–Si(3) 137.89(18), O(1)–Si(1)–O(4) 109.34(10), O(2)–Si(2)–O(4') 109.25(10), O(3)–Si(3)–O(5) 108.78(12), Si(1)–O(4)–Si(2') 156.65(14), Si(3)–O(5)–Si(3') 167.17(19).

† Synthesis of compound **1**: boric acid (0.173 g, 2.8 mmol) and tetraphenyldisiloxanediol (1.80 g, 0.043 mmol) were added to toluene (60 ml) in a Dean–Stark apparatus. The mixture was heated at reflux for 20 h. Removal of the toluene afforded a colourless solid which was redissolved and crystallised from a 3 : 1 mixture of dichloromethane–light petroleum (bp 40–60 °C). Yield: 0.791 g, 44.9%, mp 264–266 °C. Satisfactory elemental (C, H, B) analyses were obtained. IR Spectrum (KBr disc, $\nu_{\text{max}}/\text{cm}^{-1}$) 3100m, 3062m, 3025m, 1612m, 1443s, 1381vs, 1343vs, 1212m, 1125vs, 1100vs, 1080(sh)s, 1043m, 1012m, 881vs, 750s, 725vs, 700vs, 681s and 537vs; NMR (CD₂Cl₂, 294–296 K) δ (¹H) +17.5, δ (²⁹Si) –42.0.

‡ Crystal data for **1**: C₇₂H₆₀B₂O₉Si₆, *M_r* = 1259.4, colourless prismatic crystal, dimensions 0.35 × 0.35 × 0.45 mm, monoclinic, space group C2/c, *a* = 23.4572(11), *b* = 13.9213(7), *c* = 20.5184(12) Å, β = 98.001(4)°, *V* = 6635.2(6) Å³, *Z* = 4, *D_c* = 1.26 g cm⁻³; CAD4 diffractometer using the ω -2 θ mode, 7394 unique reflections, 4523 with *I* > 2.0 σ (*I*) treated as observed, 475 parameters, 2 θ_{max} = 54°, Mo–K α (λ = 0.7093 Å) radiation, *T* = 21 °C. Data corrected for Lorentz, polarisation and absorption effects. The structure was solved by direct methods (SHELX86)¹¹ and refined by full-matrix least-squares techniques using the NRCVAX¹² programs to an *R* value of 0.049, *R_w* = 0.058, GoF = 1.54. All non-hydrogen atoms were refined anisotropically; hydrogen atoms attached to carbon atoms were included as riding atoms, (C–H 0.95 Å). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

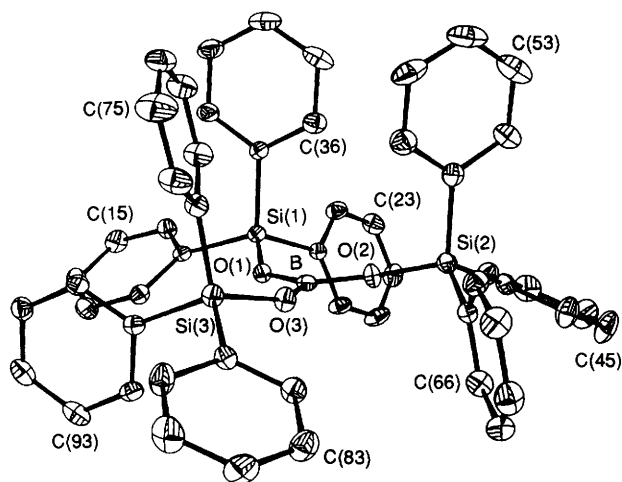


Fig. 2 A view of $B(OSiPh_3)_3$, ref. 2, with 35% probability ellipsoids

some insight into the factors controlling the formation of **1**.² In $B(OSiPh_3)_3$ (Fig. 2), the local geometry at each of the Si atoms is such that steric interactions within and between the $SiPh_3$ units causes three Si-Ph groups to be located with Si-C_{Ph} bonds [Si(1)-C(31), Si(2)-C(51) and Si(3)-C(71)] almost parallel. If the $SiPh_3$ units were replaced by $SiPh_2(OSiPh_2OH)$ units, it would be expected that an arrangement with three Si- $OSiPh_2OH$ groups present would adopt the same geometry. Subsequent reaction with a second boric acid molecule could yield **1**.

We are currently investigating the chemistry of **1** as a host molecule for both cations and anions and we are preparing other cages with different bridging groups.

We thank EOLAS (Ireland) for financial support to A. T. O'D., and NSERC (Canada) for Grants in Aid of Research to G. F.

Received, 19th July 1993; Com. 3/04215D

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