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Preliminary communication

A highly strained heterocyclosiloxane: synthesis and X-ray crystal structure of pentaphenylboracyclotrisiloxane $BSi_2O_3Ph_5$

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Abstract

The first X-ray structure determination of a neutral, uncomplexed molecular cyclotrisiloxane in which a skeletal silicon atom has been replaced by an atom of a heteroelement shows that $BSi_2O_3Ph_5$ possesses a highly strained six-membered ring with considerable bond angle distortion.

The deliberate introduction of ring-strain to cyclic inorganic molecules shows considerable promise as a means of facilitating their ring-opening polymerization to new classes of macromolecules. For example, recent work in phosphazene chemistry has shown that cyclic species which normally resist polymerization will polymerize when additional strain is induced using external, transannular ferrocenyl substituents [1]. In this case the additional ring-strain is manifested in the imposed non-planar, higher energy conformation of the phosphazene ring [2]. Recent results have also indicated that the ring-strain present in cyclic phosphazenes may be increased by the introduction of small skeletal heteroatoms. Thus, replacement of a skeletal phosphorus atom of $N_3P_3Cl_6$ by carbon (to give $N_3P_2CCl_5$) leads to a remarkable decrease in the observed polymerization temperature from 250 °C to 120 °C and provides access to polycarbophosphazenes, a new class of inorganic-organic polymers [3]. In this case, the presence of additional bond angle-strain in $N_3P_2CCl_5$ was detected by X-ray crystallography [4].

We are now exploring the introduction of ring-strain to other classes of cyclic inorganic compounds. Cyclosiloxanes comprise a well studied group of small molecules many of which polymerize to yield polyorganosiloxanes (silicones). At present, these macromolecules represent the most commercially useful class of inorganic polymers with applications as high performance oils, speciality elastomers, adhesives, and biomaterials [5]. The incorporation of small skeletal heteroatoms into cyclic siloxanes would be expected to increase the ring-strain present and therefore facilitate polymerization to polyheterosiloxanes, which should possess properties that complement and broaden those accessible with the conventional silicone

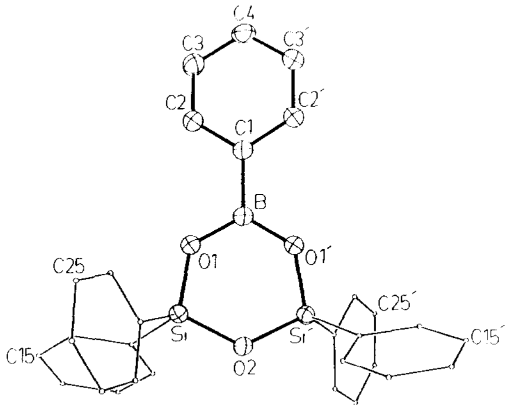

Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Si–O1 1.6388(13), Si–O2 1.6363(9), B–O1 1.3696(20), Si–O2–Si' 127.13(10), O1–Si–O2 106.55(8), B–O1–Si 128.89(14), O1–B–O1' 120.79(21).

polymer system. In this communication, we report our preliminary structural results on the introduction of additional strain to the siloxane ring system via the incorporation of a skeletal boron atom.

The borocyclotrisiloxane $BSi_2O_3Ph_5$ (**1**) was synthesized via a method similar to that previously used by Wannagat and Eisele to prepare the tetramethyl analogue $BSi_2O_3PhMe_4$ [6]. Our procedure involved the (3 + 3) cyclocondensation reaction of phenylboric acid with 1,3-dichlorotetraphenyldisiloxane in diethylether in the presence of triethylamine as a hydrogen halide acceptor [7]. Filtration [to remove $(NEt_3H)Cl$], followed by solvent removal and recrystallization of the residue from CH_2Cl_2–hexanes at −6 °C afforded colourless crystals of **1** (yield, 65%). In order to examine the structural changes arising from the replacement of a skeletal silicon atom by boron and in view of the lack of any crystallographic data on neutral, uncomplexed heterocyclotrisiloxanes [7,8] an X-ray diffraction study of a single crystal of **1** was undertaken *.

The molecular structure of **1** is shown in Fig. 1. The structural consequences of replacing a silicon atom (covalent radius 1.17 Å) by a smaller boron atom (covalent radius 0.80 Å) are dramatic [9]. This causes a considerable decrease of 0.26 Å in the distance between the two oxygen atoms O1 and O1' compared to the situation in $Si_3O_3Ph_6$ [10]. This contraction can be readily appreciated by noting the non-parallel nature of the Si–O1 and Si'–O1' bonds (see Fig. 1). The enforced decrease in the O1–O1' distance leads to a marked contraction of the Si–O2–Si' bond angle to 127.1(1)° compared to the value of 131.8(8)° in $Si_3O_3Ph_6$. The presence of

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* Crystallographic data: $C_{30}H_{25}BO_3Si_2$, $M = 500.5$, monoclinic, space group $C2/c$, $a = 15.703(6)$, $b = 10.864(3)$, $c = 17.733(4)$ Å, $\beta = 119.14(2)$, $V = 2641(14)$ Å^3, $Z = 4$, $D_c = 1.26$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu = 1.6$ cm^{-1}, $F(000) = 1048$, $R = 0.037$ for 215 parameters and 2152 reflections with $I > 3\sigma(I)$ measured on an Enraf–Nonius CAD 4 diffractometer at 293 K. The structure was solved by direct methods and refined by least squares, initially with isotropic and then with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were located and refined with isotropic thermal parameters. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

considerable angle-strain in **1** is further emphasized by a consideration of the much larger Si–O–Si bond angles in $Si_4O_4Ph_8$ [152.3(2)° and 167.4(2)°] [11] and unconstrained, linear disiloxanes such as $Me_3SiOSiMe_3$ [148.8(1)°] [12]. The additional strain present in **1** is also made evident by the significant widening of the O1–B–O1′ bond angle to 120.7(2)° compared to the analogous value in phenylboric acid [116.3(2)°] [13]. Interestingly, the O–Si–O bond angles in **1** [106.55(8)°] are only slightly different to those found in $Si_3O_3Ph_6$ [107.7(8)°]. The skeletal B–O bond lengths [1.370(2) Å] and average Si–O bond lengths [1.637(1) Å] are similar to the average values in phenylboric acid [1.371(2) Å] and $Si_3O_3Ph_6$ [1.64(1) Å], respectively. This indicates that the considerable structural distortion caused by the presence of the small boron atom is manifested mainly in changes in bond angles rather than bond lengths [14]. The six-membered BSi_2O_3 ring is approximately planar with only small (< 0.07 Å) deviations from the plane noted for Si1 and O1′. Similar, small deviations from planarity were also found in $Si_3O_3Ph_6$.

The additional bond-angle strain clearly present in **1** compared to $Si_3O_3Ph_6$ suggests that ring-opening reactions (e.g. polymerization) should be even more facile than for cyclotrisiloxanes in which small skeletal heteroatoms are not present. Studies of these and other reactions of **1** (and related species) are in progress and will be reported in a later paper.

Preparation of pentaphenylboracyclotrisiloxane, $BSi_2O_3Ph_5$

To a cooled (−78°C) solution of phenylboric acid (3.0 g, 25 mmol) and excess triethylamine (5.5 g, 55 mmol) in diethylether (1000 ml) was added slowly, dropwise a solution of 1,3-dichlorotetraphenyldisiloxane (11.3 g, 25 mmol) in the same solvent (50 ml). After warming to room temperature the reaction mixture was allowed to stir overnight. Filtration [to remove $(NEt_3H)Cl$], followed by solvent removal and recrystallization of the residue from CH_2Cl_2–hexanes at −6°C afforded colourless crystals of **1**, yield 8.1 g (65%). Data: ^{11}B NMR (CH_2Cl_2, $BF_3 \cdot OEt_2$ ref.) (δ in ppm): 28.2 (br, s). ^{13}C NMR ($CDCl_3$) (δ in ppm): 136.1 (s, *meta* B–Ph), 135.1 (s, *meta* Si–Ph), 134.7 (br s, *ipso* B–Ph), 133.7 (s, *ipso* Si–Ph), 132.4 (s, *para* B–Ph), 131.6 (s, *para* Si–Ph), 128.7 (s, *ortho* Si–Ph), 128.4 (s, *ortho* B–Ph). ^1H NMR ($CDCl_3$) (δ in ppm): 8.23, 7.88, 7.67, and 7.6-7.4 (all br, m). MS (EI) 500 (M^+, 100%).

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8 To the best of our knowledge, no X-ray crystallographic data exist for neutral, uncomplexed cyclotrisiloxanes in which a skeletal silicon atom is replaced by an atom of a heteroelement. A number of interesting metallosiloxanes have recently been studied but in neutral species where six-membered rings are present, coordination to skeletal oxygen atoms is observed. See, for example, M.B. Hursthouse, M.A. Mazid, M. Motevalli, M. Sanganee and A.C. Sullivan, J. Organomet. Chem., 381 (1990) C43 and references therein. A single example of a cycloboratrisiloxane has been previously reported but no X-ray studies were carried out: see ref. 6.

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14 It is interesting to note that the bond angle distortion observed in **1** is similar to that observed on replacement of a skeletal phosphorus atom in $N_3P_3Cl_6$ by a (smaller) carbon atom (see ref. 4).