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Comparison of the Flexibility of Eight-Membered Tetrasiloxane and Stannasiloxane Rings: A Crystallographic and Computational Study[†]

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The syntheses and crystal structures of the eight-membered *cyclo*-stannasiloxanes *cyclo*-[*t*-Bu(OH)Si(OSn*t*-Bu$_2$O)$_2$Si(OH)*t*-Bu] (**1**) and *cyclo*-{*t*-Bu$_2$Si[OSn(CH$_2$SiMe$_3$)$_2$O]$_2$Si*t*-Bu$_2$} (**2**) as well as the synthesis of the six-membered *cyclo*-stannasiloxane *cyclo*-{*t*-Bu$_2$Si[OSn(CH$_2$SiMe$_3$)$_2$]$_2$O} (**3**) are reported. Compound **1** crystallizes as its *trans* isomer, but the *cis* isomer dominates in solution. In agreement with the experimentally obtained results, ab initio and DFT calculations on the model compounds *cyclo*-(H$_2$SiO)$_4$ (**4**), *cyclo*-[H$_2$Si(OSnH$_2$)OSiH$_2$] (**5**), *cyclo*-O(H$_2$SiOSnH$_2$)$_2$O (**6**), and *cyclo*-[H$_2$Si(OSiH$_2$)OSnH$_2$] (**7**) indicate that the energetic preference to adopt puckered structures increases and the ring flexibility decreases with an increasing number of tin atoms in the ring. The rich diversity of puckered conformations is attributed to the steric demand of the different organic substituents.

Introduction

Molecular metallasiloxanes have attracted considerable attention in recent years due to their role as model compounds for structurally modified silica surfaces or minerals, their interesting physical properties, and their potential as precursors for new inorganic materials.[1−5] A rich structural diversity of eight-membered rings incorporating various heteroatoms, such as B, Al, Ge, Sn, P, Ti, Zr, Hf, Mo, and W, exists among the *cyclo*-metallasiloxanes.[6−27] Single-crystal X-ray diffraction studies show that even very similar compounds can have drastically different ring conformations. A large variety of ring conformations have also been observed in the crystal structures of *cyclo*-tetrasiloxanes.[28−39]

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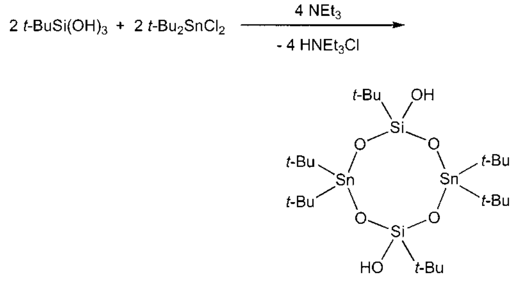
In this paper, we consider ring flexibility to be defined as a measure of the deformation energy corresponding to an appropriate dynamic ring motion, e.g., from a puckered conformation to planarity. The high flexibility of *cyclo*-tetrasiloxanes has been confirmed via experimental means such as vibrational spectroscopy,[40] as well as via computational studies on the parent compound, *cyclo*-$(H_2SiO)_4$.[41] The eight-membered *cyclo*-metallasiloxanes can be regarded as derivatives of *cyclo*-tetrasiloxanes, *cyclo*-$(R_2SiO)_4$, in which one or more silicon atoms are formally replaced by other metal atoms. To the best of our knowledge, there are no computational reports in the literature concerning the effects of substituting silicon with another metal on the flexibility of the metallasiloxane ring.

The focus of this study is the comparison of the ring flexibilities of *cyclo*-tetrasiloxanes and *cyclo*-stannasiloxanes in order to determine the effects of replacing silicon in eight-membered *cyclo*-tetrasiloxanes with tin. We first report the syntheses and characterization of two new eight-membered *cyclo*-stannasiloxanes, namely, *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] and *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$}, and classify their ring conformations according to a previously introduced classification scheme by Kök and Puff.[16] The new compounds are systematically related to the previously reported eight-membered *cyclo*-stannasiloxanes.[23]

We also report ab initio and DFT studies on *cyclo*-tetrasiloxane, *cyclo*-$(H_2SiO)_4$, and the eight-membered *cyclo*-stannasiloxanes *cyclo*-$[H_2Si(OSnH_2O)_2SiH_2]$, *cyclo*-$O(H_2SiOSnH_2)_2O$, and *cyclo*-$[H_2Si(OSiH_2O)_2SnH_2]$. In these model compounds the steric effect of the organic substituents is excluded and the direct influence of the tin and silicon atoms on the ring flexibility can be qualitatively addressed, whereas the impact of the steric demand of the organic substituents is examined via comparison with the experimentally obtained geometries obtained previously[23] and herein.

Results and Discussion

The equimolar reaction of *tert*-butylsilanetriol with di-*tert*-butyltin dichloride in the presence of the appropriate amounts of triethylamine affords *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] (**1**) in high yields (eq 1). Compound **1** was still the only stannasiloxane species formed even when the di-*tert*-butyltin dichloride:*tert*-butylsilanetriol ratio was increased to 3:2; no evidence of any substitution of the third OH group could be found.

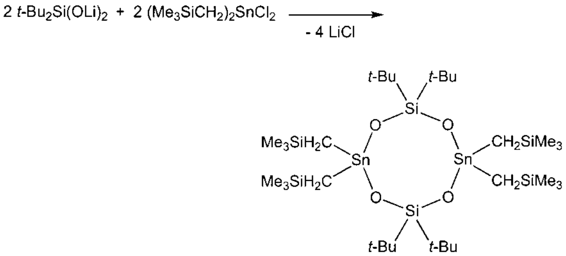


(1)

1

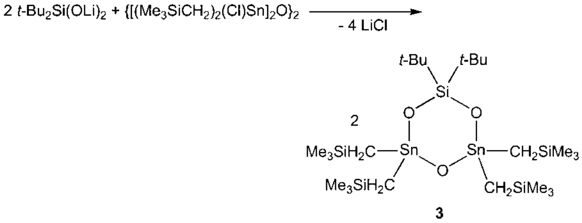
In contrast, the silanetriol $RSi(OH)_3$ (R = (2,6-$Me_2C_6H_3)NSiMe_3$) reacts with diphenyltin dichloride under comparable conditions with substitution of all hydroxy groups to afford the bicyclic compound $[RSi(OSnPh_2O)_3SiR]$.[42] The fact that all three hydroxy groups in *tert*-butylsilanetriol are reactive has been demonstrated by the synthesis of *t*-$BuSi(OSnMe_3)_3$.[43]

Reaction of dilithium di-*tert*-butylsilanediolate with bis(trimethylsilylmethyl)tin dichloride or bis(tetrakis-(trimethylsilylmethyl)dichlorodistannoxane) provides either the eight-membered ring *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$}(**2**) (eq 2) or the six-membered ring *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2]_2O$} (**3**), respectively (eq 3).



(2)

2



(3)

3

The *cyclo*-stannasiloxanes **1**, **2**, and **3** are colorless crystalline compounds that dissolve readily in organic solvents such as chloroform, toluene, or THF. According to ^{119}Sn NMR and ^{29}Si NMR spectroscopy ($CDCl_3$), *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] (**1**) consists of a mixture of two isomers in solution, *cis* ($\delta(^{119}Sn)$ −151.7, $\delta(^{29}Si)$ −47.8) and *trans* ($\delta(^{119}Sn)$ −153.8, $\delta(^{29}Si)$ −48.9), with a ratio of about 90 to 10 (Chart 1). The fact that the *cis* isomer dominates in solution was derived from the number and intensity ratios of the ^{1}H and ^{13}C NMR

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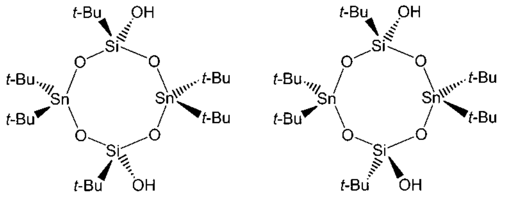
Chart 1



2, *cis* isomer **2**, *trans* isomer

resonances for the *tert*-butyl groups. Thus, the ^{1}H NMR spectrum of **1** displays three major and almost equally intense signals at 0.96 (Si-*t*-Bu), 1.30 (Sn-*t*-Bu), and 1.33 (Sn-*t*-Bu) ppm belonging to the *cis* isomer and a low-intensity signal at 0.97 (Si-*t*-Bu) belonging to the *trans* isomer. The signal for the tin-bonded *tert*-butyl group of the *trans* isomer is not visible but is likely to be superimposed with the signal for the *cis* isomer at 1.33 ppm. This view is supported by the fact that the intensity of the latter signal is slightly higher than the intensities of the two other signals assigned to the *cis* isomer. The ^{13}C NMR spectrum shows three major and almost equally intense signals for the quaternary carbons at 18.69 (Si*C*), 37.76 (Sn*C*), and 39.13 (Sn*C*) and three major and equally intense signals for the methyl carbons at 27.28, 29.65, and 29.84 ppm all belonging to the *cis* isomer. The corresponding signals of the *trans* isomer appear in the expected intensity ratio of about 1:2 at 19.0 (Si*C*) and 38.5 (Sn*C*) ppm, and at 27.44 ($SiCCH_3$) and 29.57 ($SnCCH_3$) ppm.

Given the well-established kinetic lability of Sn−O bonds in *cyclo*-stannasiloxanes,[5] the observation of both isomers suggests a dynamic equilibrium existing in solution between both isomers, which is fast on the laboratory time scale, but slow on the ^{119}Sn and ^{29}Si NMR time scale. Furthermore, the fact that the *cis* isomer of **1** is predominant in this equilibrium suggests that this isomer is thermodynamically favored. In this context it is worth mentioning that the mild hydrolysis of $PhSiCl_3$ affords the *all-cis* isomer of *cyclo*-$(Ph(OH)SiO)_4$ in high yield.[37] There was no evidence for the existence of other isomers; however, in the solid state, *all-cis cyclo*-$(Ph(OH)SiO)_4$ forms a hydrogen-bonded dimer.[37] One straightforward reason for the high yield of the *all-cis* isomer could be the directing effect of hydrogen bonding in solution. The kinetic stability of the Si−O bonds at room temperature and below (crystallization conditions) locks the molecules into the *all-cis* configuration. We suggest that the formation of a similar hydrogen-bonded dimer in solution might also be the reason for the preference of the *cis* isomer of *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] (**1**) in solution. It is worth mentioning that the related compound *cyclo*-[*t*-Bu(F)Si(OSn*t*-$Bu_2O)_2$Si(F)*t*-Bu] exists as a mixture of *cis* and *trans* isomers in solution with an approximately 41:59 ratio.[23]

The ring size of the compounds **1**−**3** is confirmed by the magnitude of the $^2J(^{119}\text{Sn}-\text{O}-^{29}\text{Si})$ and $^2J(^{119}\text{Sn}-\text{O}-^{117}\text{Sn})$ couplings, being 73/75 Hz (**1**), 76 Hz (**2**), 43 Hz (**3**), and 316 Hz (**3**), as well as by the integral ratio of the satellites with respect to the main signals.[23]

Conformational Flexibility of Eight-Membered *cyclo*-Siloxanes and *cyclo*-Stannasiloxanes. Three-dimensional geometry requires the sum of endocyclic angles of an *n*-membered ring to be less than $(n - 2) \times 180°$. Therefore, the aforementioned sum can be expressed for any eight-membered ring as $a \times 1080°$, where $a = 1$ for a planar ring and decreases as ring puckering increases. In the following discussion, ring puckering will be quantified using the "puckering factor" *a*, which can be obtained for an eight-membered ring by dividing the sum of its endocyclic angles by 1080°.

Recent computational work indicates that at the SCF/6-31G* level of theory, the puckered (S_4, $a = 0.967$) conformation of *cyclo*-$(H_2SiO)_4$ is the lowest energy conformation and is favored by only 1.05 kJ mol^{-1} over the planar conformation (D_{4h}, $a = 1$).[41] This result is consistent with the experimentally obtained gas-phase structures of *cyclo*-$(H_2SiO)_4$ (S_4, $a = 0.967$)[44] and *cyclo*-$(Me_2SiO)_4$ (S_4, $a = 0.944$).[45]

The X-ray structures of symmetrically substituted *cyclo*-tetrasiloxanes exhibit (nearly) planar conformations: *cyclo*-$(Me_2SiO)_4$ ($a = 1.000$),[28] monoclinic *cyclo*-$(Ph_2SiO)_4$ ($a = 0.998$),[32] triclinic *cyclo*-$(Ph_2SiO)_4$ (two molecules: $a = 0.995, 0.996$),[38] and *cyclo*-$(Cl_2SiO)_4$ ($a = 0.998$).[36,39] In contrast, the molecular structures of asymmetrically substituted *cyclo*-tetrasiloxanes show more puckered conformations: *cis cyclo*-{$Me_2Si[OSi(Me)Ph]_2SiMe_2$} ($a = 0.939$),[29] *trans cyclo*-{$Me_2Si[OSi(Me)Ph]_2SiMe_2$} ($a = 0.943$),[31] and *cyclo*-$O(Me_2SiOSiPh_2)_2O$ ($a = 0.959$),[30] which may be attributed to steric or crystal packing effects given the high flexibility of the parent compound. The only notable exception is *cyclo*-[*t*-$Bu_2Si(OSiMe_2O)_2Si$*t*-Bu_2] ($a = 1$),[35] in which the bulky *tert*-butyl groups induce a perfectly planar conformation. Two *cyclo*-tetrasiloxanes containing silanol groups are known, namely, *all-cis cyclo*-$[Ph(OH)SiO]_4$ ($a = 0.952$)[37] and *cis cyclo*-{$Ph_2Si[OSi(OH)MeO]_2SiPh_2$} ($a = 0.938$),[34] both of which are puckered.

In a previous work, we reported the X-ray structures of the eight-membered *cyclo*-stannasiloxanes, *cyclo*-[$Ph_2Si(OSiPh_2O)_2$Sn*t*-Bu_2] ($a = 0.949$), *cyclo*-[Ph_2Si(OSn*t*-$Bu_2O)_2SiPh_2$] ($a = 0.934$), and *cyclo*-$O(Ph_2SiOSn$*t*-$Bu_2)_2O$) ($a = 0.944$), which adopt puckered ring conformations.[23] These compounds can be regarded as derivatives of the parent *cyclo*-tetrasiloxane *cyclo*-$(Ph_2SiO)_4$, in which Ph_2SiO groups are formally replaced by *t*-Bu_2SnO groups. We also reported the solid-state structures of *cyclo*-[*t*-Bu_2Si(OSn*t*-$Bu_2O)_2Si$*t*-Bu_2] ($a = 0.992$) and *cyclo*-[*t*-Bu(F)Si(OSn*t*-$Bu_2O)_2$Si(F)*t*-Bu] ($a = 0.959$), which consist of the same ring constitution as *cyclo*-[Ph_2Si(OSn*t*-$Bu_2O)_2SiPh_2$].[23] Comparing the conformations of these three compounds shows that *cyclo*-[*t*-Bu_2Si(OSn*t*-$Bu_2O)_2Si$*t*-Bu_2] contains a significantly more planar ring than its analogues.

The molecular structures of *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] (**1**) and *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**) are shown in Figures 1 and 2, respectively. Crystal data are given in Table 1. Selected bond lengths and bond angles for **1** and **2** are listed in Tables 2 and 3, respectively. The conclusions drawn from NMR spectroscopy concerning the ring sizes and the Si−O−Sn connectivities are confirmed by their X-ray crystal structures. The ring of *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2$Si(OH)*t*-Bu] (**1**) lies across a crystallographic center of inversion like the other known *cyclo*-

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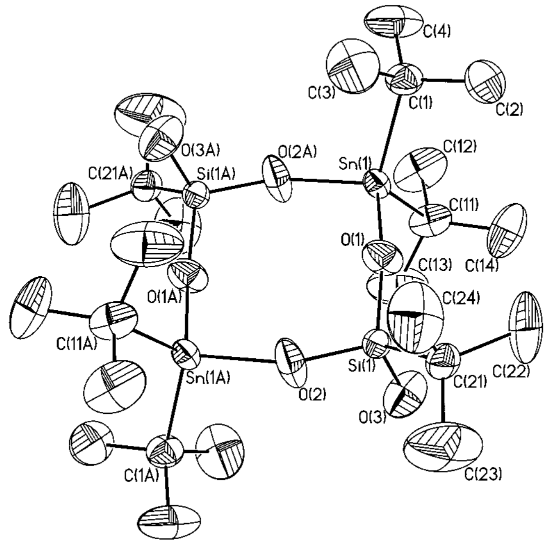

Figure 1. General view (SHELXTL-PLUS) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: a = $-x + 1$, $-y + 1$, $-z$).

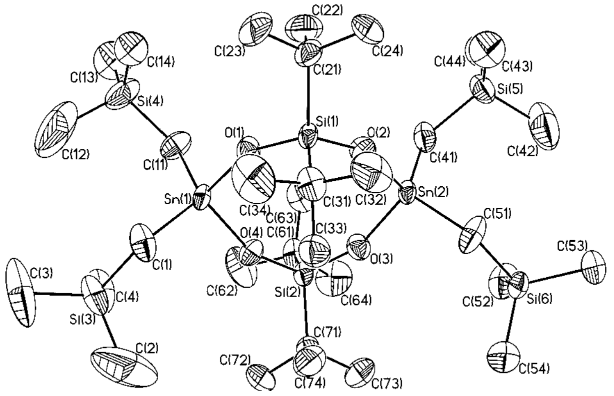

Figure 2. General view (SHELXTL-PLUS) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom numbering.

stannasiloxanes of the same ring constitution, i.e., (*cyclo*-[$Ph_2Si(OSn$*t*-$Bu_2O)_2SiPh_2$], *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2], and *cyclo*-[*t*-Bu(F)Si(OSn*t*-$Bu_2O)_2Si(F)$-*t*-Bu], but *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**) lacks such centrosymmetry.[23] This observation is attributed to the less symmetric trimethylsilylmethyl groups in **2**.

In the solid state, *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2Si$-(OH)*t*-Bu] (**1**) was isolated as the *trans* isomer. The Mössbauer spectrum of **2** shows only one parameter set (I.S. 1.30 mm s^{-1}, Q.S. 2.35 mm s^{-1}), and the ^{119}Sn MAS NMR spectrum of **2** exhibits only a single resonance at −156.7 ppm, demonstrating that the *trans* isomer is exclusively formed in the solid state. The reason that the *trans* isomer is favored over the *cis* isomer might be the inversion symmetry in the former, which allows more effective packing in the crystal lattice.

The Si−O, Si−C, Sn−O, and Sn−C bond lengths are all within expected ranges and are comparable with those of related compounds.[23] The bond angles at tin and silicon resemble slightly distorted tetrahedral coordination geometries. Using the ring classification scheme of Kök and Puff,[16] the central ring core of *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2Si(OH)$*t*-Bu] (**1**) adopts a D-type conformation and that of *cyclo*-{*t*-$Bu_2Si[OSn$-$(CH_2SiMe_3)_2O]_2Si$*t*-Bu_2} (**2**) exhibits the novel K-type conformation (Figure 3).

Table 1. Crystal Data and Structure Refinement for 1 and 2

	1	2
formula	$C_{24}H_{56}O_6Si_2Sn_2$	$C_{32}H_{80}O_4Si_6Sn_2$
fw, g/mol	734.25	934.88
cryst syst	monoclinic	triclinic
cryst size, mm	0.25 × 0.20 × 0.20	0.48 × 0.48 × 0.16
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.598(1)	12.4365(4)
b, Å	12.859(1)	13.5555(6)
c, Å	16.167(1)	16.201(2)
α, deg	90	92.469(6)
β, deg	96.287(1)	100.844(5)
γ, deg	90	103.743(3)
V, Å^3	1776.7(3)	2594.6(4)
Z	2	2
ρ_{calcd}, Mg/m^3	1.372	1.197
ρ_{measd}, Mg/m^3	1.372(4)	1.18(1)
μ, mm^{-1}	1.502	9.186
F(000)	752	976
θ range, deg	2.99 to 27.14	2.79 to 54.86
index ranges	$-11 \leq h \leq 11$ $-16 \leq k \leq 16$ $-20 \leq l \leq 20$	$0 \leq h \leq 13$ $-14 \leq k \leq 13$ $-17 \leq l \leq 16$
no. of reflns collcd	31 162[a]	6795[b]
completeness to θ_{max}	99.8%	99.2%
no. of indep reflns/R_{int}	3924/0.0460	6432/0.1289
no. of reflns obsd with ($I > 2\sigma(I)$)	2392	5563
no. refined params	187	396
GooF (F^2)	0.984	1.045
R1 (*F*) ($I > 2\sigma(I)$)	0.0387	0.0825
wR2 (F^2) (all data)	0.0985	0.2305
$(\Delta/\sigma)_{max}$	<0.001	<0.001
largest diff peak/hole, e/Å^3	0.526 and −0.555	2.391 and −2.215

[a] Mo Kα radiation. [b] Cu Kα radiation.

In the crystal lattice of the hydroxy-substituted stannasiloxane ring *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2Si(OH)$-*t*-Bu] (**1**) the molecules are connected by intermolecular O(3)−H···O(3b) hydrogen bridges of 2.94(1) Å, giving rise to an infinite chain of parallel packed eight-membered rings (Figure 4). This value is at the upper range of hydrogen bridges reported so far for organosilanols.[46] It can be best compared with the hydrogen bonds of 2.705/2.704 Å and 2.678−2.690 Å found for *t*-$BuSi(OH)_3$[47] and [*t*-$Bu(OH)_2Si]_2O$,[48] respectively.

Notably, the ring of *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2$-Si*t*-$Bu_2$} (**2**, *a* = 0.985) is significantly flatter than those of *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2Si(OH)$*t*-Bu] (**1**, *a* = 0.952), *cyclo*-[*t*-Bu(F)Si(OSn*t*-$Bu_2O)_2Si(F)$*t*-Bu] (*a* = 0.959), and *cyclo*-[$Ph_2Si(OSn$*t*-$Bu_2O)_2SiPh_2$] (*a* = 0.934), and it resembles more the almost planar conformation of *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2] (*a* = 0.992).[23] Therefore, it can be surmised that the *tert*-butyl groups at the silicon atoms cause the rings in *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2] and *cyclo*-{*t*-$Bu_2Si[OSn$-$(CH_2SiMe_3)_2O]_2Si$*t*-Bu_2} (**2**) to flatten. A similar observation was made by comparing the unsymmetrically substituted *cyclo*-tetrasiloxanes. Only in the case of the *tert*-butyl-substituted compound *cyclo*-[*t*-$Bu_2Si(OSiMe_2O)_2$-

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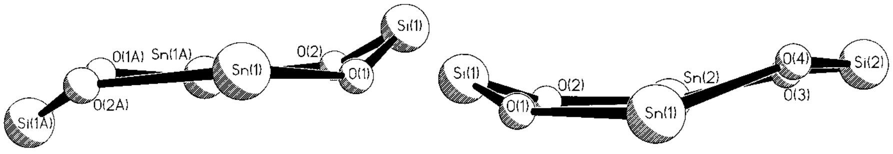


0 0 0 + 0 0 0 −
D-type

0 0 + + + 0 0 +
K-type

Figure 3. Classification scheme for eight-membered *cyclo*-stannasiloxanes **1** and **2**.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1[a]

Sn(1)−O(1)	1.936(3)	Sn(1)−O(2a)	1.953(3)
Sn(1)−C(1)	2.170(5)	Sn(1)−C(11)	2.163(5)
Si(1)−O(1)	1.596(3)	Si(1)−O(2)	1.592(3)
Si(1)−O(3)	1.634(5)	Si(1)−C(21)	1.874(4)
O(3)−H(3)	0.90(7)		
O(1)−Sn(1)−O(2a)	105.65(15)	O(1)−Si(1)−O(3)	108.6(2)
O(1)−Si(1)−O(2)	109.8(2)	Sn(1)−O(1)−Si(1)	153.0(2)
O(2)−Si(1)−O(3)	112.6(2)	Sn(1a)−O(2)−Si(1)	145.5(2)
Sn(1)−O(1)−Si(1)−O(2)	−88.4(5)	O(1)−Si(1)−O(2)−Sn(1a)	48.7(5)
Si(1)−O(2)−Sn(1a)−O(1a)	−20.2(5)	O(2)−Sn(1a)−O(1a)−Si(1a)	−67.5(5)
Sn(1a)−O(1a)−Si(1a)−O(2a)	88.4(5)	O(1a)−Si(1a)−O(2a)−Sn(1)	−48.7(5)
Si(1a)−O(2a)−Sn(1)−O(1)	20.2(5)	O(2a)−Sn(1)−O(1)−Si(1)	67.5(5)

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

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 2

Sn(1)−O(1)	1.923(7)	Sn(1)−O(4)	1.949(7)
Sn(1)−C(1)	2.119(13)	Sn(1)−C(11)	2.131(11)
Sn(2)−O(2)	1.942(7)	Sn(2)−O(3)	1.949(7)
Sn(2)−C(41)	2.098(14)	Sn(2)−C(51)	2.109(12)
Si(1)−O(1)	1.621(7)	Si(1)−O(2)	1.598(7)
Si(1)−C(21)	1.882(12)	Si(1)−C(31)	1.881(13)
Si(2)−O(3)	1.598(8)	Si(2)−O(4)	1.606(7)
Si(2)−C(61)	1.900(13)	Si(2)−C(71)	1.892(13)
O(1)−Sn(1)−O(4)	105.3(3)	Sn(1)−O(1)−Si(1)	153.9(5)
O(2)−Sn(2)−O(3)	105.8(3)	Sn(2)−O(2)−Si(1)	157.1(5)
O(2)−Si(1)−O(1)	112.4(4)	Sn(1)−O(4)−Si(2)	156.6(5)
O(3)−Si(2)−O(4)	112.6(4)	Sn(2)−O(3)−Si(2)	157.7(5)
O(2)−Si(1)−O(1)−Sn(1)	45.1(14)	O(4)−Sn(1)−O(1)−Si(1)	−13.3(14)
O(1)−Si(1)−O(2)−Sn(2)	−44.5(15)	O(3)−Sn(2)−O(2)−Si(1)	15.9(15)
O(4)−Si(2)−O(3)−Sn(2)	−21.3(15)	O(2)−Sn(2)−O(3)−Si(2)	22.8(14)
O(3)−Si(2)−O(4)−Sn(1)	43.7(12)	O(1)−Sn(1)−O(4)−Si(2)	−49.3(12)

Si*t*-Bu$_2$] (a = 1.000) was a planar conformation found (see above).[35]

The *cyclo*-tetrasiloxanes that possess planar solid-state ring geometries have identical reactivities to those that possess puckered solid-state ring geometries. However, the flatter stannasiloxane compounds, *cyclo*-[*t*-Bu$_2$Si(OSn*t*-Bu$_2$O)$_2$Si*t*-Bu$_2$] and *cyclo*-{*t*-Bu$_2$Si[OSn(CH$_2$SiMe$_3$)$_2$O]$_2$Si*t*-Bu$_2$}(**2**), are moisture-sensitive unlike the other aforementioned (more puckered) eight-membered *cyclo*-stannasiloxanes.[23] Apparently, *cyclo*-tetrasiloxanes, *cyclo*-(R$_2$SiO)$_4$, can easily adopt planar ring conformers owing to the high flexibility of the Si−O−Si linkages. However, if Si−O−Sn linkages are less flexible, the widening of the endocyclic angles that accompanies flattening leads to the possibility of increased angular strain within the ring. This idea is examined below in greater detail.

Ab Initio and DFT Studies of *cyclo*-(H$_2$SiO)$_4$ (4), *cyclo*-[H$_2$Si(OSnH$_2$O)$_2$SiH$_2$] (5), *cyclo*-O(H$_2$SiO-SnH$_2$)$_2$O (6), and *cyclo*-[H$_2$Si(OSiH$_2$O)$_2$SnH$_2$] (7). The ring compositions of the stannasiloxanes **5**−**7** are shown in Chart 2. At the SCF/(v)TZa level of theory, geometry optimizations of all three *cyclo*-stannasiloxanes **5**−**7** converged toward planar rings, regardless of starting structure. A similar observation has been previously reported for the parent *cyclo*-tetrasiloxane *cyclo*-(H$_2$SiO)$_4$ (**4**), where the planar conformation was the only minimum on the SCF/6-311G(d,p) potential energy surface.[41] The point groups, calculated energies, and selected geometric parameters of the SCF/(v)TZa optimized structures of **5**−**7** are listed in Table 4. The calculated Si−O and Sn−O bond lengths of **5**−**7** are in good agreement with the experimentally obtained parameters for **1**, **2**, and those of the already reported *cyclo*-stannasiloxanes. The calculated O−Si−O and O−Sn−O angles also agree well with experimental values; however, the experimental Si−O−Si, Si−O−Sn, and Sn−O−Sn angles are always significantly lower than the calculated values because the eight-membered rings in **1**, **2**, and the previously reported eight-membered *cyclo*-stannasiloxanes are puckered.[23] It is also noteworthy that the calculated Si−O−Sn and/or Sn−O−Sn angles in **6** and **7** are always narrower than the calculated Si−O−Si angles. Vibrational frequency calculations indicate that all three planar structures are minima on their respective potential energy surfaces at the SCF/(v)TZa level of theory. All three minima possess six vibrational modes with frequencies less than 100 cm^{-1}, and in each case, five of the six low-frequency

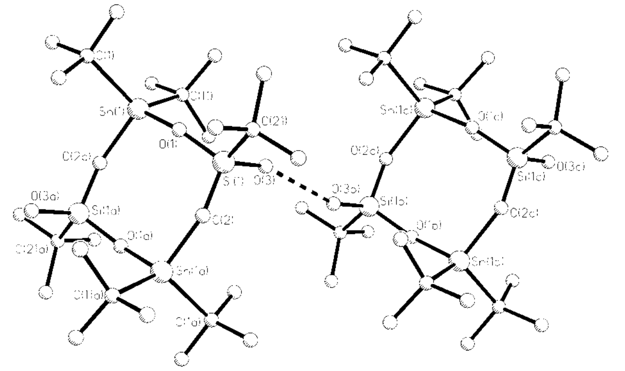
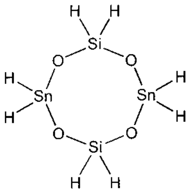


Figure 4. Side view (SHELXTL-PLUS) of the infinite chain of **1** formed by intermolecular hydrogen bridges (symmetry transformations used to generate equivalent atoms: a = $-x + 1, -y + 1, -z$; b = $-x, -y + 1, -z$).

Chart 2



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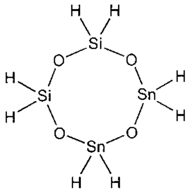

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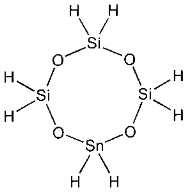

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Table 4. SCF/(v)TZa Calculated Total Energies (hartree) and Geometric Parameters (Å, deg) of the Planar Conformations of 5−7

	5	6	7
point group	D_{2h}	C_{2v}	C_{2v}
energy	−888.8227786	−888.8214265	−1174.5873477
Si−O	1.617	1.611 1.623	1.613 1.619 1.626
Sn−O	1.930	1.925 1.938	1.934
Si−O−Si		169.5	164.1
Si−O−Sn	161.2	159.3	157.8
Sn−O−Sn		157.1	
O−Si−O	111.9	111.0	109.9 110.7
O−Sn−O	105.7	106.4	105.0

vibrations correspond to out-of-plane deformations, indicating that the rings in **5**−**7** are very flexible.

The geometry optimizations of **5**−**7** were repeated at the B3LYP/(v)TZb level of theory to determine if the inclusion of electron correlation effects and the use of a more extended basis set would reproduce the experimental observation of puckering within the compounds *cyclo*-[*t*-Bu(OH)Si(OSn*t*-$Bu_2O)_2Si(OH)$*t*-Bu] (**1**), *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**), and the previously published eight-membered *cyclo*-stannasiloxanes. The significantly higher cost of this method precluded the performance of a full conformational study at this level of theory. However, the results herein are sufficient to provide an insight into the relative flexibilities of eight-membered *cyclo*-stannasiloxanes. The D_{4h} and S_4 conformations of the parent compound *cyclo*-$(H_2SiO)_4$ (**4**) were also revisited at this level of theory for comparison.

At the B3LYP/(v)TZb level of theory, the S_4 conformation of *cyclo*-$(H_2SiO)_4$ (**4**) is calculated to be only 0.6 kJ mol^{-1} lower in energy than the planar D_{4h} conformation. This result is consistent with published electron diffraction data which indicate that the S_4 conformation is the most stable for both *cyclo*-$(H_2SiO)_4$ (**4**) and *cyclo*-$(Me_2SiO)_4$.[44,45] Furthermore, the very small energy difference between the planar and puckered conformations of **1** is consistent with experimental vibrational data that indicates that *cyclo*-$(Me_2SiO)_4$ is extremely flexible.[40]

Two stationary points, one corresponding to a planar ring and the other to a puckered ring, were located at the B3LYP/(v)TZb level of theory for each of **5**−**7**. The calculated energies, selected geometric parameters, and *a* values of the planar and puckered conformations of **4**−**7** are listed in Tables 5 and 6, respectively. Side-on views of the puckered conformations of **4**−**7** are shown in Figure 5. The B3LYP/(v)TZb calculated Si−O and Sn−O bond lengths are systematically longer than the SCF/(v)TZa calculated values by approximately 0.01 and 0.02 Å, respectively, but are still in excellent agreement with the experimental bond lengths observed in compounds **1**, **2**, and the previously published eight-membered *cyclo*-stannasiloxanes.[23]

In agreement with the SCF/(v)TZa results, the Si−O−Sn and/or Sn−O−Sn angles in the B3LYP/(v)TZb optimized structures of both planar and puckered conformations of *cyclo*-$O(H_2SiOSnH_2)_2O$ (**6**) and *cyclo*-$[H_2Si(OSiH_2O)_2SnH_2]$ (**7**) adopt smaller values compared to the Si−O−Si angles. However, at the B3LYP/(v)TZb level of theory, all four eight-membered rings are predicted to favor puckered structures. Furthermore, with increasing Sn substitution, the energy difference between the puckered and planar conformations increases, while *a* decreases. All of these facts indicate that substitution of silicon by tin atoms causes the angle at oxygen to become slightly less flexible and to prefer smaller values, hence resulting in a more puckered and less floppy ring. The experimentally obtained geometries of the series *cyclo*-$[Ph_2Si(OSiPh_2O)_2Sn$*t*-$Bu_2]$ ($a = 0.949$), *cyclo*-$[Ph_2Si(OSn$*t*-$Bu_2O)_2SiPh_2]$ ($a = 0.934$), *cyclo*-$O(Ph_2SiOSn$*t*-$Bu_2)_2O)$ ($a = 0.944$) appear to obey this trend. However, the stannasiloxane rings are still sufficiently flexible that steric or crystal-packing effects could cause further ring distortion to occur, as evidenced by the range of experimentally observed *a* values.

With the exception of the compounds *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**) and *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2] the *a* values of the crystal structures (see above) lie reasonably close to the values for the calculated parent compounds. The *a* values for *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**) and *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2] both indicate that their rings are significantly flatter than the other rings in their class, which is attributable to the steric demand of the *t*-Bu_2Si groups. The planar conformation of *cyclo*-$[H_2Si(OSnH_2O)_2SiH_2]$ (**5**) is calculated to be 8.7 kJ mol^{-1} less stable than its puckered conformation at the B3LYP/(v)TZb level of theory. We postulate that a substantial part of this energy difference arises from ring strain owing to the wider Si−O−Sn angles in the planar conformation. This view is supported by the increased reactivity of *cyclo*-{*t*-$Bu_2Si[OSn(CH_2SiMe_3)_2O]_2Si$*t*-$Bu_2$} (**2**) and *cyclo*-[*t*-$Bu_2Si(OSn$*t*-$Bu_2O)_2Si$*t*-Bu_2][23] compared to their more puckered analogues.

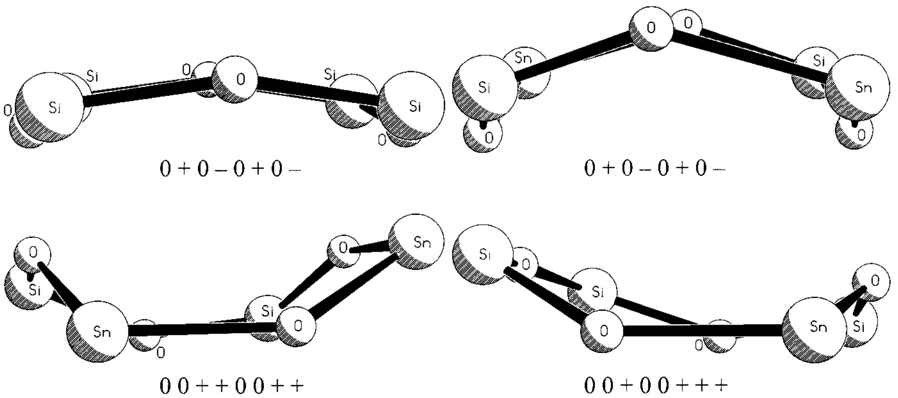

Figure 5. Side view of the B3LYP/(v)TZb optimized puckered conformations of **4**−**7**.

Table 5. B3LYP/(v)TZb Calculated Total Energies (hartree) and Geometric Parameters (Å, deg) of the Planar Conformations of 4−7

	4	**5**	**6**	**7**
point group	D_{4h}	D_{2h}	C_{2v}	C_{2v}
energy	−1464.2982950	−891.8952813	−891.8947313	−1178.0978428
Si−O	1.631	1.625	1.621 1.630	1.622 1.627 1.634
Sn−O		1.947	1.944 1.958	1.952
Si−O−Si	159.0		173.8	163.2
Si−O−Sn		159.1	153.5	155.0
Sn−O−Sn			155.9	
O−Si−O	111.0	113.7	112.1	111.2 112.3
O−Sn−O		108.0	109.5	107.9

Table 6. B3LYP/(v)TZb Calculated Total Energies (hartree) and Geometric Parameters (Å, deg) of the Puckered Conformations of 4−7

	4	**5**	**6**	**7**
point group	S_4	D_2	C_1	C_1
energy	−1464.2985136	−891.8985956	−891.8967578	−1178.0989348
Si−O	1.633	1.633	1.626−1.640	1.628−1.639
Sn−O		1.961	1.953−1.969	1.960 1.962
Si−O−Si	154.1		148.5	151.2 158.4
Si−O−Sn		141.8	140.1 144.4	142.6 143.3
Sn−O−Sn			141.2	
O−Si−O	110.9	112.7	111.5 112.0	111.2−112.1
O−Sn−O		106.7	106.9 108.2	106.1
rel energy (kJ mol^{-1})[a]	−0.6	−8.7	−5.3	−2.9
a	0.981	0.931	0.938	0.960

[a] Relative to planar conformation.

Conclusion

The present study indicates that while eight-membered *cyclo*-stannasiloxanes possess a significant amount of flexibility, they are less flexible than eight-membered *cyclo*-tetrasiloxanes. Apparently, the ring flexibility decreases with increasing tin substitution.

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk and vacuum-line techniques. Solvents were distilled from the appropriate desiccants prior to use. Literature procedures were used to prepare t-BuSi(OH)$_3$,[47] t-Bu$_2$Si(OH)$_2$,[49] t-Bu$_2$SnCl$_2$,[50] (Me$_3$SiCH$_2$)$_2$SnCl$_2$,[51] and {[(Me$_3$SiCH$_2$)$_2$(Cl)Sn]$_2$O}$_2$.[51]

Solution NMR spectra were recorded with a Bruker DRX 400 spectrometer at 149.21 (^{119}Sn), 79.49 (^{29}Si), 100.62 (^{13}C), and 400.13 (^{1}H) MHz in CDCl$_3$. Chemical shifts (δ) are given in ppm and are referenced against Me$_4$Sn (^{119}Sn) and Me$_4$Si (^{29}Si, ^{13}C, ^{1}H). The ^{119}Sn MAS NMR spectrum of compound **1** was obtained using a Bruker MSL 400 spectrometer using cross-polarization and high-power proton decoupling. Tetracyclohexyltin, (c-C$_6$H$_{11}$)$_4$Sn, was used as a second reference (δ −97.35 ppm) and to optimize Hartmann−Hahn CP matching conditions. However, we could not obtain reasonable ^{119}Sn MAS NMR spectra of the trimethylsilylmethyl-containing stannasiloxanes **2** and **3**. The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Model 1106). The densities of single crystals were determined using a Micromeritics Accu Pyc 11330.

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1,1,3,5,5,7-Hexa-*tert*-butyl-3,7-dihydroxy-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (1). A solution of di-*tert*-butyltin dichloride (3.04 g, 10.0 mmol) in diethyl ether (30 mL) was added to a mixture of *tert*-butylsilanetriol (1.36 g, 10.0 mmol) and triethylamine (2.02 g, 2.79 mL, 20.0 mmol) in diethyl ether (40 mL). Precipitation of triethylammonium chloride occurred immediately. After the precipitate was filtered, the solution was concentrated to approximately 10 mL and colorless crystals of **1** (3.21 g, 4.37 mmol, 87%, mp 196 °C) were deposited upon standing at −10 °C.

^{1}H NMR: δ 1.33 (18H, $^{3}J(^{1}\mathrm{H}-^{117/119}\mathrm{Sn}) = 96/100$ Hz; SnC*Me*$_{3}$, *cis* isomer); 1.30 (18H, $^{3}J(^{1}\mathrm{H}-^{117/119}\mathrm{Sn}) = 96/100$ Hz; SnC*Me*$_{3}$, *cis* isomer); 0.97 (SiC*Me*$_{3}$, *trans* isomer) 0.96 (18H; SiC*Me*$_{3}$, *cis* isomer). The signal for the tin-bonded *tert*-butyl group of the *trans* isomer is not visible and is likely to be superimposed with the signal at 1.33. ^{13}C NMR: δ 39.13 ($^{1}J(^{13}\mathrm{C}-^{117/119}\mathrm{Sn}) =$ 484/506 Hz; Sn*C*Me$_{3}$, *cis* isomer); 38.52 ($^{1}J(^{13}\mathrm{C}-^{117/119}\mathrm{Sn}) =$ 493/516 Hz; Sn*C*Me$_{3}$, *trans* isomer); 37.76 ($^{1}J(^{13}\mathrm{C}-^{117/119}\mathrm{Sn}) =$ 499/522 Hz; Sn*C*Me$_{3}$, *cis* isomer); 29.84 (SnC*Me*$_{3}$; *cis* isomer) 29.65 (SnC*Me*$_{3}$, *cis* isomer); 29.57 (SnC*Me*$_{3}$, *trans* isomer); 27.44; (SiC*Me*$_{3}$, *trans* isomer); 27.28 (SiC*Me*$_{3}$, *cis* isomer); 19.03 (Si*C*Me$_{3}$, *trans* isomer);18.69 (Si*C*Me$_{3}$, *cis* isomer). ^{29}Si NMR: δ −47.9 ($^{2}J(^{29}\mathrm{Si}-\mathrm{O}-^{117/119}\mathrm{Sn}) = 73$ Hz; integral 9, *cis* isomer); −48.9 ($^{2}J(^{29}\mathrm{Si}-\mathrm{O}-^{117/119}\mathrm{Sn}) = 75$ Hz; integral 1, *trans* isomer). ^{119}Sn NMR: δ −151.7 ($^{2}J(^{119}\mathrm{Sn}-\mathrm{O}-^{29}\mathrm{Si}) = 73$ Hz; integral 9, *cis* isomer); −153.8 ($^{2}J(^{119}\mathrm{Sn}-\mathrm{O}-^{29}\mathrm{Si}) = 74$ Hz; integral 1, *trans* isomer). ^{119}Sn MAS NMR: δ −156.7. IR (KBr): ν_{OH} 3696s, 3665s, 3465br cm^{-1}. Mössbauer spectrum: I.S. 1.30 mm s^{-1}, Q.S. 2.35 mm s^{-1}. Anal. Calcd for $C_{24}H_{56}O_{6}Si_{2}Sn_{2}$ (734.35): C, 39.26; H, 7.69. Found: C, 38.9; H, 8.2.

3,3,7,7-Tetra-*tert*-butyl-1,1,5,5-tetrakis(trimethylsilylmethyl)-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (2). To a solution of di-*tert*-butylsilanediol (882 mg, 5.00 mmol) in toluene (20 mL) at 0 °C was added via syringe a solution of butyllithium (2 M, 5 mL, 10.00 mmol) in hexane. The resulting mixture was stirred overnight before a solution of bis(trimethylsilyl)tin dichloride (1.82 g, 5.00 mmol) in toluene (30 mL) was added. The hexane was distilled off and the mixture heated at reflux for 12 h. The colorless precipitate of lithium chloride was removed via filtration and the solvent reduced to approximately 5 mL. Upon cooling to −10 °C, colorless crystals of **2** (2.15 g, 2.3 mmol, 92%, mp 150 °C) were deposited.

^{1}H NMR: δ 1.01 (36H; C*Me*$_{3}$); 0.40 (8H, $^{2}J(^{1}\mathrm{H}-^{117/119}\mathrm{Sn}) =$ 104/109 Hz; C*H*$_{2}$); 0.19 (16H; Si*Me*$_{3}$). ^{13}C NMR: δ 28.8 (C*Me*$_{3}$); 21.1 (*C*Me$_{3}$); 7.4 ($^{1}J(^{13}\mathrm{C}-^{117/119}\mathrm{Sn}) = 407/426$ Hz; *C*H$_{2}$Si); 2.0 (Si*Me*$_{3}$). ^{29}Si NMR: δ 0.9 ($^{2}J(^{29}\mathrm{Si}-\mathrm{C}-^{117/119}\mathrm{Sn}) = 21$ Hz); −23.3 ($^{2}J(^{29}\mathrm{Si}-\mathrm{O}-^{117/119}\mathrm{Sn}) = 76$ Hz). ^{119}Sn NMR: δ −42.7 ($^{2}J(^{119}\mathrm{Sn}-\mathrm{O}-^{29}\mathrm{Si}) = 77$ Hz). Anal. Calcd for $C_{32}H_{80}O_{4}Si_{6}Sn_{2}$ (934.97): C, 41.11; H, 8.62. Found: C, 41.1; H, 8.8.

5,5-Di-*tert*-butyl-1,1,3,3-tetrakis(trimethylsilylmethyl)-2,4,6-trioxa-5-sila-1,3-distannacyclohexane (3). To a suspension of di-*tert*-butylsilanediol (353 mg, 2.00 mmol) in hexane (10 mL) at 0 °C was added via syringe a solution of butyllithium (1.4 M, 2.86 mL, 4.00 mmol) in hexane. The resulting mixture was stirred overnight at room temperature. Bis[tetrakis(trimethylsilylmethyl)dichlorodistannoxane] (1.35 g, 1.00 mmol) in hexane (40 mL) was subsequently added, and the reaction mixture was heated at reflux for 10 h. The lithium chloride precipitate was removed via filtration and the solvent was evaporated to dryness, leaving a colorless residue of **3** (1.53 g, 1.96 mmol, 98%, mp 112 °C).

^{1}H NMR: δ 1.02 (18H; C*Me*$_{3}$); 0.35 (16H, $^{2}J(^{1}\mathrm{H}-^{117/119}\mathrm{Sn}) =$ 95/99 Hz; C*H*$_{2}$); 0.16 (32H; Si*Me*$_{3}$). ^{13}C NMR: δ 28.4 (C*Me*$_{3}$); 21.1 (*C*Me$_{3}$); 8.1 ($^{1}J(^{13}\mathrm{C}-^{117/119}\mathrm{Sn}) = 373/390$ Hz; *C*H$_{2}$Si); 1.8 (Si*Me*$_{3}$). ^{29}Si NMR: δ 1.1 ($^{2}J(^{29}\mathrm{Si}-\mathrm{C}-^{117/119}\mathrm{Sn}) = 20$ Hz); −15.8 ($^{2}J(^{29}\mathrm{Si}-\mathrm{O}-^{117/119}\mathrm{Sn}) = 43$ Hz). ^{119}Sn NMR: δ 25.5 ($^{2}J(^{119}\mathrm{Sn}-\mathrm{O}-^{117}\mathrm{Sn}) = 316$ Hz). Anal. Calcd for $C_{24}H_{62}O_{3}Si_{5}Sn_{2}$ (776.65): C, 37.12; H, 8.05. Found: C, 37.1; H, 8.3.

Crystallography. Intensity data for **1** were collected on a Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα radiation at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at 2 × 5 s per frame with a detector−θ-offset of 5°. The crystal-to-detector distance was 2.7 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysis of the duplicate reflections revealed no evidence for any decay. Intensity data for **2** were collected on a Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation at 291 K. Three standard reflections were recorded every 60 min, and an anisotropic intensity loss of up to 8.4% was detected during X-ray exposure. The structures were solved by direct methods (SHELXS97)[52] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL97).[53] The H atoms of the *t*-Bu groups of **1** were placed in geometrically calculated positions using a riding model and refined with a common isotropic temperature factor (C−H$_{\mathrm{tert.}}$ C−H 0.97 Å, U_{iso} 0.209(8) Å^{2}), and the H atom of one disordered OH group was located in the difference Fourier map and refined isotropically (O(3)−H(3) 0.90(7) Å, U_{iso} 0.12(3) Å^{2}). The occupancy of the disordered fragment (OH)Si was refined at 0.817(4) (Si(1), O(3), H(3)) and 0.183(4) (Si(1′), O(3′), respectively, whereas no H atom was located near O(3′). The H atoms of **2** were placed in geometrically calculated positions using a riding model and refined with common isotropic temperature factors for different C−H types (C$_{\mathrm{prim.}}$−H 0.96 Å, C$_{\mathrm{sec.}}$−H 0.97 Å, U_{iso} 0.169(9) Å^{2}). Disordered SiMe$_{3}$ groups were found with an occupancy of 0.6 for (13), C(14), C(43), C(44) and of 0.4 for (13′), C(14′), C(43′), C(44′), which were refined isotropically. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 54. The figures were created by SHELXTL-Plus.[55] Crystallographic data are given in Table 1, and selected geometric parameters for **1** and **2** are given in Tables 2 and 3.

Computational Methods

All ab initio and DFT molecular orbital calculations were performed using the GAUSSIAN 98 suite of programs.[56] Geometry optimizations and vibrational frequency calculations were performed for **5**−**7** using standard gradient techniques at the Hartree−Fock SCF level of theory. The all-electron 6-311+G(d) basis set was used for H, O, and Si, whereas the valence-triple-ζ (quasi-relativistic) pseudopotential basis set of Stoll et al.,[57] supplemented with a single d-polarization function from Huzinaga,[58] was used for Sn. Diffuse functions were added to Sn by repeating the outermost basis functions and multiplying their exponents by a factor of one-third. This combination of basis sets will be referred to as "(v)TZa" throughout this paper. Geometry optimizations were also performed for **4**−**7** using the B3LYP hybrid DFT-HF method

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with the 6-311+G(2df) basis set for H, O, and Si. The same basis set as above was used for Sn; however the d-polarization function was replaced with a two-membered d-polarization set from Huzinaga,[58] and a further f-polarization function, $f(\zeta)_{Sn} = 0.286$, optimized using the method of Höllwarth et al.,[59] was added. This combination of basis sets will be referred to as "(v)TZb" throughout this paper.

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for **1** and **2**; calculated geometries (SCF/(v)TZa and B3LYP/(v)TZb) and vibrational frequencies (SCF/(v)TZa) of **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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