Structural Characterization of 1,3-Cyclodisiloxanes

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Four single-crystal X-ray analyses are presented for 1,3-cyclodisiloxanes: tetramesitylcyclodisiloxane–benzene (**1**), two crystalline forms of tetramesitylcyclodisiloxane–toluene (**2a** and **2b**), and *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane (**3**). For all of these crystals the cross-ring silicon–silicon distances are 238–239 pm, and the Si–O distances are 167–168 pm. These crystal structures are compared with those of four previously reported cyclodisiloxanes, and the implications for chemical bonding in cyclodisiloxanes are discussed.

Introduction

Cyclic siloxanes $(R_2SiO)_n$, where *n* has a value of 3 or greater, have been known for a long time and are of considerable commercial importance.[1] The first example of a cyclodisiloxane ($n = 2$), tetramesitylcyclodisiloxane, was reported only in 1983.[2] Shortly afterward a crystal structure of a toluene solvate of this compound, $(Mes_2SiO)_2 \cdot C_7H_8$ (**2a**), was published.[3] In this structure, the nonbonded Si···Si distance was reported as 231 pm, slightly shorter than the average silicon–silicon single-bond distance of 234–235 pm. In a paper published in 1985,[4] the structure of compound **2a** was compared to those of two other cyclodisiloxanes, *trans*-1,3-dimesityl-1,3-di-*tert*-butylcyclodisiloxane (**4**) and *cis*-1,3-bis[bis(trimethylsilyl)amino]-1,3-dimesitylcyclodisiloxane (**5**), which showed transannular Si···Si distances of 240 and 235 pm. The Si···Si separations in these cyclodisiloxanes are all within the known range of Si–Si single-bond distances. This observation raised the question of the nature of the bonding in these molecules, spawning a theoretical controversy which still continues.

Theoretical calculations have been done mainly on the unsubstituted cyclodisiloxane, $(H_2SiO)_2$. Most of the early papers found no bonding interaction between the silicon atoms;[5–7] the short silicon–silicon separation was explained in terms of high strength or polarity of the Si–O bonds[6,7] or strong repulsions between lone pairs on the oxygen atoms,[7] forcing the silicon atoms into close proximity. NMR studies confirm the view that there is no σ bonding between the silicons. The silicon–silicon spin coupling, J_{Si-Si}, in an unsymmetrically substituted cyclodisiloxane was found to be only 4 Hz;[8] for silicon atoms forming a normal Si–Si σ bond, ${}^1J_{Si-Si}$ should be approximately 80–90 Hz.[9] In a 1987 paper, however, Grev and Schaefer proposed that although σ bonding between the silicons was nonexistent, a residual π interaction took place (an "unsupported π-bond").[10] A similar view has been advanced by Liang and Allen, who described the cross-ring interactions in cyclodisiloxane and related compounds in terms of "σ-bridged π-bonding".[11] π interactions of this type would not necessarily require Fermi contact and so would be consistent with small Si–Si spin coupling. Subsequent papers have come down on opposite sides of the bonding question. Thus, Somogyi and Tamás report calculations of Mayer's bond orders and find small but characteristic Si···Si bond orders indicating a Si···Si bond.[12] On the other hand, Gordon *et al.* conclude that any bonding between silicon atoms in cyclodisiloxanes must be negligible.[13]

Short cross-ring M···M distances, raising the question of M–M bonding, have recently been observed for cyclometalloxanes of other group 4 elements. The cyclodistannoxane $(R_2SnO)_2$, where R = $(Me_3Si)_2CH$, was found to have a Sn···Sn separation of 294 pm, compared to a normal Sn–Sn single-bond distance of 281 pm.[14] This compound exhibited an unexpected low-energy electronic transition, perhaps indicative of Sn···Sn interaction in an excited state. Similar unexpected UV absorption bands have been found for cyclodisiloxanes.[4] Short Ge···Ge separation distances have also been observed for two 1,3-cyclodigermoxanes.[15] In addition, it has been pointed out that the cyclodisiloxane structure may be an important feature of the surface structure of baked silica.[16]

In view of the countinuing interest in the bonding in 1,3-cyclodisiloxanes and related compounds, we decided to take a closer look at the structural evidence in this class

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[⊕] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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Table 1. Structural Data for Compounds 1–7[a]

compd	R	R′	temp (K)	Si···Si	Si–O	O···O	Si–O–Si	O–Si–O	site sym	ref
1·C_6H_6	Mes	Mes	113	239.1(2)	167.3(2)	234.1(3)	91.2(1)	88.8(1)	D_2	*b*
2a·C_7H_8	Mes	Mes	193	238.2(2)	167.0(2) 167.9(2)	235.2(4)	90.6(1)	89.2(1)	C_2	*b*
2b·C_7H_8	Mes	Mes	113	239.0(1)	167.0(3) 167.3(3) 167.5(2) 167.8(3)	234.4(5)	91.1(1) 91.1(1)	89.0(1) 88.7(1)	C_1	*b*
3	Mes	Ad	113	239.6(1)	167.7(2) 168.2(2)	235.4(3)	91.0(1)	89.0(1)	C_i	*b*
4	Mes	*tert*-butyl	230	239.6(1)	167.6(2) 167.9(2)	234.9(3)	91.1(1)	88.9(1)	C_i	4
5	Mes	$N(SiMe_3)_2$	250	234.9(1)	166.3(3) 166.7(3)	235.8(4)	89.7(1) 89.4(1)	90.2(1) 89.8(1)	C_1	4
6	Is	Is	150	243.1(2)	169.2(4) 169.9(4)	237.7(7)	91.3(2) 91.2(2)	89.0(2) 88.5(2)	C_1	17
7	Tb	Tip	300	239.9(3)	166.7(5) 167.5(5) 167.7(5) 168.2(5)	231.2(9)	91.7(2) 91.2(3)	87.5(3) 87.0(3)	C_1	18

[a] Benzene solvate of tetramesitylcylodisiloxane (**1**) at both 295 and 113 K, toluene solvate of tetramesitylcyclosiloxane at both 193 and 113 K (**2a**,**b**), *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisloxane (**3**), *trans*-1,3-dimesityl-1,3-di-*tert*-butylcyclodisiloxane (**4**), *cis*-1,3-bis[bis(trimethylsilyl)amino]-1,3-dimesitylcyclodisiloxane (**5**), tetrakis(2,4,6-triisopropylphenyl)cyclodisiloxane (**6**), and *cis*-1,3-bis[2,4,6-tris(bis(trimethylsilyl)methyl)phenyl]-1,3-dimesitylcyclodisiloxane (**7**). Interatomic distances are given in pm and angles in degrees. [b] This work.

of molecule. When tetramesitylcyclodisiloxane was crystallized from toluene, at −14 °C, we obtained either one of two polymorphic forms of the toluene solvate: the tetragonal form **2a** and the new monoclinic form **2b**. Both compounds were stable at low temperature. In successive experiments the crystalline form varied in seemingly random fashion, but "seeding" with either polymorph induced crystallization of that form only. The crystal structures of both **2a** and **2b** were determined, as were those for a benzene solvate of tetramesitylcyclodisiloxane (**1**) and for *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane (**3**). In this paper these new cyclodisiloxane structures, and the redetermined structure of **2a**, will be summarized and compared with the structures of four other cyclodisiloxanes: **4**, **5**, tetrakis(2,4,6-triisopropylphenyl)cyclodisiloxane (**6**),[17] and *cis*-1,3-bis[2,4,6-tris(bis(trimethylsilyl)methyl)phenyl]-1,3-dimesitylcyclodisiloxane (**7**).[18]

Results and Discussion

Tetramesitylcyclodisiloxane, of which X-ray-quality crystals of the benzene solvate **1** and toluene solvates **2a**,**b** were grown, was synthesized by the oxidation of tetramesityldisilene[19] with air or oxygen at room temperature. *trans*-1,3-Bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane (**3**) was synthesized by bubbling oxygen into a solution of 1,2-bis(1-adamantyl)dimesityldisilene at −78 °C.[20] The cyclodisiloxane products were purified by recrystallization.[21]

Important geometric features of the crystal structures are summarized in Table 1, along with corresponding information for other known cyclodisiloxane structures (**4**–**7**). Thermal ellipsoid diagrams for **1** and **3** are shown in Figures 1 and 2, respectively. Crystallographic information for the four structures is summarized in Table 2.

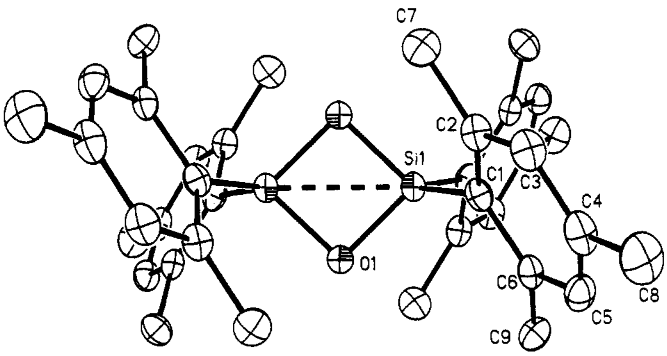

Figure 1. Thermal ellipsoid plot of tetramesitylcyclodisiloxane as its benzene solvate (**1**) with hydrogens omitted for clarity (50% probability).

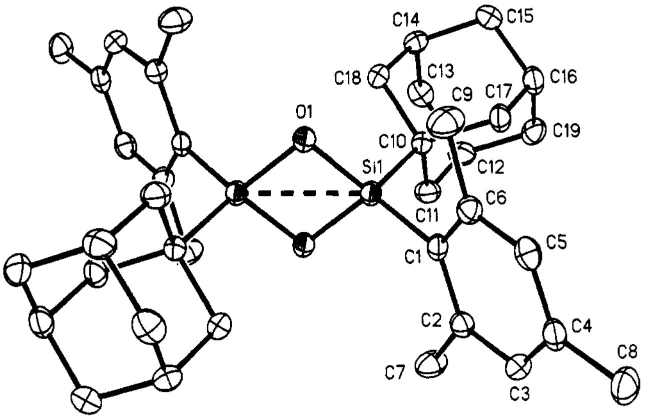

Figure 2. Thermal ellipsoid plot of *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane (**3**) with hydrogens omitted for clarity (50% probability).

The four structures obtained, **1**, **2a**,**b**, and **3**, as well as that of the *tert*-butyl compound **4** are very similar in most respects. The Si_2O_2 ring is planar within experimental error in each case, and the Si–Si distances span the narrow range from 238.2(2) to 239.6(1) pm. The Si–O distances all fall between 167.0(3) and 168.2(2) pm, and the Si–O–Si angles range from 90.6(1) to 91.2(1)°.

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Table 2. Summary of Crystallographic Data for Compounds 1 (at 295 and 113 K), 2, and 3[a]

	1	2a	2b	3
empirical formula	$C_{36}H_{44}O_2Si_2{\cdot}C_6H_6$	$C_{36}H_{44}O_2Si_2{\cdot}C_7H_8$	$C_{36}H_{44}O_2Si_2{\cdot}C_7H_8$	$C_{38}H_{52}O_2Si_2$
fw	643.0	657.0	657.0	597.0
cryst dimens, mm	0.5 × 0.2 × 0.2	0.5 × 0.5 × 0.2	0.4 × 0.4 × 0.1	0.3 × 0.25 × 0.2
cryst syst	orthorhombic	tetragonal	monoclinic	triclinic
space group	*Ccca*	$I4_1/a$	$C2/c$	$P\bar{1}$
cell params				
a, Å	12.0405(10)	12.200(2)	25.869(7)	8.158(3)
b, Å	20.075(3)	12.200(2)	14.605(2)	10.242(4)
c, Å	14.5942(13)	52.342(10)	20.446(2)	10.412(4)
α, deg	90	90	90	107.62(3)
β, deg	90	90	102.984(10)	91.94(3)
γ, deg	90	90	90	103.42(3)
V, Å^3	3527.6(4)	7791(2)	7527(2)	801.4(5)
Z	4	8	8	1
density (calcd), g/mL	1.211	1.120	1.160	1.237
abs coeff, mm^{-1}	1.162	1.073	1.110	0.144
F(000)	1384	2832	2832	324
temp, K	113(2)	193(2)	113(2)	113(2)
2θ range, deg	4.0–114.0	4.0–114.0	4.0–114.0	3.5–50.0
scan type	2θ–θ	2θ–θ	2θ–θ	Wyckoff
scan speed (in ω), deg/min	2–40	2–20	3–40	2–20
scan range	0.64	1.04	1.12	0.60
no. of data	1196	2628	5022	2836
largest diff peak, e/Å^3	0.38	0.65	0.46	0.39
largest diff hole, e/Å^3	−0.33	−0.44	−0.40	−0.28
$R(1)$ ($F \geq 4\sigma(F)$)	0.0505	0.0680	0.0593	0.0422
$R_w(2)$ (all)	0.1657	0.1943	0.2105	0.1139
goodness of fit	1.131	1.071	1.163	1.039

[a] Benzene solvate of tetramesitylcylodisiloxane (**1**) at both 295 and 113 K, toluene solvate of tetramesitylcyclodisiloxane (**2a,b**), and *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane (**3**).

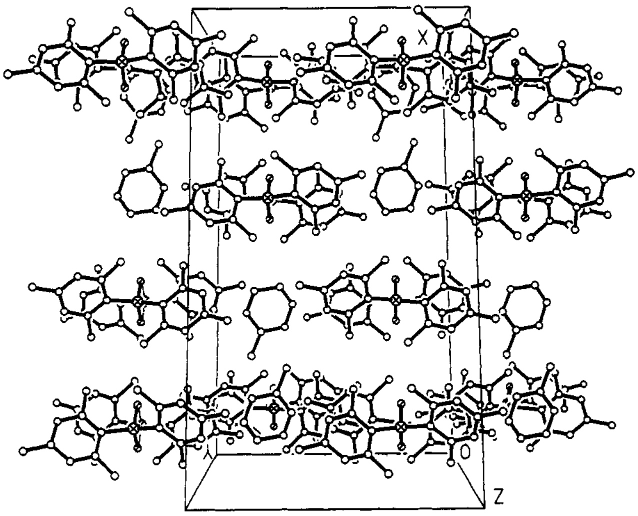

Figure 3. Packing diagram for the tetragonal toluene solvate of tetramesitylcyclodisiloxane (**2a**).

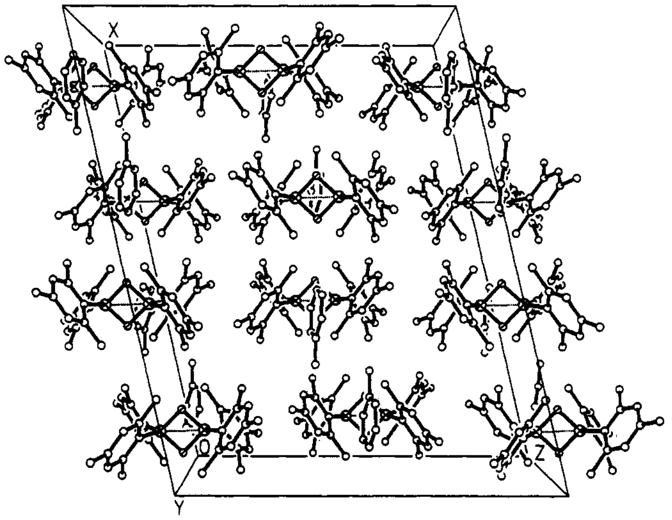

Figure 4. Packing diagram for the monoclinic toluene solvate of tetramesitylcyclodisiloxane (**2b**).

These results are consistent with Nagase and Kudo's theoretical calculations of $(H_2SiO)_2$ at the HF/6-31G* level.[6] Nagase and Kudo calculated the Si–O and Si···Si distances at 167.1 and 239.4 pm and Si–O–Si and O–Si–O angles of 91.5 and 88.5°. Our results are also in agreement with Grev and Schaefer's theoretical calculations for $(H_2SiO)_2$: Si–O = 166.1 pm, nonbonded Si···Si = 238.3 pm, Si–O–Si = 91.7°.[10]

In the toluene solvates **2a,b**, the toluene occupies disordered positions in the lattice. Packing diagrams for **2a,b** are shown as Figures 3 and 4. The toluene molecules in the solvent sites were refined with distance restraints. The occupancies of these molecules were refined to sum to 1 for the respective sites and had occupancies of 0.511(6) and 0.489(6) for **2a** and 0.635(7) and 0.365(7) for **2b**.

The structures of the other three cyclodisiloxanes **5–7** each show slight but significant differences from **1–4**. For compound **5**, the reported Si···Si distance is shorter, 234.9(1) pm. This difference may be due to an electronic effect of the unusual nitrogen substituent. This molecule also has a nonplanar Si_2O_2 ring, with a dihedral angle of 170°. In **6**, the Si···Si distance is lengthened to 243.1(2) pm, probably to relieve severe steric interactions between the bulky triisopropylphenyl substituents.

In the structure of the *cis* cyclodisiloxane **7**,[18] the Si···Si and Si–O distances are similar to those of **1–4**, but the Si_2O_2 ring is nonplanar. The distortion from planarity probably relieves steric repulsion between the extremely large bis(trimethylsilyl)methyl substituents on the *cis* aromatic rings.

This leaves only the first reported structure for the tetragonal toluene solvate **2a**,[2] for which the originally reported structure is very different from our redetermined structure of the same compound and from all other

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1[a]

	x	*y*	*z*	*U*(eq)
Si(1)	0	1904(1)	2500	18(1)
O(1)	972(2)	2500	2500	18(1)
C(1)	110(2)	1423(1)	1410(2)	20(1)
C(2)	–653(2)	1472(1)	677(1)	23(1)
C(3)	–414(2)	1148(1)	–147(2)	26(1)
C(4)	550(2)	795(1)	–289(2)	28(1)
C(5)	1289(2)	743(1)	433(2)	26(1)
C(6)	1084(2)	1044(1)	1278(1)	21(1)
C(7)	–1705(2)	1868(1)	733(2)	29(1)
C(8)	801(3)	479(1)	–1206(2)	37(1)
C(9)	1939(2)	967(1)	2023(1)	27(1)
C(1S)	567(2)	2503(1)	6683(2)	34(1)
C(2S)	1144(4)	2500	7500	30(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2a[a]

	x	*y*	*z*	*U*(eq)
Si(1)	449(1)	8367(1)	1060(1)	28(1)
O(1)	853(2)	7052(2)	1049(1)	32(1)
C(1)	893(2)	8943(2)	1373(1)	31(1)
C(2)	180(2)	9227(3)	1576(1)	37(1)
C(3)	615(3)	9578(3)	1806(1)	45(1)
C(4)	1733(3)	9675(3)	1845(1)	50(1)
C(5)	2429(3)	9392(3)	1647(1)	47(1)
C(6)	2032(2)	9022(2)	1415(1)	35(1)
C(7)	–1060(3)	9152(3)	1558(1)	49(1)
C(8)	2192(4)	10080(4)	2097(1)	76(1)
C(9)	2851(3)	8690(3)	1212(1)	44(1)
C(10)	797(2)	9218(2)	776(1)	29(1)
C(11)	415(3)	10309(2)	772(1)	34(1)
C(12)	612(3)	10967(3)	562(1)	47(1)
C(13)	1169(3)	10596(3)	349(1)	49(1)
C(14)	1535(3)	9526(3)	353(1)	47(1)
C(15)	1358(3)	8836(2)	558(1)	40(1)
C(16)	–219(3)	10800(3)	993(1)	46(1)
C(17)	1349(5)	11328(3)	120(1)	79(2)
C(18)	1787(4)	7667(3)	537(1)	59(1)
C(1A)	5000	7500	–134(2)	290(38)
C(2A)	5000	7500	147(1)	159(9)
C(3A)	5283(13)	6553(4)	280(1)	206(20)
C(4A)	5288(10)	6555(3)	546(1)	154(7)
C(5A)	5000	7500	679(1)	138(8)
C(2B)	5000	7500	441(1)	127(7)
C(3B)	5239(15)	6541(4)	308(1)	178(18)
C(4B)	5252(12)	6544(3)	43(1)	161(7)
C(5B)	5000	7500	–91(1)	227(29)
C(1B)	5640(45)	5571(17)	449(2)	302(31)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

cyclodisiloxane structures. Besides a very short Si···Si distance of 231 pm, this crystal structure gave Si–O bonds of unequal length, 165 and 172 pm, and a ring structure with the Si···Si distance shorter than the O···O distance. How can this earlier result be accounted for? One possibility is that the discrepancies stem from systematic errors in the original determination of **2a**, resulting both from the crystal-disordered toluene molecule and from residual overlap of adjacent diffraction maxima, due to the long *c* axial length of 52.42(1) Å and the use of Mo Kα radiation. The relatively high discrepancy factors ($R(F) = 0.079$, $R_w(F) = 0.100$ for observed data $|F_o| > 3\sigma|F_o|$) obtained for the structural analysis for **2a** in this earlier determination may support this interpretation. In any case, in view of the consistency of the tetramesityldisiloxane structure in **1**, **2a** (redetermined), and **2b**, we believe that the new structure for **2a** should replace the earlier determination.

Table 5. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2b[a]

	x	*y*	*z*	*U*(eq)
Si(1)	1165(1)	2498(1)	5939(1)	25(1)
Si(2)	1142(1)	2427(1)	4765(1)	25(1)
O(1)	1618(1)	2451(2)	5471(1)	27(1)
O(2)	689(1)	2454(2)	5236(1)	29(1)
C(1)	1126(2)	3619(3)	6363(2)	29(1)
C(2)	1485(2)	4350(3)	6372(2)	35(1)
C(3)	1384(2)	5192(3)	6646(2)	42(1)
C(4)	939(2)	5348(3)	6895(2)	45(1)
C(5)	593(2)	4627(3)	6888(2)	43(1)
C(6)	676(2)	3773(3)	6630(2)	33(1)
C(7)	1972(2)	4279(3)	6085(2)	45(1)
C(8)	832(2)	6278(3)	7168(3)	65(2)
C(9)	272(2)	3024(3)	6626(2)	41(1)
C(10)	1230(2)	1448(3)	6475(2)	30(1)
C(11)	1692(2)	1371(3)	7004(2)	30(1)
C(12)	1802(2)	554(3)	7354(2)	39(1)
C(13)	1473(2)	–202(3)	7212(2)	43(1)
C(14)	1023(2)	–113(3)	6708(2)	40(1)
C(15)	893(2)	675(3)	6331(2)	32(1)
C(16)	2066(2)	2164(3)	7203(2)	37(1)
C(17)	1611(2)	–1092(3)	7595(3)	58(1)
C(18)	403(2)	661(3)	5765(2)	44(1)
C(19)	1190(2)	3494(3)	4280(2)	29(1)
C(20)	1640(2)	3594(3)	4018(2)	35(1)
C(21)	1744(2)	4420(3)	3723(2)	47(1)
C(22)	1400(2)	5151(3)	3671(2)	53(1)
C(23)	948(2)	5038(3)	3910(2)	51(1)
C(24)	830(2)	4241(3)	4221(2)	39(1)
C(25)	2038(2)	2819(3)	4056(2)	42(1)
C(26)	1518(3)	6046(3)	3362(3)	77(2)
C(27)	338(2)	4219(3)	4503(2)	50(1)
C(28)	1086(2)	1327(3)	4288(2)	27(1)
C(29)	1433(2)	572(3)	4457(2)	32(1)
C(30)	1324(2)	–241(3)	4101(2)	36(1)
C(31)	882(2)	–355(3)	3580(2)	38(1)
C(32)	547(2)	386(3)	3415(2)	38(1)
C(33)	637(2)	1214(3)	3752(2)	32(1)
C(34)	1925(2)	601(3)	5026(2)	43(1)
C(35)	772(2)	–1254(3)	3216(2)	52(1)
C(36)	241(2)	1980(3)	3544(2)	41(1)
C(1S)	3144(3)	2165(5)	9462(4)	49(2)
C(2S)	3573(4)	1620(6)	9739(5)	59(3)
C(3S)	4074(4)	1928(6)	9891(4)	70(3)
C(4S)	4159(4)	2910(8)	9783(6)	82(4)
C(5S)	3763(4)	3393(6)	9510(5)	81(3)
C(6S)	3240(4)	3086(6)	9364(5)	64(3)
C(7S)	2598(3)	1789(7)	9296(5)	61(2)
C(1S′)	3652(4)	2519(9)	9644(7)	62(5)
C(2S′)	3386(6)	1707(10)	9770(9)	65(5)
C(3S′)	2863(6)	1622(11)	9529(10)	91(6)
C(4S′)	2581(5)	2275(11)	9104(8)	73(5)
C(5S′)	2833(5)	3046(10)	8969(8)	80(5)
C(6S′)	3369(5)	3143(9)	9219(7)	53(5)
C(7S′)	4237(5)	2569(12)	9857(8)	52(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Summary

In the crystal structures of seven 1,3-cyclodisiloxanes the Si···Si distances span the range from 234.9(1) to 243.1(1) pm, clustering around 239 pm. This separation is well within the bonding distance for Si–Si single bonds,[22] leaving open the question of chemical bonding in these molecules. The ring structures of cyclodisiloxanes are in quite good agreement with theoretical calculations on the parent molecule, $(H_2SiO)_2$.

Experimental Section

Syntheses. Tetramesitylcyclodisiloxane was synthesized by exposing a benzene solution of tetramesityldisilene[19] to air at

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[22] Si–Si σ bond lengths from 234 to 270 pm have been recorded. See: Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 79.

room temperature. The yellow tetramesityldisilene decolorizes over a period of a few hours, and crystals of **1** suitable for crystallography grew upon slow evaportion of the benzene. Oxidation of tetramesityldisilene can also be carried out by bubbling oxygen into a solution of the disilene. This procedure was used for **2a**, which was then recrystallized from toluene. The compound *trans*-1,3-bis(1-adamantyl)-1,3-dimesitylcyclodisiloxane was synthesized by bubbling oxygen into a benzene solution of *trans*-1,2-bis(1-adamantyl)-1,2-dimesityldisilene at −78 °C.[20] Oxidation of the disilene is completed within minutes; recrystallization from THF gave X-ray-quality crystals. The ^{1}H NMR spectra of the 1,3-cyclodisiloxane products matched those given in the original publications.[2–4,20]

Structure Determinations. Crystals of **2a,b** were grown from a toluene solution of tetramesityldisiloxane at approximately −14 °C. These crystals rapidly lost solvent when the solution was warmed to room temperature, and also when the crystals were exposed to air. To prevent loss of crystallinity, the solution containing the crystals was kept cold (−23 °C) and the crystals were immediately coated with a layer of Paratone-N upon removal from the solution. A crystal was selected and cut to a suitable size and then mounted on a thin glass fiber for X-ray analysis.

The X-ray crystallographic experiments were performed on a Siemens P4f diffractometer equipped with a low-temperature device; an Mo Kα X-radiation source (λ = 0.710 73 Å) was used for data acquisition of **3**, and Cu Kα (λ = 1.541 78 Å) was used for compounds **1** and **2a,b**.

The structures were solved by direct methods with the SHELXTL PLUS program and refined by the full-matrix least-squares refinement method on F^2 using the SHELXL-93 program.[23,24] The crystal systems and the space groups for all compounds were determined from the intensity data. The crystal systems were determined by merging symmetry-equivalent data. The space groups were determined from systematic absences and from statistical tests for center of symmetry on the intensity data and confirmed by the structure solution and refinement. In the final refinement cycles the non-hydrogen atoms were assumed to vibrate anisotropically, while the hydrogen atoms were included as idealized isotropic fixed contributors; the refinement converged to unweighted and weighted agreement factors of $R(1) = 0.0505$ and $R_w(2) = 0.1657$ for **1**, $R(1) = 0.0680$ and $R_w(2) = 0.1943$ for **2a**, $R(1) = 0.0593$ and $R_w(2) = 0.2105$ for **2b**, and $R(1) = 0.0422$ and $R_w(2) = 0.1139$ for **3**. The values for $R(1)$ are determined for data with $F > 4\sigma(F)$, and the values for $R_w(2)$ are determined for all data. The principal mean-square displacements for the silicon and neighboring atoms in **1** and **3** indicate that these atoms have similar, nearly isotropic thermal motion. The two compounds with disordered solvent, **2a,b** have values for the U_{ij} terms of the silicon and neighboring atoms somewhat larger than those found in **1** and **3**. A riding model[25] was applied to determine if the interatomic distances should be corrected for thermal motion. A 2/1 model was found to increase all of the distances reported in Table 1 by 1 esd or less. Thus, the interatomic distances reported in this manuscript are not correct for thermal motion. Crystal data and experimental details for the structure determination of all three compounds are provided in Table 2.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **1**, **2a,b**, and **3** (30 pages). Ordering information is given on any current masthead page.

OM930831W

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[23] The structure were solved using: Sheldrick, G. M. SHELXTL PLUS, Version 4.2; Siemens Analytical X-ray Instruments, Madison, WI, 1990. Refinements were carried out using the SHELXL-93 program: Sheldrick, G. M. *J. Appl. Crystallogr.*, in press. Scattering factors were taken from: *International Tables for Crystallography*; Kluwer: Boston, MA, 1992; Vol C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2.

[24] The structures were initially refined with the SHELXTL PLUS software, which refines structural parameters on F's. These results lead to relatively large values for the goodness-of-fit statistics, S. At the urging of a reviewer, the structures were re-refined with the SHELXL-93 program, which minimizes the weighted differences in F^2_s and coincidentally produces S values much closer to 1.0. The refinement on F^2_s resulted in geometric results nearly identical (within 2 esd's) with the results from the earlier refinements, except for the distances to the oxygen of **1**. The Si–O distance in **1** changed from 167.8(1) to 167.3(2) pm, and the O···O distance changed from 239.4(3) to 234.1(3) pm. Even these differences in interatomic geometry are within the ranges of the corresponding interactions detailed in Table 1.

[25] Johnson, C. K. *Crystallographic Computing*; Munskgaard: Copenhagen, 1970; pp 220–226.