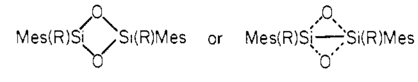
Isomer **2** is a pale yellow and not thermochromic when heated. It does show a reversible decolorization when cooled to −196 °C. **2** is more stable thermally than **1**, decomposing only above 220 °C after melting to a light yellow liquid at 165–173 °C. The nitrogen-substituted disilene isomers, **3a** and **3b**, are orange-red at room temperature (Figure 1). Upon cooling to −196 °C, **3b**, but not **3a**, shows a reversible change to yellow. As solid powders both **1** and **3** react with oxygen rapidly, being converted to their oxidation products upon simple exposure to the atmosphere within a few minutes at room temperature. Solid **2** react much more slowly, with a half-lifetime for oxidaton in air of several hours. Therefore **2** may be transferred from one vessel to another without the protection of an inert atmosphere, although it should be stored under nitrogen or argon. All three compounds oxidize in air to give analogous products, the cyclodisiloxanes **4–6**. The unusual structure of **4** and its implications for chemical bonding are described in the accompanying communication.[8]



4, R = mesityl
5, R = $N(SiMe_3)_2$
6, R = *tert*-butyl

Acknowledgment. Research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-82-0067 and by the National Science Foundational Science Foundation under Grant CHE-81-21112.

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(8) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.*, following paper in this issue.

Tetramesitylcyclodisiloxane: A Cyclic Siloxane with an Unusual Structure

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Cyclosiloxanes, $(R_2SiO)_n$, are compounds of considerable commercial importance as precursors to silicone polymers.[1] Although a large number of ring sizes can be obtained by the hydrolysis of difunctional silanes, the first members of this series, the cyclodisiloxanes, are almost unknown.[2] We report herein the unexpected structure of the recently reported tetramesitylcyclodisiloxane (**1**).[3] Compound **1** is produced nearly quantitatively from tetramesityldisilene (**2**) when the latter is simply exposed to atmospheric oxygen.[3] The cyclodisiloxane is a white powder (mp 215 °C) with surprising stability; it survives gas chromatography at 310 °C, prolonged heating in refluxing Decalin, and lengthy photolysis at 254 nm.

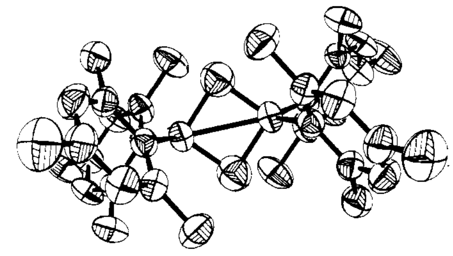


Figure 1. ORTEP drawing of tetramesitylcyclodisiloxane.

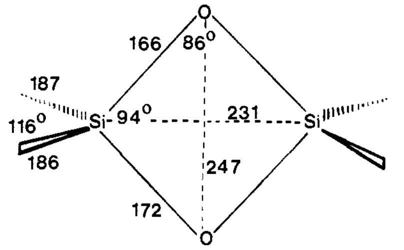
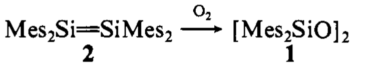


Figure 2. Important bond lengths (pm) and angles in **1**.



$$\underset{\mathbf{2}}{Mes_2Si{=}SiMes_2} \xrightarrow{O_2} \underset{\mathbf{1}}{[Mes_2SiO]_2}$$

Mes = 2,4,6-trimethylphenyl

An X-ray structure determination was undertaken, in order to understand the structural features that contribute to the stability of **1**. Crystals of the toluene solvate of **1** ($C_{36}H_{44}Si_2O_2{\cdot}C_7H_8$, *m* = 657.06) were obtained by slow cooling of a saturated toluene solution of **1** from room temperature to −10 °C. Compound **1** crystallizes in the tetragonal space group ($I4_1/a$) with $a = 1221.2$ pm and $c = 5242.5$ pm (−30 ± 5 °C, $\lambda_{Mo\ K\bar{\alpha}} = 71.037$ pm), $D_{calcd} = 1.12$ g/cm³, and $z = 8$.[4] Figure 1 is an ORTEP diagram of **1** which shows the silicon–oxygen ring structure. Important bond lengths and angles are displayed in Figure 2. The ring is nearly planar, the dihedral angle between the Si–Si–O three-member planes being 6°. The two independent silicon–oxygen bond lengths are 166 and 172 pm, somewhat longer than those found for other cyclic siloxanes (161–165 pm).[5] The Si–O–Si angle is 86°, highly constrained compared to normal siloxane bond angles of 140–180°.[6] A striking feature of this structure is the silicon–silicon distance of 231 pm, somewhat *shorter* than the normal Si–Si single-bond length of 234 pm. The distance between the oxygen atoms is 247 pm, slightly less than the sum of the Van der Waals radii for oxygen, ~280 pm.

Each silicon is coplanar with the attached carbon atoms and the other silicon atom. A slight twist (11°) about the silicon–silicon axis is observed for the two C–Si–C planes; the siloxane ring is roughly orthogonal to these planes. The molecular structure

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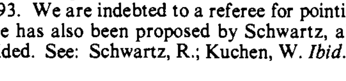
[†] University of Utah.

(1) Noll, W. "Chemistry and Technology of Silicones"; Academic Press: New York, 1968.

(2) An unstable silica polymorph, orthorombic silica, has been reported to contain the cyclodisiloxane structure unit



It reacts with water at room temperature. Weiss, V. A.; Weiss, A. Z. *Anorg. Allg. Chem.* **1954**, *276*, 93. We are indebted to a referee for pointing out that a disilaoxetane structure has also been proposed by Schwartz, although no structure proof was provided. See: Schwartz, R.; Kuchen, W. *Ibid.* **1955**, *279*, 84.

(3) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. West, R.; Fink, M. J.; Michl, J. *Science* (Washington, D.C.) **1981**, *214*, 1343.

(4) With $z = 8$ there is only $^1/_2$ formula unit per asymmetric unit. This is accommodated by the molecule being located on a 2-fold axis ($^1/_2$, $^1/_4$, *z*) that relates the two silicon atoms and the two oxygen atoms. The solvent molecule is distorted with the two independent overlapping quarter molecules also located on a 2-fold axis (0, $^1/_4$, *z*). The structure was solved by direct methods and refined by full-matrix least-squares refinement based on *F* using the 2292 data with $F_o > 3\sigma(F_o; R = 0.079$, GOF = 1.48). Tables of the final atomic coordinates, anisotropic thermal parameters, and selected distances and angles are given as supplementary material.

(5) Kiss, J.; Mencze, G. *Acta Crystallogr., Sect B* 1975, *B31*, 1214.

(6) Examples: $Me_3SiOSiMe_3$, 149°;[7] $(Me_2SIO)_4$, 143°,[8] $(Ph_2SiO)_4$, 160°;[9] $Ph_3SiOSiPh_3$, 180°.[10]

(7) Barrow, M. J.; Ebsworth, E. A. V.; Hardine, M. M. *Acta Crystallogr., Sect. B* 1979, *B35*, 2093.

(8) Steinfink, H.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1955**, *8*, 420.

(9) Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 522.

(10) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978**, *B34*, 124–128.

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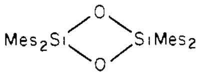
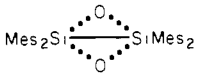
can be described as arising from a severely distorted trigonal-bipyramidal geometry about the silicons, with each silicon occupying an equatorial position of the other and the oxygens bridging adjacent apices.

The nature of bonding in the siloxane ring of **1** raises interesting questions. Two possible models will be considered: **1a**, the diamond-shaped distortion in the central ring, which places the two oxygen atoms 247 pm apart and the two silicon atoms only 231 pm apart, is the result of very severe lone pair–lone pair respulsions between the oxygen atoms. This repulsion overwhelms both the nonbonded repulsion between the silicon atoms and the bond angle preferences of the ring atoms. The Si–O bonds are lengthened because of strain in the ring, as well as by O–O repulsion. **1b**, a localized two-electron bond exists between the silicon atoms, leading to the short Si–Si distance and the observed distortion of the ring, at the cost of introducing an unfavorable, very small Si–O–Si bond angle. There is a delocalized, four-center six-electron bond about the periphery of the ring, accounting for the lengthened Si–O distances. If this view is adopted, the oxygen addition reaction breaks only the π and not the σ component of the Si═Si double bond in **2**.



1a



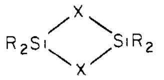
1b

Atomic orbitals on the silicon atoms in **1** must interact strongly, but it is not yet certain if the interaction is bonding or antibonding. Detailed theoretical calculations on model compounds may be instructive.[11] Treatment of **1** with lithium aluminum hydride leads to **3**, the product of cleavage of the cyclodisiloxane ring. However reduction of **1** with lithium naphthalide at −78 °C followed by quenching with water leads to the disilanediol **4**; the presence of a silicon–silicon bond in **4** suggests that one may likewise be present in **1**.

$$\underset{\mathbf{3}}{(\mathrm{Mes})_2\mathrm{SiHOH}} \xleftarrow[\mathrm{Et_2O}]{\mathrm{LiAlH_4}} \mathbf{1} \xrightarrow[\mathrm{THF},\ -78\ ^\circ\mathrm{C}]{\mathrm{Li/C_{10}H_8}} \rightarrow \xrightarrow[\mathrm{H^+}]{\mathrm{H_2O}} \underset{\mathbf{4}}{\mathrm{Mes_2SiOH{-}SiOHMes_2}}$$

Mes = 2,4,6-trimethylphenyl

The isoelectronic ring systems **5**–**7** do not show unusual silicon–silicon distances, the closest being 259 pm found in **5**. The cyclodithiane **8**, however, has a planar structure with a very small Si–S–Si angle (75°), giving a silicon–silicon distance of 234 pm.[16] The structure of **8** suggests that bonding between silicon and chalcogens in other small rings might also result in pentacoordination about the silicon.



5, R = Ph; X = NPh[12]
6, R = Cl; X = CH_2[13]
7, R = Ph; X = $SiPh_2$[14]
8, R = Me; X = S[15]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force System Command, USAF, under Grant AFOSR 82-0067, and by National Science Foundation Grant CHE-81-21122.

Supplementary Material Available: Final atomic coordinates, anisotropic thermal parameters, and selected distances and angles for **1** (3 pages). Ordering information is given on any current masthead page.

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(11) A CNDO calculation with unspecified geometry for $(H_2SiO)_2$ and $(Me_2SiO)_2$ showed significant Si–Si bond indices of 0.2 to 0.3 (Kirichenko, E. A.; Ermakov, A. I.; Samsonova, I. N. *Russ. J. Phys. Chem.* **1977**, *51*, 146). An MNDO calculation on $(H_2SiO)_2$ suggests only a weak antibonding interaction between the silicon atoms. In addition, MNDO geometry optimization leads to a severe diamond-shaped distortion of the ring in the opposite sense from that observed, with the Si–Si distances moving to 260 pm. This result may reflect the replacement of mesityl by hydrogen in the calculation, or may be due to an inherent defect of the method.

(12) Parkanyi, L.; Dunaj-Jurco, M.; Bihatsi, L.; Hencsei, P. *Cryst. Struct. Commun.* **1980**, *9*, 1049.

(13) Vilkov, L. V.; Kusakov, M. M.; Nametkin, N. S.; Oppengeim, V. D. *Akad. Nauk SSSR Proc.* **1968**, *181*, 1038.

(14) Parkanyi, L.; Sasvari, K.; Barta, I. *Acta Crystallogr., Sect. B* **1978**, *B34*, 883.

(15) Yokoi, M.; Nomura, T.; Yamasaki, K. *J. Am. Chem. Soc.* **1955**, *77*, 4484. Yokoi, M. *Bull. Soc. Jpn.* **1957**, *30*, 1, 100.

(16) The authors of this study did not comment on this unusual silicon–silicon distance, obtained from an electron diffraction study. The precise geometry about the silicon is not known for **8** due to assumptions in the trial models.

Electron Attachment to $Cr(CO)_6$ at Threshold Energies[†]

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Received July 22, 1983

Using electron transmission spectroscopy[1] (ETS), we have recently shown[2] resonance behavior in the electron scattering cross sections from threshold to about 4 eV for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. The resonances observed were assigned by using bound-state multiple-scattering (MS) Xα SCF MO calculations,[3] which predicted several anion states that were either bound or within 1 eV of threshold. Recently, an ab initio restricted Hartree–Fock (RHF) SCF MO calculation[4] on $Cr(CO)_6^-$ was reported that gave as the lowest energy anion a $^2T_{1u}$ state, 1.54 eV *above* threshold. A completely new assignment of the ETS features was suggested. No other properties were reported from the RHF calculation, and no interpretation was given for the several features below 1 eV in the electron transmission spectrum. A time-of-flight mass spectrometer has recently been appended to our ETS apparatus in order to monitor anions from dissociative attachment with the same high resolution (50 meV) that characterizes the ETS experiment. Using this instrument along with new computational capabilities, we are in a position to address the question of the nature of the interaction of low-energy electrons with $Cr(CO)_6$.

In Figure 1 we show the negative ion current from $Cr(CO)_6$ as a function of incident electron energy. The chief features of this spectrum—a large peak near 0.5 eV with shoulders between 1 and 2 eV and between 2 and 3 eV—correspond to the prominent features of the electron transmission spectrum. The vast majority of the ions observed are $Cr(CO)_5^-$ except near 1.6 eV where $Cr(CO)_4^-$ contributes about 15% to the total. The production of $Cr(CO)_4^-$ is clearly associated with features "B" in the electron transmission spectrum,[2] which we identified with processes involving the $3t_{2u}$ orbital. It is apparent that electron attachment readily occurs at energies below 1 eV, in sharp contrast to the RHF results.

In order to interpret our results we have performed continuum MS-Xα calculations on $Cr(CO)_6$ using the method described by Davenport et al.[5] We have generated self-consistent potentials

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[†] Supported by NSF CHE81-21125. From a dissertation to be submitted to the Graduate School, University of Maryland, by J. K. Olthoff in partial fulfillment of the requirements for the PhD degree in Physics.

[‡] Department of Chemistry.

[§] Department of Physics.

(1) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 344.

(2) Giordan, J. C.; Moore, J. H.; Tossell, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 6632.

(3) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.

(4) Vanquickenborne, L. G.; Verhulst, J. *J. Am. Chem. Soc.* **1983**, *105*, 1769.

(5) Davenport, J. W.; Ho, W.; Schrieffer, J. R. *Phys. Rev.* **1978**, *B17*, 3115.

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