Organometallics 1989, *8*, 709–716

reflections monitored every 7000 s; 7866 reflections (including standards) measured. Data corrected for Lorentz, polarization, and crystal decay (based on values of standards; 11% decay; maximum rescale factor on F_o = 1.222). After 2502 systematically absent or zero F_o data were rejected and 144 symmetry equivalent reflections (R_{merge} = 0.045) were averaged, a data set of 4968 reflections was obtained.

After several recrystallizations from methanol some small colorless plate shaped crystals were obtained (by W.J.C.). The largest available crystal of dimensions only 0.045 × 0.095 × 0.175 mm was used to collect the above weak data set [after excluding standards, only 1687 (22%) of the above 7614 data were considered observed using the criteria $I \geq 2\sigma(I)$]. Weaknesses in the data led to both $P2_1/c$ and $P2_1/n$ as possible space groups. The latter was shown to be correct. The crystal packing which consists of layers of molecules 1 and 2 parallel to the *ab* face in which the *x* and *z* (but not *y*) coordinates of the two molecules are related by $x_2 \approx {}^1/_2 + x_1$ and $z_2 \approx z_1$ leads to the pseudoabsence $h0l$, $l = 2n$, and helps explain some of the weakness of other sections of the data set.

The structure was solved by the use of direct methods (after several attempts and only after renormalization of several parity groups) to locate two fragments and some spurious peaks. In the early stages of refinement only heavily damped least squares gave meaningful results. All missing atoms were then located, and H atoms in the Ad groups were placed in calculated positions with fixed temperature factors. Hydrogen atoms in the CH_3 groups and the C(*n*1)–H atoms (representing 12% of the electron density) were not included. Refinement of anisotropic temperature factors was not possible (too few reflections available) and least-squares refinements minimizing $\sum w\Delta F^2$ then converged (maximum Δ/σ = 0.12) to the residuals R = 0.1212 (wR = 0.1207) for 1103 reflections with $F > 3\sigma(F)$. Weights in the final cycles were given by $w = [\sigma^2(F) + 0.00166F^2]^{-1}$ and a final ΔF map contained no peaks > 0.46 e Å^{-3}. Final positional parameters, bond lengths/bond angles, and structure factors have been deposited as supplementary material.

Acknowledgment. The authors are grateful to the Natural Science and Engineering Research Council of Canada for financial support of this research and for a scholarship for K.M.B.

Registry No. **1a**, 117959-04-3; **1b**, 96760-14-4; **1c**, 117959-09-8; **1d**, 117959-10-1; **1e**, 117959-11-2; **1f**, 117959-12-3; **1g**, 81671-43-4; **1i**, 97551-01-4; **2b**, 117959-16-7; **2f**, 117959-31-6; **2g**, 117959-31-6; **2g** (2,3-dimethylbutadiene cycloadduct), 117959-39-4; **2g** (anthracene cycloadduct), 117959-40-7; **2h**, 81671-50-3; **3a**, 117959-05-4; **3b**, 117959-06-5; **3c**, 109242-61-7; **3g**, 4110-02-5; **4a** (isomer 1), 117959-14-5; **4a** (isomer 2), 117982-86-2; **4b** (isomer 1), 117959-18-9; **4b** (isomer 2), 117959-19-0; **4c** (isomer 1), 117959-23-6; **4c** (isomer 2), 117959-24-7; **4d** (isomer 1), 117959-25-8; **4d** (isomer 2), 117959-26-9; **4e** (isomer 1), 117959-29-2; **4e** (isomer 2), 117959-30-5; **4f** (isomer 1), 117959-33-8; **4f** (isomer 2), 117959-34-9; **4g**, 117959-38-3; **4i**, 117959-41-8; **5a**, 117959-13-4; **5c**, 117959-22-5; **5e** (isomer 1), 118099-30-2; **5e** (isomer 2), 117959-27-0; **5g**, 117982-89-5; **6b**, 117959-17-8; **6f**, 117959-32-7; **7b** (isomer 1), 117959-20-3; **7b** (isomer 2), 117959-21-4; **7f** (isomer 1), 117959-35-0; **7f** (isomer 2), 117959-36-1; **7g**, 117959-38-3; **7h**, 117959-42-9; **7i**, 117959-41-8; **9b**, 96760-17-7; **10b**, 117959-15-6; **10e$_1$**, 118015-90-0; **10e$_2$**, 117959-28-1; **10e$_3$**, 118015-89-7; **11d** (isomer 1), 117982-87-3; **11d** (isomer 2), 117982-88-4; ClCOAd, 2094-72-6; $(Me_3Si)_2(t\text{-}Bu)Si(CH_2)_4OCOAd$, 117959-07-6; ClCO(*t*-Bu), 3282-30-2; ClCOMeS, 938-18-1; $ClCOCEt_3$, 35354-15-5; ClCO(BCO), 21891-38-3; methyltris(trimethylsilyl)silane, 2003-86-3; *tert*-butyltris(trimethylsilyl)silane, 104475-59-4; *tert*-butyltrichlorosilane, 18171-74-9; phenyltris(trimethylsilyl)silane, 4235-65-8; tris(trimethylsilyl)silyl bromide, 5089-31-6; 2,3-dimethylbutadiene, 513-81-5; anthracene, 120-12-7.

Supplementary Material Available: Tables of fractional coordinates and bond distances and angles for **7b** (5 pages); a listing of structure factors (4 pages). Ordering information is given on any current masthead page.

Crystal Structures of Four Sterically Crowded 1,3-Disilacyclobutanes

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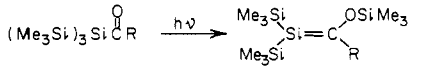
Received June 15, 1988

The crystal structures of the four 1,3-disilacyclobutanes $(R_1R_2SiCR_3R_4)_2$ [**1**, R_1 = Me, R_2 = $OSiMe_3$, R_3 = 1-Ad, R_4 = $SiMe_2t$-Bu; **2**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMe(*t*-Bu)($OSiMe_3$) (*R*,*R*:*S*,*S*); **3**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMePh($OSiMe_3$) (*R*,*R*:*S*,*S*); **4**, R_1 = R_2 = Me, R_3 = 1-Ad, R_4 = SiMePh($OSiMe_3$) (*R*,*S*:*S*,*R*)] whose syntheses by the photolyses of the appropriate (1-adamantylcarbonyl)phenyl- or (1-adamantylcarbonyl)*tert*-butylbis(trimethylsilyl)silane are reported in the previous paper are herein described and discussed. All four compounds contain sterically crowded but essentially planar (fold angles ≤ 5.9°) 1,3-disilacyclobutane rings. Despite the differences in the nature of the R_2 and R_4 substituents, the individual bond lengths and bond angles in the two independent molecules of **1** and in **2**–**4** do not deviate significantly from average values obtained from the dimensions of all the molecules, although the ⟨Si–C⟩ distance [1.962 Å] is significantly longer than a standard Si–C single bond length and is ca. 0.04 Å longer than values observed in other disilacyclobutanes. Additional evidence of steric crowding in these molecules can be seen in the lengthening of the C(ring)–Ad bond lengths to 1.624 Å (average). The significant increases in the already elongated C(ring)–R_4 bond lengths seem to be consistent with approximate cone angles calculated for the R_4 silicon substituents. Similarly, angle deformations result in differences in the maximum and minimum bond angles at each ring atom and in the *tert*-butyl groups of up to 13°. Finally, in the disiloxane moieties the Si–O–Si bond angles vary from 137° to 166° and there is an obvious correlation between the Si–O bond length and the included Si–O–Si angle.

Introduction

The photolysis of tris(trimethylsilyl)acylsilanes is a well-established route to highly substituted silenes.[1]



$$(Me_3Si)_3Si\overset{O}{\overset{\|}{C}}R \xrightarrow{h\nu} (Me_3Si)_2Si{=}C(OSiMe_3)R$$

This mild route has been used to prepare stable silenes (R = 1-adamantyl, CEt_3, mesityl, 1-methylcyclohexyl)[2] and has enabled us to investigate the physical properties and

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[1] (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* 1979, *101*, 83. (b) Brook, A. G.; Kallury, R. K. M. R.; Poon, Y. C. *Organometallics* 1982, *1*, 987.

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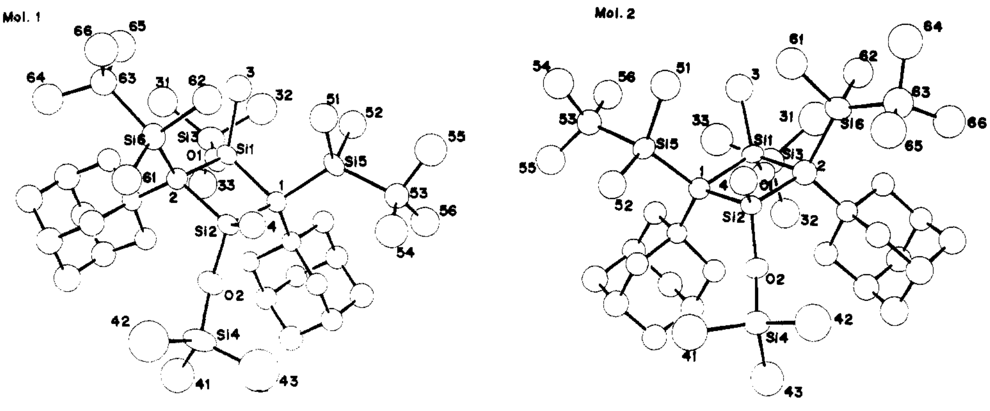
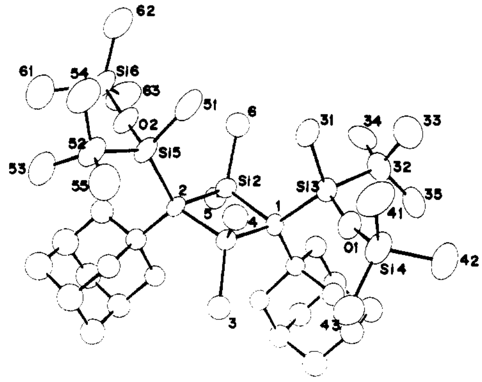


1, molecule 1 1, molecule 2



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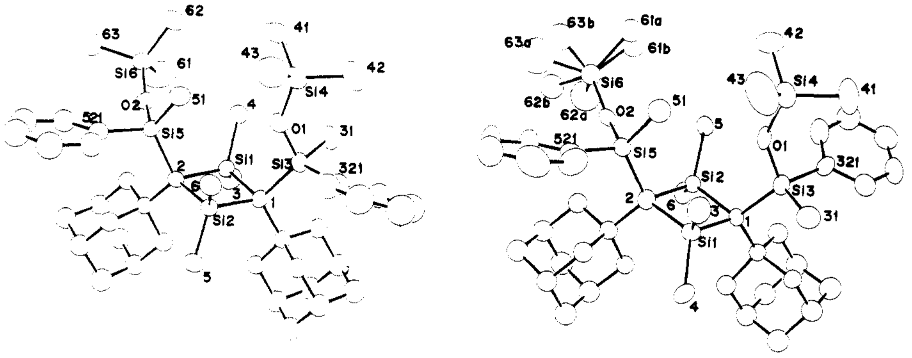
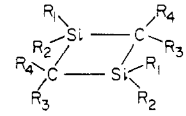


3 4

Figure 1. ORTEP views of the two independent molecules in 1,3-disilacyclobutane 1 and of 1,3-disilacyclobutanes **2**, **3**, and **4** showing the crystallographic numbering of principal atoms in each structure. Thermal ellipsoids are drawn at the 50% probability level.

chemistry of these compounds with relative ease.[2,3] It was of interest to prepare silenes with substituents other than trimethylsilyl groups at the unsaturated silicon atom, and thus, the photolysis of bis(trimethylsilyl)alkyl- and bis(trimethylsilyl)arylacylsilanes was investigated.[4] As expected these acylsilanes rearranged under photolytic conditions to the expected silenes. However, the initially formed silenes underwent further rearrangement to give differently substituted silenes which, in the absence of trapping reagents, dimerized in the usual head-to-tail manner to give 1,3-disilacyclobutanes (Scheme I). Details of this rearrangement are discussed in the preceding paper[5] while in this paper we report details of the crystal structure determinations of 1,3-disilacyclobutanes 1–4 and a detailed comparison of their structures. These 1,3-disilacyclobutanes are of interest not only as a result of this unprecedented rearrangement but also due to recent interest shown in small-ring silacarbocycle chemistry.[6]



1: R_1 = Me ; R_2 = $OSiMe_3$; R_3 = 1-Ad ; R_4 = $SiMe_2$t-Bu

2: R_1 = R_2 = Me ; R_3 = 1-Ad ; R_4 = SiMet-Bu($OSiMe_3$) (R,R : S,S)

3: R_1 = R_2 = Me ; R_3 = 1-Ad ; R_4 = SiMePh($OSiMe_3$) (R,R : S,S)

4: R_1 = R_2 = Me ; R_3 = 1-Ad ; R_4 = SiMePh($OSiMe_3$) (R,S : S,R)

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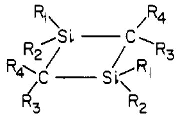
(2) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr.* **1985**, *C41*, 1632. (c) Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

(3) (a) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246. (b) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

(4) A preliminary communication has been published: Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 4338.

(5) See preceding paper.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg)



1: R_1 = Me; R_2 = $OSiMe_3$; R_3 = 1-Ad; R_4 = $SiMe_2$*t*-Bu

2: R_1 = R_2 = Me; R_3 = 1-Ad; R_4 = SiMe*t*-Bu($OSiMe_3$) (R,R : S,S)

3: R_1 = R_2 = Me; R_3 = 1-Ad; R_4 = SiMePh($OSiMe_3$) (R,R : S,S)

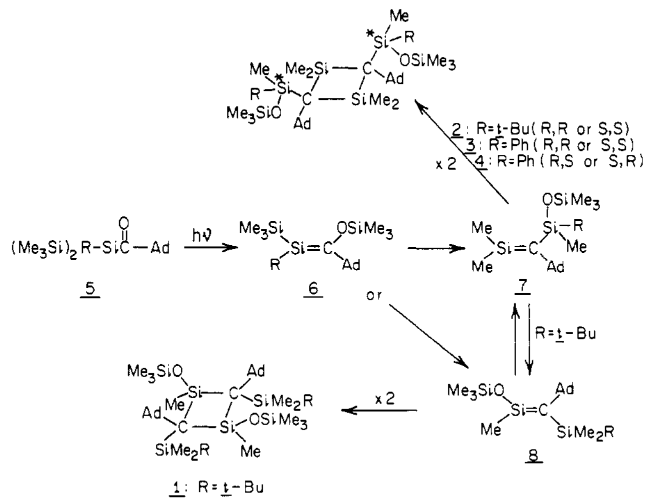
4: R_1 = R_2 = Me; R_3 = 1-Ad; R_4 = SiMePh($OSiMe_3$) (R,S : S,R)

	1		2	3	4
	molecule 1	molecule 2			
		Bond Lengths			
Si1–C1	1.972 (9)	1.961 (9)	1.977 (7)	1.959 (3)	1.959 (10)
Si1–C2	1.966 (9)	1.946 (10)	1.958 (6)	1.957 (5)	1.962 (10)
Si1–R_1	1.883 (11)	1.879 (11)	1.912 (8)	1.882 (3)	1.860 (10)
Si1–R_2	1.631 (6)	1.640 (7)	1.894 (7)	1.884 (5)	1.905 (10)
Si2–C1	1.958 (9)	1.973 (9)	1.970 (7)	1.952 (4)	1.965 (9)
Si2–C2	1.953 (9)	1.959 (10)	1.984 (6)	1.959 (3)	1.958 (10)
Si2–R_1	1.869 (10)	1.875 (10)	1.901 (7)	1.887 (5)	1.880 (10)
Si2–R_2	1.639 (6)	1.634 (6)	1.895 (8)	1.878 (3)	1.895 (10)
C1–R_3	1.616 (12)	1.610 (12)	1.622 (9)	1.627 (4)	1.610 (13)
C1–R_4	1.986 (8)	1.981 (9)	1.961 (7)	1.925 (5)	1.928 (9)
C2–R_3	1.637 (12)	1.628 (13)	1.622 (9)	1.625 (6)	1.644 (13)
C2–R_4	1.984 (9)	1.978 (9)	1.966 (6)	1.930 (3)	1.904 (10)
		Bond Angles			
C1–Si1–C2	95.1 (4)	96.0 (4)	96.0 (3)	95.0 (2)	95.0 (4)
C1–Si1–R_1	120.7 (4)	112.9 (4)	115.9 (3)	119.1 (2)	114.5 (4)
C1–Si1–R_2	111.5 (3)	115.3 (3)	117.2 (3)	113.2 (2)	116.4 (4)
C2–Si1–R_1	113.5 (4)	119.5 (4)	119.5 (3)	120.2 (2)	112.0 (4)
C2–Si1–R_2	115.9 (3)	112.5 (4)	113.0 (3)	112.9 (2)	121.3 (5)
R_1–Si1–R_2	101.2 (4)	101.4 (4)	96.6 (3)	97.5 (2)	98.7 (5)
C1–Si2–C2	96.0 (4)	95.2 (4)	95.4 (3)	95.2 (2)	95.0 (4)
C1–Si2–R_1	112.7 (4)	119.5 (4)	118.9 (3)	118.9 (2)	113.0 (4)
C1–Si2–R_2	115.2 (3)	111.8 (3)	114.8 (3)	112.7 (2)	120.9 (4)
C2–Si2–R_1	120.7 (4)	113.8 (4)	116.5 (3)	116.6 (2)	115.4 (4)
C2–Si2–R_2	111.2 (3)	116.2 (3)	116.5 (3)	117.1 (1)	116.4 (4)
R_1–Si2–R_2	101.9 (4)	101.3 (4)	96.3 (3)	97.8 (2)	97.5 (5)
Si1–C1–Si2	84.2 (3)	83.9 (3)	84.0 (3)	84.9 (2)	84.9 (4)
Si1–C1–R_3	119.1 (5)	114.8 (5)	118.6 (5)	119.8 (2)	121.4 (6)
Si1–C1–R_4	107.3 (4)	119.1 (4)	108.8 (3)	108.5 (2)	108.6 (5)
Si2–C1–R_3	114.8 (5)	117.7 (5)	116.5 (4)	116.3 (3)	114.1 (6)
Si2–C1–R_4	119.8 (4)	108.9 (4)	117.4 (4)	117.4 (2)	117.6 (5)
R_3–C1–R_4	109.8 (5)	110.3 (5)	109.6 (4)	108.5 (3)	109.0 (6)
Si1–C2–Si2	84.5 (3)	84.7 (4)	84.2 (2)	84.8 (2)	85.0 (4)
Si1–C2–R_3	112.9 (5)	119.4 (6)	115.8 (4)	117.3 (2)	113.5 (6)
Si1–C2–R_4	120.2 (4)	107.5 (4)	117.9 (3)	109.9 (2)	118.3 (5)
Si2–C2–R_3	119.4 (5)	113.9 (6)	118.0 (4)	117.7 (3)	119.5 (6)
Si2–C2–R_4	108.2 (4)	121.1 (5)	111.3 (3)	115.4 (2)	109.3 (5)
R_3–C2–R_4	110.0 (5)	108.8 (6)	108.4 (4)	109.8 (2)	109.7 (6)

Results and Discussion

Compounds 1–4 all contain the 1,3-disilacyclobutane moiety with different R_2 and R_4 substituents at silicon and carbon, respectively (Figure 1). The silyl substituents (R_4) in compounds 2, 3, and 4 are chiral, and the relative configuration of the two silyl substituents in each compound is indicated above. Both independent molecules in the asymmetric unit of disilacyclobutane 1 and disilacyclobutanes 2 and 3 have approximately twofold symmetry with the twofold axis perpendicular to the center of the Si_2C_2 ring, whereas disilacyclobutane 4 has approximately *m* symmetry. The dimensions of the independent molecules of compound 1 are very similar (Table I), and the results of a least-squares fit of the two molecules using the program BMFIT[7] (supplementary material) show that the atoms

Scheme I



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(6) (a) Fritz, G. *Angew. Chem.* 1987, *99*, 1150. (b) Fritz, G.; Matern, E. *Carbosilanes Syntheses and Reactions*; Springer-Verlag: Berlin, 1986.

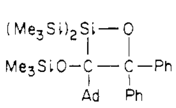
Table II. Average Bond Lengths[a] and Bond Angles for the Disilacyclobutane Moieties

Bond Lengths (Å)			
Si(ring)–C(ring)	1.962	C(ring)–Ad	1.624
Si(ring)–Me	1.885	C(ring)–$SiMe_2$(*t*-Bu)	1.982
Si–O	1.636	C(ring)–SiMePh($OSiMe_3$)	1.922
		C(ring)–SiMe(*t*-Bu)($OSiMe_3$)	1.964
Bond Angles (deg)			
C(ring)–Si–C(ring)	95.4	Si(ring)–C–Si(ring)	84.5
C(ring)–Si–R_1[b]	117.7	[112.7–120.9]	
C(ring)–Si–R_2[b]	114.1	[111.2–117.1]	
R_1–Si–R_2	99.0	[96.3–101.9]	
Si(ring)–C–R_3[b]	116.8	[107.5–121.4]	
Si(ring)–C–R_4[b]	113.6	[107.3–121.1]	
R_3–C–R_4	109.4	[108.4–110.3]	

[a] Standard Si–C and Si–O bond lengths for four-coordinate silicon are 1.872 (1) and 1.610 (4) Å, respectively.[8] [b] The small fold in each disilacyclobutane ring makes the C(1 or 2)–Si–R_1 angle different from the C(1 or 2)–Si–R_2 angle, likewise, the Si(1 or 2)–C–R_3 angle is different from the Si(1 or 2)–C–R_4 angle.

in the two disilacyclobutane rings fit to within 0.036 Å. The remaining deviations of atoms are within 0.45 Å. In the unit cell, the mean plane through the Si_2C_2 ring of molecule 2 makes an angle of 8° with the corresponding mean plane of molecule 1. Compounds **3** and **4** differ only in the relative configurations of the R_4 substituent. Thus, the results of a least-squares fit of molecules **3** and **4** indicate that the two molecules fit one another within 0.49 Å except in the region of Si(6) which is of opposite configuration in the two molecules (supplementary material).

Despite the difference in the nature of the R_2 and R_4 substituents, individual Si(ring)–C(ring), C(ring)–Ad, and Si(ring)–Me bond lengths and the endocyclic C–Si–C and Si–C–Si bond angles in the five molecules do not deviate significantly from average values obtained from the dimensions of all the molecules (Tables I and II). All of the molecules must be considered to be sterically crowded since the endocyclic Si–C bond lengths are all significantly longer (average Si(ring)–C(ring) distance is 1.962 Å; Table II) than standard values for four-coordinate silicon (standard Si–C bond length = 1.872 (1) Å[8]), as are most of the Si–O bond distances (average Si–O for **1**–**4** = 1.636 Å; standard Si–O bond length = 1.610 (4) Å[8]). These endocyclic Si–C bond lengths are considerably longer than the analogous bond lengths in other disilacyclobutanes[9,10] (by ca. 0.04 Å) but are comparable to the Si–C bond lengths of some sterically crowded alkyllithiums[11a] and organocuprates,[11] of the sterically hindered siloxetane **9** (Si–C = 1.963 Å),[3a] and of 1-mesityl-2,3,4-tri-*tert*-butyl-1-silacyclobutadiene (Si–C = 1.928 (3) Å, Si–C(sp^3), and 1.837 (3) Å, Si–C(sp^2), in the ring and 1.933 (3) Å, C–$SiMe_3$ exo ring).[12] Longer Si–C bond lengths have been observed in the sterically crowded 1,2-disilacyclobutane **10**[13] (Si–C bond length = 2.00 Å) and the disiloxetane **11**[14] (Si–C = 2.028 Å). The lengthening of the Si(ring)–C(ring) bonds in the 1,3-disilacyclobutanes **1**–**4** is even more extreme in view of the small endocyclic C–Si–C bond angle values, implying that the Si(ring)–C(ring) bonds in these compounds must be bent. Additional evidence of strain in these molecules can be seen in the lengthening of the C(ring)–Ad distances to 1.624 Å (cf. normal C–C bond length = ca. 1.54 Å), which is comparable to the lengthened central C–C bonds of sterically hindered ethanes,[15] and in the lengthening of the C(ring)–R_4 distances (Table II). The average C(ring)–R_4 distances to the different R_4 groups vary significantly: C–R_4 = 1.922 Å for –SiMePh($OSiMe_3$), 1.964 Å for –SiMe(*t*-Bu)($OSiMe_3$), and 1.982 Å for –$SiMe_2$(*t*-Bu). The increase in these distances is consistent with the increasing size of the groups as indicated by their cone angles θ.[16] The cone angles of silicon ligands have been shown to be equal to the cone angles of the corresponding phosphorus ligands[17] and thus, on the basis of the cone angle values calculated for phosphorus ligands,[16] the cone angles for the –SiMePh($OSiMe_3$), –SiMe(*t*-Bu)($OSiMe_3$), and –$SiMe_2$(*t*-Bu) groups were estimated to be 126°, 138°, and 139°, respectively.[18] The cone angle for the trimethylsiloxy substituent was assumed to be <118° (115°), which is not unreasonable considering that the cone angles of alkoxy substituents are generally 10–35° smaller than their alkyl counterparts.



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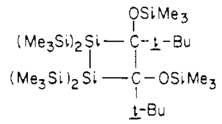

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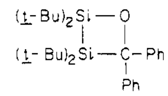

11

An alternative way to relieve steric strain is for there to be angle deformations or for the molecules to fold. Surprisingly, the fold angles for the present molecules are quite small (2–6°; Table III), much smaller than the values observed in cyclobutanes (35°[19]), the siloxetane **9** (20.1°[3a]), and other 1,3 disilacyclobutanes (e.g. 17.9°[9]). As a result of the fold, the C(ring)–Si(ring)–R_1 bond angles differ by several degrees from the C(ring)–Si(ring)–R_2 bond angles, as do the Si(ring)–C(ring)–R_3 and Si(ring)–C(ring)–R_4 bond angles. With different R groups there is obviously much more variation in these angles than the variations in the other ring dimensions (Tables I and II). At each ring Si or C atom one or two of these bond angles are contracted down due to steric interactions, although no consistent trends are apparent. This does result in differences between the maximum and minimum bond angles at each ring atom of up to 12.8° (the smallest difference is 4.1°). In general, the angle deformations are slightly larger at the carbon atoms. Variation in the C(ring)–Si(ring)–R and Si(ring)–C(ring)–R angles have also been observed in a folded 1,3-disilacyclobutane;[9] however, the corresponding angles observed in a planar 1,3-disilacyclobutane[10] are virtually identical with those observed in the present compounds.

The bond lengths and bond angles within the adamantyl and phenyl groups do not deviate significantly from normal values; however, the bond angles to these groups and other groups are somewhat distorted (supplementary material). For example, the angles at the Si atoms in the R_4 groups, that is, C(ring)–Si–Me, –Ph, –$OSiMe_3$, and –*t*-Bu are consistently larger than tetrahedral values, with bond angles of up to 124.7° being observed, and accordingly, the

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(18) $\theta(SiR_1R_2R_3) = {}^1/_3\theta[P(R_1)_3] + {}^1/_3\theta[P(R_2)_3] + {}^1/_3\theta[P(R_3)_3]$.

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Table III. Ring Puckering Amplitudes (Å)

atom of plane 1	1 molecule 1	1 molecule 2	2	3	4
Si1	0.027 (3)	−0.028 (3)	−0.038 (2)	0.029 (1)	0.015 (3)
Si2	0.027 (3)	−0.028 (3)	−0.037 (2)	0.029 (1)	0.015 (3)
C1	−0.027 (10)	0.028 (10)	0.037 (6)	−0.029 (4)	−0.015 (11)
C2	−0.027 (10)	0.028 (11)	0.038 (6)	−0.029 (4)	−0.015 (11)
θ (deg)[a]	4.2	4.4	5.9	4.6	2.4
Δ[a] (Å)	−0.107 (10)	0.111 (10)	0.150 (6)	−0.116 (4)	−0.061 (11)

[a] θ is defined as the angle between the planes Si1–Si2–C1 and Si1–Si2–C2; Δ is the distance of atom C2 from the plane through Si1–Si2–C1.

Table IV. Crystal Data, Details of Intensity Measurements, and Structure Refinements[a]

	$C_{42}H_{84}O_2Si_6$ (1)	$C_{42}H_{84}O_2Si_6$ (2)	$C_{46}H_{76}O_2Si_6$ (3)	$C_{46}H_{76}O_2Si_6$ (4)
system	triclinic	orthorhombic	triclinic	monoclinic
a, Å	16.194 (6)	19.435 (2)	11.751 (2)	19.359 (7)
b, Å	16.404 (3)	17.975 (3)	14.997 (3)	11.408 (4)
c, Å	19.421 (4)	26.983 (5)	16.965 (6)	23.431 (11)
α, deg	78.42 (2)	90.0	63.29 (3)	90.0
β, deg	82.03 (3)	90.0	67.25 (2)	109.75 (4)
γ, deg	88.34 (2)	90.0	73.10 (2)	90.0
V, Å^3	5006	9426	2438	4870
fw	789.6	789.6	829.5	829.5
Z/D_{calcd}, g cm^{-3}	4/1.05	8/1.11	2/1.13	4/1.13
space group	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P2_1/c$
μ(Mo K$\bar{\alpha}$), cm^{-1}	1.9	2.0	2.0	2.0
reflns in cell	25	25	25	25
detmn (no./2θ range, deg)	14.4–32.2	23.6–31.0	14.0–28.4	8.1–27.6
scan range, deg	0.85 + 0.35 tan θ	0.60 + 0.35 tan θ	0.65 + 0.35 tan θ	0.75 + 0.35 tan θ
max scan time, s	65	65	65	60
max 2θ, deg	45	50	55	48
quadrants	$h,\pm k,\pm l$	h,k,l	$h,\pm k,\pm l$	$\pm h,k,l$
std reflns (no./interval, s)	3/8200	3/8000	3/8500	3/6500
no. of data colld	13 434	10 068	11 433	8467
cryst size faces d, mm	{1,0,0}: 0.094 (1,0,$\bar{1}$): 0.125 ($\bar{1}$,0,1): 0.125 (1,$\bar{1}$,0): 0.150 ($\bar{1}$,1,0): 0.150	{0,1,0}: 0.075 {1,0,0}: 0.075 {0,0,1}: 0.100 (0,2,$\bar{1}$): 0.075 (0,2,1): 0.080 (0,$\bar{2}$,$\bar{1}$): 0.080	{0,1,0}: 0.138 (1,1,1): 0.063 ($\bar{1}$,$\bar{1}$,$\bar{1}$): 0.063 (0,1,1): 0.113 (1,0,0): 0.150	{0,0,1}: 0.088 {0,1,0}: 0.106 {1,0,0}: 0.037
av decline in std reflns (%)	−12.8	−25.0	−6.3	−0.9
rescale factors (CHORT)				
max	1.204	1.380	1.111	
min	0.976	0.952	0.978	
no. of zero F_o/sys abs rejd	2059	2390	1061	2090
no. of data averaged		651		155
$R_{merge}(F)$		0.037		0.056
no. of nonzero data	11012	6745	10083	5935
no. of obsd data	4739[b] $I > 3\sigma(I)$	2899 $I > 3\sigma(I)$	6947 $I > 3\sigma(I)$	2695 $I > 2.5\sigma(I)$
structure soln[c]	direct methods (MULTAN 11), least squares, Fourier, and ΔF Fourier calculations			
final R factors				
R	0.0837	0.0635	0.0688	0.0823
wR	0.1043	0.0582	0.0741	0.0950
max Δ/σ	0.050	0.25	0.150	0.41
weights, p	0.10[d]	0.000 27[e]	0.000 34[e]	0.080[d]
S	1.59	NA	NA	1.44
max peak final ΔF map, e Å^{-3}	1.05 (nr. Si)	0.38	0.86	0.43

[a] Enraf-Nonius CAD4 diffractometer; $\theta/2\theta$ mode; Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å); graphite monochromator; T = 298 K. [b] For compound 1, refinement below ~11% was not possible with the complete data set and there was very poor agreement at low (sin θ)/λ (R factors > 15%). Accordingly, the 1248 observed data with (sin θ)/λ < 0.25 were rejected in subsequent cycles of least squares. Refinement then proceeded routinely to give the indicated R factors. [c] Programs: Enraf-Nonius SDP package on PDP 11/23 or SHELX on Gould 9705 computers. Scattering curves stored in programs were taken from ref 23. [d] $w = 4F^2[\sigma^2(I) + (pF^2)^2]^{-1}$. [e] $w = [\sigma^2(F) + pF^2]^{-1}$.

remaining angles (i.e. Me–Si–Ph, Me–Si–t-Bu, Me–Si–OSiMe$_3$, etc.) are smaller. Values as small as 98.9° were observed. This implies that the groups on the central Si atoms of the R_4 moieties are folding back, most probably to relieve steric strain.

Notably, the increase in the average C(ring)–Si–R angles for the R_4 substituents in each compound correlates well with the sizes of the R groups. Thus, in compound 2 the ⟨CSiO⟩, ⟨CSiMe⟩, and ⟨CSiBu⟩ angles are 106.1, 114.3, and 124.0° (⟨OSiMe⟩, ⟨OSiBu⟩, and ⟨MeSiBu⟩ are 103.7, 105.4, and 101.3°, respectively), while in compounds 3 and 4 the corresponding ⟨CSiO⟩, ⟨CSiMe⟩, and ⟨CSiPh⟩ bond angles are 110.6, 114.6, and 116.9° respectively (with ⟨OSiMe⟩, ⟨OSiPh⟩ and ⟨MeSiPh⟩ of 105.3, 103.5, and 104.8°). However, in compound 1 the ⟨CSiBu⟩ [124.3°] is significantly larger than the ⟨CSiMe⟩ average angle [111.6°] but comparable to the corresponding angles in compound 2. However, there is no difference in the ⟨MeSiMe⟩ and ⟨MeSiBu⟩ angles in compound 1. In arriving at these angles, it should be noted that angle differences of up to 5.3° between comparable angles in compounds 3 or 4 due to the change in configuration of the

Table V. Final Atomic Positional and Thermal Parameters for Compounds 1–4[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Compound 1									
Si11	0.4749 (2)	0.3977 (2)	0.7339 (1)	2.67 (6)	Si21	0.1017 (2)	0.1850 (2)	0.2901 (1)	2.95 (6)
Si12	0.4609 (2)	0.2397 (2)	0.7281 (1)	2.56 (6)	Si22	–0.0370 (2)	0.1892 (2)	0.2332 (1)	2.67 (6)
Si13	0.4319 (2)	0.5280 (2)	0.8348 (2)	4.33 (8)	Si23	0.2979 (2)	0.1969 (3)	0.2595 (2)	4.78 (9)
Si14	0.4106 (2)	0.0621 (2)	0.8213 (2)	4.43 (8)	Si24	–0.1137 (2)	0.2278 (2)	0.0889 (2)	3.38(7)
Si15	0.3622 (2)	0.3835 (2)	0.6147 (2)	3.34 (7)	Si25	–0.0462 (2)	0.3241 (2)	0.3337 (2)	3.15 (7)
Si16	0.6528 (2)	0.2908 (2)	0.6899 (2)	3.43 (7)	Si26	0.0162 (3)	0.0080 (2)	0.3400 (2)	4.57 (8)
O11	0.4440 (5)	0.4444 (4)	0.7996 (4)	3.5 (2)	O21	0.1985 (5)	0.1975 (5)	0.2518 (4)	3.7 (2)
O12	0.4272 (5)	0.1620 (4)	0.7923 (3)	3.2 (2)	O22	–0.0513 (4)	0.2128 (4)	0.1499 (3)	3.0 (2)
C11	0.3836 (6)	0.3338 (6)	0.7124 (5)	2.7 (2)*	C21	0.0256 (6)	0.2763 (6)	0.2603 (5)	2.7 (2)*
C12	0.5488 (6)	0.3013 (6)	0.7549 (5)	2.8 (2)*	C22	0.0435 (7)	0.1005 (7)	0.2579 (6)	3.6 (2)*
C13	0.5259 (8)	0.4862 (8)	0.6655 (7)	4.7 (3)*	C23	0.1150 (8)	0.1705 (8)	0.3863 (7)	4.9 (3)*
C14	0.4816 (7)	0.1874 (7)	0.6503 (6)	3.9 (2)*	C24	–0.1464 (8)	0.1642 (8)	0.2777 (6)	4.1 (2)*
C15	0.2969 (6)	0.3229 (6)	0.7657 (5)	2.6 (2)*	C25	0.0667 (6)	0.3498 (6)	0.1978 (5)	2.6 (2)*
C16	0.2403 (7)	0.4005 (7)	0.7546 (6)	3.4 (2)*	C26	0.0040 (7)	0.4162 (7)	0.1712 (5)	3.1 (2)*
C17	0.1577 (7)	0.3879 (7)	0.8022 (6)	3.7 (2)*	C27	0.0450 (7)	0.4881 (8)	0.1136 (6)	4.0 (2)*
C18	0.1716 (7)	0.3686 (7)	0.8806 (6)	3.5 (2)*	C28	0.0833 (7)	0.4546 (7)	0.0520 (6)	3.9 (2)*
C19	0.2234 (7)	0.2907 (7)	0.8939 (6)	3.6 (2)*	C29	0.1494 (7)	0.3914 (7)	0.0752 (6)	3.7 (2)*
C110	0.3094 (6)	0.3041 (6)	0.8448 (5)	2.8 (2)*	C210	0.1112 (7)	0.3213 (7)	0.1305 (5)	3.2 (2)*
C111	0.2475 (7)	0.2491 (7)	0.7539 (5)	3.1 (2)*	C211	0.1348 (7)	0.3939 (7)	0.2242 (6)	3.5 (2)*
C112	0.1643 (7)	0.2376 (7)	0.8010 (6)	3.4 (2)*	C212	0.1744 (7)	0.4660 (7)	0.1685 (6)	3.8 (2)*
C113	0.1117 (8)	0.3179 (8)	0.7881 (6)	4.2 (2)*	C213	0.1096 (8)	0.5310 (8)	0.1439 (6)	4.5 (3)*
C114	0.1771 (8)	0.2183 (8)	0.8772 (6)	4.0 (2)*	C214	0.2162 (8)	0.4347 (8)	0.1040 (6)	4.3 (2)*
C115	0.5677 (6)	0.2815 (6)	0.8373 (5)	2.6 (2)*	C215	0.0874 (6)	0.0622 (6)	0.1907 (5)	2.8 (2)*
C116	0.4893 (7)	0.2686 (7)	0.8923 (5)	3.2 (2)*	C216	0.0240 (7)	0.0182 (7)	0.1601 (6)	3.6 (2)*
C117	0.5131 (8)	0.2533 (8)	0.9678 (6)	4.3 (2)*	C217	0.0647 (8)	–0.0215 (8)	0.0978 (6)	4.5 (3)*
C118	0.5625 (8)	0.1739 (8)	0.9816 (7)	4.8 (3)*	C218	0.1048 (8)	0.0467 (8)	0.0398 (7)	4.8 (3)*
C119	0.6429 (8)	0.1863 (8)	0.9291 (6)	4.4 (3)*	C219	0.1681 (8)	0.0877 (8)	0.0675 (6)	4.2 (2)*
C120	0.6217 (7)	0.2034 (7)	0.8535 (6)	3.9 (2)*	C220	0.1329 (7)	0.1287 (7)	0.1288 (6)	3.5 (2)*
C121	0.6158 (7)	0.3547 (7)	0.8513 (6)	3.5 (2)*	C221	0.1557 (7)	–0.0029 (7)	0.2128 (5)	3.3 (2)*
C122	0.6396 (8)	0.3385 (8)	0.9261 (7)	4.5 (3)*	C222	0.1951 (7)	–0.0401 (7)	0.1505 (6)	3.4 (2)*
C123	0.5594 (8)	0.3255 (8)	0.9797 (6)	4.5 (3)*	C223	0.1304 (8)	–0.0843 (8)	0.1226 (6)	4.5 (3)*
C124	0.6905 (8)	0.2593 (8)	0.9405 (7)	4.7 (3)*	C224	0.2377 (8)	0.0262 (8)	0.0903 (6)	4.1 (2)*
C131	0.534 (1)	0.565 (1)	0.8500 (9)	7.0 (4)*	C231	0.327 (1)	0.094 (1)	0.311 (1)	8.1 (4)*
C132	0.366 (1)	0.501 (1)	0.9217 (8)	6.5 (3)*	C232	0.356 (1)	0.214 (1)	0.1691 (8)	6.6 (3)*
C133	0.380 (1)	0.611 (1)	0.7747 (9)	7.6 (4)*	C233	0.322 (1)	0.284 (1)	0.304 (1)	7.9 (4)*
C141	0.367 (1)	0.047 (1)	0.9162 (9)	7.2 (4)*	C241	–0.185 (1)	0.315 (1)	0.1010 (8)	6.3 (3)*
C142	0.510 (1)	0.001 (1)	0.813 (1)	9.0 (5)*	C242	–0.172 (1)	0.131 (1)	0.0901 (8)	6.5 (3)*
C143	0.336 (1)	0.025 (1)	0.771 (1)	9.8 (5)*	C243	–0.049 (1)	0.257 (1)	0.0011 (8)	6.1 (3)*
C151	0.4562 (8)	0.3875 (8)	0.5467 (7)	4.7 (3)*	C251	–0.0896 (8)	0.2443 (8)	0.4146 (7)	4.9 (3)*
C152	0.3343 (8)	0.4966 (8)	0.6068 (7)	5.0 (3)*	C252	–0.1451 (8)	0.3661 (8)	0.2993 (6)	4.1 (2)*
C153	0.2794 (7)	0.3398 (7)	0.5655 (6)	3.6 (2)*	C253	–0.0102 (7)	0.4098 (7)	0.3798 (6)	3.7 (2)*
C154	0.295 (1)	0.250 (1)	0.5612 (8)	6.0 (3)*	C254	–0.0773 (9)	0.4169 (9)	0.4422 (7)	5.3 (3)*
C155	0.296 (1)	0.391 (1)	0.4866 (8)	6.0 (3)*	C255	–0.0024 (9)	0.4983 (9)	0.3361 (7)	5.1 (3)*
C156	0.1891 (9)	0.3521 (9)	0.5905 (7)	5.3 (3)*	C256	0.0723 (9)	0.3859 (9)	0.4111 (7)	5.2 (3)*
C161	0.6809 (8)	0.1775 (8)	0.6953 (7)	4.8 (3)*	C261	–0.0530 (9)	0.0448 (9)	0.4137 (7)	5.4 (3)*
C162	0.6390 (8)	0.3267 (8)	0.5938 (7)	4.8 (3)*	C262	0.1128 (9)	–0.0332 (9)	0.3798 (7)	5.5 (3)*
C163	0.7580 (8)	0.3451 (8)	0.6919 (6)	4.0 (2)*	C263	–0.0458 (8)	–0.0932 (8)	0.3382 (7)	4.9 (3)*
C164	0.8071 (9)	0.3085 (9)	0.7547 (7)	5.5 (3)*	C264	–0.061 (1)	–0.139 (1)	0.4175 (8)	6.4 (3)*
C165	0.748 (1)	0.440 (1)	0.6859 (8)	6.1 (3)*	C265	–0.129 (1)	–0.071 (1)	0.3112 (8)	6.4 (3)*
C166	0.184 (1)	0.667 (1)	0.3759 (8)	6.1 (3)*	C266	0.0029 (9)	–0.1554 (9)	0.2994 (7)	5.6 (3)*
Compound **2**[b]									
Si1	8984 (1)	1166 (1)	1991 (1)	25.9 (6)	C22	9224 (4)	2728 (3)	1264 (2)	30 (2)*
Si3	8019 (1)	1037 (1)	2949 (1)	30.5 (6)	C23	9648 (4)	3199 (4)	904 (3)	40 (2)*
O1	8657 (3)	605 (2)	3215 (2)	36 (2)	C24	9176 (4)	3471 (4)	480 (3)	48 (2)*
Si4	9134 (1)	-12 (1)	3495 (1)	43.9 (7)	C25	8903 (4)	2781 (4)	209 (3)	52 (2)*
C1	8433 (4)	1735 (3)	2477 (3)	25 (2)*	C26	9483 (4)	2329 (4)	13 (3)	53 (2)*
C3	9958 (4)	1300 (4)	2028 (3)	35 (2)*	C27	9959 (4)	2056 (4)	437 (3)	48 (2)*
C4	8989 (4)	117 (4)	2055 (3)	39 (2)*	C28	9535 (4)	1586 (4)	809 (3)	36 (2)*
Si2	7882 (1)	2016 (1)	1893 (1)	27.7 (6)	C29	8483 (4)	2297 (4)	582 (3)	39 (2)*
Si5	7969 (1)	768 (1)	1018 (1)	34.9 (6)	C210	10239 (4)	2746 (4)	696 (3)	44 (2)*
O2	7376 (3)	1226 (3)	724 (2)	41 (2)	C31	7501 (4)	282 (4)	2649 (3)	41 (2)
Si6	6736 (1)	1495 (1)	376 (1)	46.6 (7)	C32	7406 (5)	1339 (4)	3493 (3)	45 (2)
C2	8484 (3)	1510 (3)	1404 (2)	24 (2)*	C33	7102 (5)	592 (5)	3701 (3)	62 (3)
C5	7696 (4)	3039 (4)	1777 (3)	36 (2)*	C34	6793 (4)	1790 (5)	3299 (3)	62 (3)
C6	6951 (4)	1703 (4)	1913 (3)	42 (2)*	C35	7727 (5)	1724 (4)	3939 (3)	54 (3)
C11	8800 (4)	2410 (4)	2777 (3)	27 (2)*	C41	8799 (5)	–959 (4)	3346 (3)	58 (3)
C12	9239 (4)	2112 (4)	3216 (3)	34 (2)*	C42	9115 (5)	154 (5)	4174 (3)	63 (3)
C13	9582 (4)	2757 (4)	3506 (3)	40 (2)*	C43	10044 (4)	94 (4)	3287 (3)	51 (2)
C14	9033 (4)	3269 (4)	3717 (3)	45 (2)*	C51	7457 (5)	90 (4)	1399 (3)	49 (2)
C15	8600 (4)	3587 (4)	3294 (3)	41 (2)*	C52	8384 (5)	104 (4)	523 (3)	48 (3)
C16	9072 (4)	4037 (4)	2954 (3)	43 (2)*	C53	8625 (5)	439 (4)	27 (3)	61 (3)
C17	9626 (4)	3519 (4)	2746 (3)	38 (2)*	C54	7804 (5)	–451 (5)	375 (3)	68 (3)
C18	9284 (4)	2884 (4)	2452 (3)	28 (2)*	C55	8967 (5)	–364 (4)	740 (3)	64 (3)
C19	8261 (4)	2947 (4)	2993 (3)	34 (2)*	C61	7030 (4)	1501 (5)	-281 (3)	70 (3)
C110	10051 (4)	3202 (4)	3167 (3)	45 (2)*	C62	6001 (4)	851 (5)	465 (3)	59 (3)
C21	8920 (4)	2023 (3)	1022 (2)	30 (2)*	C63	6475 (5)	2441 (5)	557 (4)	73 (3)

Table V (Continued)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Compound 3									
Si1	0.1261 (1)	0.2246 (1)	0.8203 (1)	19.7 (2)	C24	−0.4129 (4)	0.3020 (4)	0.9206 (3)	47.8 (9)*
Si2	0.0241 (1)	0.3441 (1)	0.6870 (1)	18.8 (2)	C25	−0.3220 (4)	0.2120 (3)	0.9610 (3)	43.0 (9)*
Si3	0.0430 (1)	0.4447 (1)	0.8192 (1)	23.6 (3)	C26	−0.1886 (4)	0.2267 (3)	0.8952 (3)	32.8 (7)*
Si4	0.2658 (1)	0.5628 (1)	0.7072 (1)	37.1 (4)	C27	−0.1605 (4)	0.3157 (3)	0.9770 (3)	35.1 (7)*
Si5	0.3179 (1)	0.2483 (1)	0.6210 (1)	21.5 (2)	C28	−0.2933 (4)	0.3009 (3)	1.0433 (3)	44.2 (9)*
Si6	0.5484 (1)	0.1113 (1)	0.6966 (1)	29.5 (3)	C29	−0.3282 (4)	0.2043 (4)	1.0550 (3)	48.9 (9)*
O1	0.1707 (2)	0.4833 (2)	0.7363 (2)	27.2 (8)	C210	−0.3847 (4)	0.3916 (3)	1.0039 (3)	46.8 (9)*
O2	0.4191 (2)	0.1613 (2)	0.6699 (2)	27.2 (8)	C31	0.0821 (4)	0.4026 (3)	0.9297 (3)	35.5 (16)
C1	−0.0080 (3)	0.3393 (2)	0.8106 (2)	19.8 (9)	C321	−0.0675 (4)	0.5675 (3)	0.8065 (3)	36.9 (8)*
C2	0.1507 (3)	0.2242 (2)	0.6996 (2)	19.3 (9)	C322	−0.1445 (4)	0.5936 (4)	0.8814 (3)	48.2 (9)*
C3	0.1012 (4)	0.1053 (3)	0.9269 (3)	30.8 (8)	C323	−0.2150 (5)	0.6910 (4)	0.8670 (4)	63.3 (13)*
C4	0.2683 (4)	0.2496 (3)	0.8287 (3)	26.8 (8)	C324	−0.2076 (5)	0.7592 (4)	0.7800 (4)	67.4 (13)*
C5	−0.1105 (4)	0.3447 (3)	0.6521 (3)	26.7 (11)	C325	−0.1348 (5)	0.7362 (4)	0.7049 (4)	63.7 (13)*
C6	0.0748 (4)	0.4664 (3)	0.5932 (3)	25.7 (10)	C326	−0.0639 (4)	0.6396 (4)	0.7180 (3)	48.2 (9)*
C11	0.1191 (3)	0.1263 (3)	0.6985 (2)	26.5 (6)*	C41	0.4165 (5)	0.4905 (5)	0.7266 (5)	62 (2)
C12	−0.0062 (4)	0.0943 (3)	0.7694 (3)	33.7 (7)*	C42	0.2010 (6)	0.6435 (4)	0.7761 (5)	58 (2)
C13	−0.0350 (4)	−0.0002 (3)	0.7701 (3)	40.2 (8)*	C43	0.2905 (6)	0.6439 (4)	0.5842 (4)	58 (2)
C14	0.0677 (4)	−0.0877 (3)	0.7949 (3)	42.2 (9)*	C51	0.3604 (4)	0.3724 (3)	0.5920 (3)	29.2 (8)
C15	0.1921 (4)	−0.0598 (3)	0.7230 (3)	36.8 (8)*	C521	0.3625 (4)	0.2450 (3)	0.5021 (3)	33.8 (7)*
C16	0.2203 (3)	0.0347 (3)	0.7220 (3)	30.4 (7)*	C522	0.4419 (4)	0.1652 (3)	0.4796 (3)	43.4 (9)*
C17	0.1107 (4)	0.1446 (3)	0.6033 (3)	33.6 (7)*	C523	0.4786 (5)	0.1661 (4)	0.3905 (4)	54.9 (11)*
C18	0.0841 (4)	0.0494 (3)	0.6036 (3)	41.0 (9)*	C524	0.4380 (5)	0.2459 (4)	0.3237 (4)	59.9 (12)*
C19	−0.0403 (4)	0.0216 (3)	0.6750 (3)	47.1 (9)*	C525	0.3581 (5)	0.3267 (4)	0.3423 (4)	56.5 (11)*
C110	0.1878 (4)	−0.0376 (3)	0.6271 (3)	41.4 (9)*	C526	0.3212 (4)	0.3253 (3)	0.4317 (3)	44.8 (9)*
C21	−0.1483 (3)	0.3230 (3)	0.8805 (2)	28.1 (6)*	C61	0.5131 (6)	0.0098 (4)	0.8126 (5)	63 (2)
C22	−0.2459 (4)	0.4119 (3)	0.8432 (3)	34.0 (7)*	C62	0.6183 (4)	0.2055 (4)	0.6987 (4)	43.4 (16)
C23	−0.3782 (4)	0.3985 (3)	0.9099 (3)	41.9 (9)*	C63	0.6615 (5)	0.0570 (5)	0.6119 (4)	52 (2)
Compound 4									
Si1	0.7175 (2)	0.2355 (3)	0.3737 (1)	2.55 (7)	C27	0.8383 (5)	0.384 (1)	0.4944 (4)	2.8 (2)*
Si2	0.8072 (2)	0.0961 (3)	0.4563 (1)	2.41 (7)	C28	0.8636 (6)	0.498 (1)	0.5321 (5)	4.0 (3)*
Si3	0.7404 (2)	−0.0034 (3)	0.3146 (1)	2.82 (7)	C29	0.8048 (6)	0.591 (1)	0.5103 (5)	4.0 (3)*
Si4	0.6160 (2)	−0.1737 (4)	0.3092 (2)	4.8 (1)	C31	0.6874 (6)	0.054 (1)	0.2350 (5)	3.8 (3)
Si5	0.6630 (2)	0.1447 (3)	0.4862 (1)	2.77 (7)	C41	0.6277 (9)	−0.253 (2)	0.2441 (6)	8.3 (5)
Si6	0.7056 (2)	−0.0013 (4)	0.6082 (1)	4.57 (9)	C42	0.6271 (9)	−0.282 (1)	0.3704 (6)	8.2 (5)
O1	0.6786 (4)	−0.0702 (7)	0.3361 (3)	3.2 (2)	C43	0.5250 (9)	−0.109 (2)	0.2868 (8)	9.5 (6)
O2	0.7041 (4)	0.0818 (6)	0.5520 (3)	2.9 (2)	C51	0.6078 (6)	0.028 (1)	0.4370 (5)	3.9 (3)
C1	0.7903 (6)	0.1195 (9)	0.3695 (4)	2.2 (3)	C61A	0.696 (1)	−0.160 (2)	0.587 (1)	4.2 (6)*
C2	0.7368 (5)	0.216 (1)	0.4609 (4)	2.8 (3)	C61B	0.740 (1)	−0.150 (3)	0.602 (1)	5.8 (7)*
C3	0.6212 (6)	0.198 (1)	0.3280 (5)	3.8 (3)	C62A	0.809 (2)	0.027 (3)	0.664 (1)	8.2 (9)*
C4	0.7229 (6)	0.386 (1)	0.3398 (4)	3.7 (3)	C62B	0.754 (1)	0.069 (2)	0.680 (1)	5.1 (7)*
C5	0.7863 (6)	−0.057 (1)	0.4747 (5)	3.1 (3)	C63A	0.648 (2)	0.046 (4)	0.652 (2)	12 (1)*
C6	0.9028 (6)	0.107 (1)	0.5142 (5)	3.4 (3)	C63B	0.599 (1)	−0.014 (3)	0.605 (1)	5.3 (7)*
C11	0.8624 (5)	0.158 (1)	0.3546 (4)	2.5 (2)*	C110	1.0207 (7)	0.215 (1)	0.3906 (5)	4.4 (3)*
C12	0.8952 (6)	0.276 (1)	0.3845 (5)	3.3 (3)*	C210	0.8789 (6)	0.468 (1)	0.5993 (5)	4.4 (3)*
C13	0.9640 (6)	0.308 (1)	0.3704 (5)	3.9 (3)*	C321	0.8000 (6)	−0.129 (1)	0.3063 (5)	3.7 (3)
C14	0.9438 (6)	0.327 (1)	0.3030 (5)	4.2 (3)*	C322	0.8246 (7)	−0.144 (1)	0.2580 (5)	4.4 (3)
C15	0.9121 (6)	0.211 (1)	0.2701 (5)	3.8 (3)*	C323	0.8696 (7)	−0.236 (1)	0.2543 (6)	5.8 (4)
C16	0.8455 (6)	0.177 (1)	0.2854 (5)	2.7 (2)*	C324	0.8884 (7)	−0.318 (1)	0.2976 (6)	6.0 (4)
C17	0.9234 (6)	0.064 (1)	0.3746 (5)	3.5 (3)*	C325	0.8642 (8)	−0.308 (1)	0.3466 (6)	5.9 (4)
C18	0.9913 (6)	0.100 (1)	0.3600 (5)	4.1 (3)*	C326	0.8230 (7)	−0.215 (1)	0.3508 (5)	4.9 (4)
C19	0.9696 (6)	0.116 (1)	0.2903 (5)	4.4 (3)*	C521	0.5914 (6)	0.241 (1)	0.4987 (5)	3.4 (3)
C21	0.7667 (5)	0.336 (1)	0.5005 (5)	2.8 (2)*	C522	0.5286 (6)	0.276 (1)	0.4494 (6)	5.3 (4)
C22	0.7830 (6)	0.312 (1)	0.5697 (5)	3.2 (3)*	C523	0.4715 (7)	0.338 (1)	0.4584 (7)	6.8 (5)
C23	0.8095 (6)	0.426 (1)	0.6070 (5)	3.8 (3)*	C524	0.4752 (7)	0.370 (1)	0.5163 (7)	7.4 (4)
C24	0.7493 (6)	0.518 (1)	0.5858 (5)	3.7 (3)*	C525	0.5350 (7)	0.336 (1)	0.5644 (6)	6.0 (4)
C25	0.7358 (6)	0.547 (1)	0.5181 (5)	3.3 (3)*	C526	0.5905 (6)	0.276 (1)	0.5552 (6)	4.9 (3)
C26	0.7097 (6)	0.432 (1)	0.4806 (5)	3.1 (3)*					

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Positional parameters x, y, $z \times 10^4$.

R_4 substituent have been averaged while the maximum difference between corresponding angles of compounds **3** and **4** is much smaller [only 2.3°].

In the R_4 substituents the average Si–Me bond lengths are 1.883, 1.877, and 1.878 Å in compounds **1**, **2**, and **3**/**4**, respectively. All of these values are significantly longer than the average Si–Me bond lengths in the $OSiMe_3$ substituents [1.859 Å (**1**), 1.858 Å (**2**), 1.849 Å (**3**), and 1.839 Å (**4**)].

Likewise, the crowding of the *tert*-butyl groups in **1** and **2** is also reflected in the lengthening of the Si–C(*t*-Bu) bonds to an average value of 1.965 Å and a compression of the Me–C–Me bond angles (average value 107.4°). The Si–C–Me bond angles were also distorted with the difference between the maximum and minimum Si–C–Me angles ranging up to 13.2° (supplementary material). Related distortions of other sterically crowded *tert*-butyl groups have been noted previously.[20]

The disiloxane moieties of 1,3-disilacyclobutanes **1**–**4** have bent configurations with the Si–O–Si bond angles

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[20] For example: (a) Cheng, P.-T.; Nyburg, S. C.; Thankachan, C.; Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 654. (b) Cheng, P.-T.; Nyburg, S. C. *Acta Crystallogr.* **1978**, *B34*, 3001.

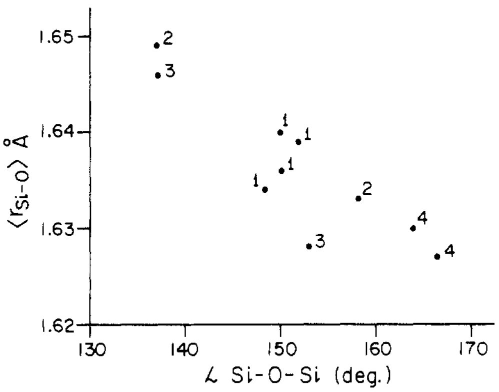

Figure 2. Relationship between silicon–oxygen bond lengths and included Si–O–Si bond angles in the trimethylsiloxy groups of compounds 1–4.

varying between 137° and 166°. Organodisiloxanes, in general, usually have either bent configurations with Si–O–Si angles between 140° and 160° or linear configurations, i.e. Si–O–Si angle of 180°.[21] In the present compounds there is a correlation between the Si–O bond lengths and the Si–O–Si bond angle (Figure 2). Similar correlations have been commented upon elsewhere[21] and have been treated theoretically.[22]

In conclusion, the 1,3-disilacyclobutanes 1–4 are all very similar in structure with relatively planar central Si_2C_2 rings in which the Si–C bond lengths are significantly elongated. All four molecules are sterically crowded, and steric strains have been relieved or lessened by a variety of means including lengthening of various Si–O, Si–C, or C–C bonds and significant angle deformations at each Si or C atom or by changes in the SiOSi angles of the siloxy substituents.

Experimental Section

The preparations (by photolysis of the appropriate acylsilanes) isolation, purifications, and physical properties (melting points and NMR and MS spectra) of the four 1,3-disilacyclobutanes whose crystal structures are herein reported have been described in detail in the preceding paper.[5] The correspondence between the compound numbering in the two papers is as follows: 1,3-disilacyclobutane 1 = dimer **9b**; 1,3-disilacyclobutane 2 = dimer **10b**; 1,3-disilacyclobutane 3 (*R,R* or *S,S*) = dimer $\mathbf{10e}_1$; 1,3-disilacyclobutane 4 (*R,S* or *S,R*) = dimer $\mathbf{10e}_2$.

X-ray Crystallography. Crystals of compound 1 were sealed in 0.2–0.3 mm Lindemann capillaries as a precautionary measure; all other crystals were glued to thin fibers. Crystal data on all four compounds were obtained on an Enraf-Nonius CAD4 diffractometer by the use of graphite-monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å) at 298 K and are summarized in Table IV which also contains a summary of the intensity measurements and structure refinements undertaken. Lorentz and polarization corrections were applied to all data collected. For compounds 1–3 the intensity data sets were rescaled for the effects of slow systematic declines in the intensities of the standard reflections after each data reduction. No absorption corrections were considered necessary in view of the small size of μ(Mo K$\bar{\alpha}$) for each compound. Averaging of symmetry equivalent reflections and the exclusion of systematically absent or zero F_0 data gave the totals of nonzero data indicated in Table IV. All four structures were solved by the use of direct methods to locate the majority of the non-hydrogen atoms in each structure. Least-squares refinements minimizing $\sum w\Delta F^2$ and Fourier calculations then located the remaining atoms. Hydrogen atoms when included were located in ΔF maps or were placed in calculated positions with common temperature factors for each substituent group. Some disorder in the $OSi(6)Me_3$ group in compound 4 resulted in two alternative arrangements of the methyl positions. No hydrogen atoms were included for this group. Suitable weighting schemes were applied and blocked least-squares refinements eventually converged to the indicated final residuals. As noted in Table IV, the low $(\sin\theta)/\lambda$ data for compound 1 were considered unreliable possibly due to the overlap from adjacent reflections (profiles somewhat broad) and have been excluded in the final refinements.

For all four structures neutral atom scattering curves stored in the programs were originally taken from ref 23a. Computing was performed on PDP11/23 and Gould 9705 computers using programs in the SDP package and SHELX.[23] The final atomic positional parameters for all four structures are given in Table V.

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Registry No. 1, 96760-17-7; 2, 118243-25-7; 3, 118015-90-0; 4, 117959-28-1.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positions, results of best molecular fits, and supplementary bond lengths and bond angles for compounds 1–4 (17 pages); listings of final structure factor amplitudes for compounds 1–4 (129 pages). Ordering information is given on any current masthead page.

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