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Crystal and molecular structure of $[i\text{-}Pr_2Si]_4$ and $[(Me_3SiCH_2)_2Si]_4$ and some structural properties of cyclopolysilanes, $[R^1R^2Si]_n (n = 3\text{-}6)$

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The crystal structures of octaisopropylcyclotetrasilane $[i\text{-}Pr_2Si]_4$ (1) and octakis(trimethylsilylmethyl)cyclotetrasilane $[(Me_3SiCH_2)_2Si]_4$ (2) have been determined by means of X-ray diffraction analysis. Various crystallographic and structural data for the two compounds were recorded. The Si_4 rings of the compounds are nonplanar with quite large dihedral angles of 37.1° in (1) and 36.6° in (2), being comparable to that (36.8)° for $[t\text{-}BuMeSi]_4$ reported previously and other characteristic features in the structures of (1) and (2) were described. Some structural properties of the cyclic catenation systems, $[R^1R^2Si]_n$ ($n = 3$–6), including (1) and (2) were also discussed from a comparative viewpoint with respect to the ring shape and the relationship between ring size and Si-Si bond length.

Keywords: Organometallics, cyclic catenation systems, peralkylcyclopolysilanes, peralkylcyclotetrasilanes, crystal and molecular structures, dihedral angles, cyclotetrasilane ring shapes

INTRODUCTION

Although the chemistry of peralkylcyclopolysilanes $[R^1R^2Si]_n$ ($n = 3$–7) bearing alkyl groups other than methyl, has been considerably developed in recent years, only a few crystal structures for each particular ring size (n) have been determined by X-ray diffraction methods and little is known about the structural details for these cyclopolysilanes. Most recently we reported that the crystal and molecular structures of the first peralkylcyclotrisilane, $[(t\text{-}BuCH_2)_2Si]_3$,[1] had been determined and that the Si-Si bond length in the Si_3 ring is the longest among those for various peralkylcyclopolysilanes and is comparable with that in the first perarylcyclotrisilane, $[(2,6\text{-}Me_2C_6H_3)_2Si]_3$.[2]

In recent papers we also described the syntheses of a series of octaalkylcyclotetrasilanes $[R^1R^2Si]_4$, including $R^1{=}R^2{=}i\text{-}Pr$ and Me_3SiCH_2 substituents, in workable yields from the lithium-mediated reductive couplings of the corresponding dialkyldichlorosilanes[3–7] and tetraalkyldichlorodisilanes in tetrahydrofuran (THF).[8] In the four-membered cyclopolysilanes, the structures of octamethylcyclotetrasilane, $[Me_2Si]_4$[9] and octakis(trimethylsilyl)cyclotetrasilane, $[(Me_3Si)_2Si]_4$[10] have been shown by X-ray analysis to be planar, while the structures of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilanes, $[t\text{-}BuMeSi]_4$,[11] and octaphenylcyclotetrasilane, $[Ph_2Si]_4$,[12] are of folded shape with varying dihedral angles. Thus, it is of some interest to determine the structures of the title compounds by X-ray analysis and to compare the crystallographic data with those of the cyclopolysilanes, $[R^1R^2Si]_n$ ($n = 3, 5, 6$).

To date, some crystallographic and structural data for a series of the catenation system, $[R^1R^2Si]_n$ ($n = 3$–6), together with the data of the title compounds, have been documented. However there are no reports on the comparisons of structural features covering the whole members of these cyclopolysilanes. This paper also deals with such structural properties as the ring shape on Si_4 cycles, and the relationship between the ring size and Si-Si bond length in rings.

It has recently been found that cyclopolysilanes of the type discussed in this work have some important applications, e.g. as Si=Si precursors,[5,13] silylene precursors[5,13a,14] electron donors,[6,15] ceramic precursors[16] and so on. Thus, the present work would provide potentially useful information about the applied aspects of the series of cyclopolysilanes.

EXPERIMENTAL

Materials

Preparation of octaisopropylcyclotetrasilane (1) and octakis(trimethylsilylmethyl)cyclotetrasilane (2).

[i-Pr_2Si]$_4$ (1): This compound [^{29}Si NMR (δ, TMS) (C_6D_6)-5.45; other spectral data, ref. 6] was prepared by the condensation of diisopropyldichlorosilane (or *sym*-tetraisopropyldichlorodisilane) with lithium in THF as previously described.[3,5,7]

Single crystals for X-ray analysis were obtained by slow recrystallization from ethanol and by slow sublimation at ca. 200° in an evacuated sealed tube.

[$(Me_3SiCH_2)_2Si$]$_4$ (2): This compound was obtained according to the following scheme:

$$\underset{(3)}{Me_3SiCH_2Cl} \xrightarrow{Li} \underset{(4)}{Me_3SiCH_2Li}$$

$$\xrightarrow{H_2SiCl_2} \underset{(5)}{(Me_3SiCH_2)_2SiH_2}$$

$$(5) \xrightarrow[PdCl_2]{CCl_4} \underset{(6)}{(Me_3SiCH_2)_2SiCl_2}$$

$$\xrightarrow[THF]{Li} \underset{(2)}{[(Me_3SiCH_2)_2Si]_4}$$

A solution containing (4) in petroleum-ether (350 cm^3; olefin-free) was prepared from lithium (2% Na alloy) (9.3 g, 1.30 g-atom) and 3 (52.8 g, 430 mmol) under Ar with irradiation (100 W ultrasound) and refluxing for 6 h, and titrated with a standard solution of *s*-BuOH/xylene using *o*-phenanthrolin as indicator[17] ((4): 360 mmol, 83% yield based on 3 used).

To the solution containing (4), which was cooled in an ice-salt bath, a cold solution of H_2SiCl_2 (12.5 cm^3; 15.3 g 151 mmol; liquified in a calibrated tube by cooling in an ice-salt bath) in *n*-hexane (15 cm^3) was added slowly under Ar and stirred for 10 h, during which time the mixture was allowed to warm up to room temperature. At this time, no H_2SiCl_2 remained (an amine test was negative).* The resulting mixture was worked up to give liquid bis(trimethylsilylmethyl)silane, (5), bp 107–113°C/104 mm Hg; 27.3 g (88%); n_D^{20} 1.4382; ^{1}H NMR (δ, TMS) (CCl_4)-0.22 (t, CH_2), 0.07(s, $SiCH_3$), (22H), 3.80(q, SiH, 2H) ($J_{SiH\text{-}CH_2}=4.6$ Hz); IR (cm^{-1}) (neat, sandwich) 2120(SiH), 1245($SiCH_3$); Analysis, Found: C, 46.77; H, 11.75%, Calcd. for $C_8H_{24}Si_3$: C, 46.98; H, 11.83%.

To a mixture of CCl_4 (61.5 g, 400 mmol) and $PdCl_2$ (0.2660 g, 3 mol% relative to the hydrosilane used), compound (5) (10.23 g, 50 mmol) was added over 30 min with magnetic stirring under N_2. After stirring for 1 h followed by evaporating the excess CCl_4, the mixture gave bis(trimethylsilylmethyl)dichlorosilane, (6); bp 110–130°C/55 mm Hg; 11.53 g (83%); ^{1}H NMR (δ, TMS) (CCl_4) 0.16(s, $SiCH_3$, 18H), 0.45(s, CH_2, 4H); IR (cm^{-1}) (neat, sandwich) 1250 ($SiCH_3$); Analysis, Found: C, 35.29; H, 8.19%; Calcd. for $C_8H_{22}Cl_2Si_3$: C, 35.14; H, 8.11%.

According to the reported method,[7] compound (2) [^{29}Si NMR (δ, TMS) ($CDCl_3$) 0.73 (Me_3SiCH_2) and -21.44 (ring Si); other spectral data, ref. 7] was obtained by reductive coupling of (6) with lithium. The crystals for X-ray analysis were obtained by slow recrystallization from ethanol.

Measurement of crystal data

The molecular structures of the title compounds were determined by the X-ray diffraction method. The crystal data and diffraction intensities were measured on a four-circle diffractometer (Rigaku-Denki; Model AFC-4) in the $\omega/2\theta$ scan mode, using Mo–Kα radiation ($\lambda=0.71069$) for (1) and Cu-Kα ($\lambda=1.5418$) for (2), with a graphite monochromator. Reflections were collected with 2θ up to 45° and 80° for (1) and (2), respectively. The reflections of the higher angles were too weak to detect. The intensities of three standard reflections were measured every 50 reflections. In compound (1), an 8% decline between the standard intensities in both the initial and final stages of the collections was observed, while such

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*A spot test by adding triethylamine to a small amount of the reaction mixture showed no white turbidity due to the formation of a quaternary ammonium salt or amine-chlorosilane complex; see ref. 18.

Table 1 Crystal data and collection parameters for [i-Pr$_2$Si]$_4$ and [Me$_3$SiCH$_2$)$_2$Si]$_4$

	[i-Pr$_2$Si]$_4$ (1)	[(Me$_3$SiCH$_2$)$_2$Si]$_4$ (2)
Molecular weight	457.060	810.073
Crystal system	Tetragonal	Monoclinic
Space group	I41/acd	P21/c
Cell constants		
a(Å)	17.950 (2)	24.208 (1)
b(Å)	17.950 (2)	22.620 (1)
c(Å)	18.990 (3)	29.142 (2)
α(°)	90.00	90.00
β(°)	90.00	134.37 (1)
γ(°)	90.00	90.00
Cell volume (Å^3)	6109.1 (1.1)	11407.7 (1.6)
Molecules in unit cell (Z)	8	8
ρ(calcd) (g.cm^{-3})	0.9936	9.9445
Crystal size (mm)	0.1 × 0.1 × 0.6	0.1 × 0.1 × 0.8
Radiation	MoKα	CuKα
Monochromator	Graphite	Graphite
Reflection, data used ($\lvert F_0 \rvert > 3\sigma(\lvert F_0 \rvert)$)	493	3043
Scan range (width)(°)	2θ (3 ~ 45)	2θ (3 ~ 80)
Scan speed (degree·min^{-1})	4	8
R factor	7.1	7.7

a large decline was not in compound (2). The values of $\lvert F_0 \rvert$ were obtained from the intensity data by applying corrections to the decline. Total numbers of 495 reflections for (1) and of 3043 for (2) with ($\lvert F_0 \rvert > 3\sigma \lvert (F_0) \rvert$) were used for the analyses, since in the collected reflections (1106 for (1) and 7155 for (2)) many zero-intensity reflections were included. No correction was made for the absorptions. The dimensions of the crystals, the unit cell parameters, and other crystal data are given in Table 1. The crystal data and X-ray structural data of compound (1) were obtained from the single crystal prepared by the recrystallization from ethanol.

It should be noted that, for molecule (1) the single crystal of which was formed by the sublimation as mentioned above, the crystal data and the unit cell parameters were completely the same as those of the crystal obtained by the recrystallization from ethanol. Therefore, further X-ray analyses for the crystal prepared by sublimation were not necessary.

Table 2 Fractional atomic coordinates (×10^4) and equivalent isotropic thermal parameters in [i-Pr$_2$Si]$_4$ (1)

$$\mathrm{Beq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$$

Atom	X	Y	Z	Beq
SI	5753 (1)	3012 (1)	1394 (2)	3.2 (0.1)
C1	5828 (6)	3195 (5)	2391 (5)	5.2 (0.3)
C2	6008 (7)	4005 (6)	2569 (7)	6.5 (0.4)
C3	6306 (7)	2670 (8)	2797 (6)	7.8 (0.5)
C4	6536 (5)	3467 (5)	861 (5)	4.5 (0.3)
C5	6497 (6)	4326 (6)	797 (6)	6.4 (0.4)
C6	7316 (5)	3227 (6)	1116 (7)	6.7 (0.4)

Determination of the structures

The structures of (1) and (2) were solved by the direct method using MULTAN 78 program.[19] Refinements for the atom positions were carried out by the block-diagonal least squares method using anisotropic temperature factors for non-hydrogen atoms.* The parameters of the hydrogen atoms were not refined. The final R-factors for (1) and (2) are listed in Table 1, and the final parameters in Table 2 for (1) and in Table 3 for (2) (molecules A and B). All the calculations were performed with UNICS III

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*The hydrogen atoms in (1) were placed at the calculated positions, assuming the C—H bond length to be 1.10 Å and the four C—H bonds to be arranged in a tetrahedral angle around the carbon atoms. The terminal hydrogens in the substituent (Me$_2$CH) were also assumed to be at gauche positions to each other. In (2) the temperature factors of the methyl carbon of the substituent (Me$_3$SiCH$_2$) were so large that the hydrogen atoms in the methyl were neglected in the calculations.

Table 3 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters in $[(Me_3SiCH_2)_2Si]_4$ (2)

$Beq = 4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$

Atom	*X*	*Y*	*Z*	Beq
Molecule A				
SI1A	4250 (4)	−9 (4)	2590 (4)	6.2 (0.6)
SI2A	3040 (4)	−11 (4)	2287 (3)	5.9 (0.6)
SI3A	3250 (4)	1014 (4)	2558 (4)	6.3 (0.6)
SI4A	4070 (4)	1026 (4)	2379 (4)	6.3 (0.6)
C1A	5067 (14)	−68 (12)	3478 (11)	7.2 (1.9)
C2A	4378 (17)	−574 (14)	2180 (13)	9.6 (2.5)
C3A	2235 (13)	−65 (14)	1379 (11)	7.8 (1.9)
C4A	2857 (14)	−584 (14)	2671 (13)	8.1 (2.3)
C5A	2387 (15)	1505 (11)	1984 (12)	6.6 (2.2)
C6A	3739 (15)	1141 (11)	3406 (11)	6.9 (2.1)
C7A	3563 (17)	1224 (13)	1538 (12)	8.4 (2.3)
C8A	4961 (16)	1512 (11)	2993 (12)	7.3 (2.3)
SI5A	5616 (5)	−772 (4)	3908 (4)	8.3 (0.7)
SI6A	4252 (5)	−498 (4)	1487 (4)	8.4 (0.7)
SI7A	1660 (5)	−742 (4)	923 (4)	9.4 (0.7)
SI8A	3076 (5)	−563 (4)	3400 (4)	7.9 (0.7)
SI9A	1493 (5)	1503 (4)	1854 (4)	8.7 (0.7)
SI10A	4254 (6)	1833 (4)	3889 (4)	8.5 (0.7)
SI11A	3106 (6)	1932 (5)	1105 (5)	10.1 (0.9)
SI12A	5835 (6)	1556 (5)	3120 (5)	10.3 (0.9)
C9A	6314 (18)	−897 (15)	3844 (16)	11.4 (3.2)
C10A	6183 (18)	−686 (20)	4782 (14)	14.2 (2.9)
C11A	4931 (19)	−1426 (12)	3556 (15)	10.4 (3.0)
C12A	4495 (19)	−1239 (15)	1360 (16)	11.2 (3.2)
C13A	4895 (18)	98 (14)	1600 (16)	10.6 (3.2)
C14A	3215 (17)	−344 (17)	729 (14)	11.6 (2.6)
C15A	1158 (19)	−620 (15)	52 (14)	11.7 (2.8)
C16A	2332 (20)	−1402 (15)	1258 (16)	11.9 (3.4)
C17A	901 (18)	−859 (15)	953 (16)	11.2 (3.0)
C18A	2489 (18)	10 (14)	3350 (16)	10.3 (3.0)
C19A	2774 (18)	−1279 (14)	3468 (15)	9.8 (3.0)
C20A	4115 (15)	−455 (16)	4138 (12)	9.9 (2.3)
C21A	1741 (21)	1817 (15)	2589 (16)	11.6 (3.6)
C22A	1093 (16)	712 (13)	1691 (15)	9.7 (2.6)
C23A	745 (17)	1962 (14)	1133 (14)	10.5 (2.6)
C24A	4031 (24)	1943 (14)	4388 (17)	12.5 (4.0)
C25A	5352 (22)	1717 (16)	4471 (16)	13.2 (3.4)
C26A	4003 (19)	2529 (12)	3403 (14)	10.4 (3.0)
C27A	3413 (23)	2158 (17)	693 (16)	13.3 (3.8)
C28A	2030 (23)	1818 (16)	478 (18)	13.8 (3.8)
C29A	3345 (23)	2556 (14)	1643 (17)	13.2 (4.0)
C30A	6563 (21)	2053 (19)	3833 (20)	17.8 (4.0)
C31A	6339 (18)	814 (16)	3346 (19)	14.1 (3.4)
C32A	5541 (24)	1806 (22)	2332 (21)	18.6 (4.8)

Table 3 Continued

Atom	*X*	*Y*	*Z*	Beq
Molecule B				
SI1B	9471 (4)	−18 (4)	2908 (4)	6.6 (0.6)
SI2B	8106 (4)	−9 (4)	2230 (4)	6.1 (0.6)
SI3B	8140 (4)	1002 (4)	2026 (4)	6.3 (0.6)
SI4B	9434 (4)	1020 (4)	3064 (4)	6.3 (0.6)
C1B	9732 (15)	−106 (11)	2442 (12)	7.4 (2.0)
C2B	9979 (18)	−591 (17)	3554 (14)	11.5 (2.9)
C3B	7763 (16)	−60 (12)	2644 (12)	8.1 (2.3)
C4B	7594 (16)	−593 (15)	1570 (13)	9.4 (2.4)
C5B	7497 (15)	1545 (12)	1934 (12)	7.5 (2.1)
C6B	8056 (13)	1081 (11)	1327 (10)	5.9 (1.8)
C7B	9441 (17)	1125 (13)	3716 (12)	8.8 (2.4)
C8B	10127 (16)	1561 (13)	3191 (13)	8.8 (2.3)
SI5B	9573 (6)	−745 (4)	1948 (5)	9.9 (0.8)
SI6B	10982 (5)	−813 (4)	4213 (4)	9.3 (0.7)
SI7B	7964 (6)	−666 (5)	3185 (5)	10.1 (0.9)
SI8B	6580 (5)	−711 (4)	879 (4)	9.3 (0.7)
SI9B	6417 (5)	1598 (4)	1274 (5)	9.0 (0.8)
SI10B	8356 (5)	1766 (4)	1179 (4)	7.6 (0.7)
SI11B	9202 (6)	1816 (4)	3885 (4)	9.8 (0.9)
SI12B	11196 (5)	1520 (4)	3876 (4)	8.4 (0.6)
C9B	10445 (20)	−871 (18)	2069 (19)	14.4 (3.9)
C10B	9433 (23)	−1443 (17)	2206 (21)	15.7 (4.7)
C11B	8709 (20)	−616 (22)	1075 (14)	15.8 (3.1)
C12B	11537 (17)	−881 (14)	3987 (14)	10.0 (2.7)
C13B	11016 (22)	−1557 (17)	4485 (19)	14.4 (4.0)
C14B	11440 (24)	−314 (21)	4909 (17)	17.4 (3.7)
C15B	7130 (22)	−737 (16)	3094 (20)	14.9 (4.4)
C16B	8127 (21)	−1384 (16)	2986 (19)	13.3 (3.9)
C17B	8818 (22)	−490 (19)	4026 (16)	14.2 (3.6)
C18B	6456 (21)	−1348 (18)	448 (18)	15.1 (3.5)
C19B	6178 (19)	−59 (18)	319 (15)	13.5 (2.8)
C20B	5994 (16)	−830 (14)	1092 (14)	9.0 (2.6)
C21B	5975 (16)	929 (16)	1306 (17)	12.2 (3.0)
C22B	6072 (18)	2285 (14)	1383 (17)	11.2 (3.3)
C23B	6094 (17)	1692 (15)	473 (14)	10.7 (2.6)
C24B	9311 (19)	1598 (17)	1432 (17)	11.9 (3.3)
C25B	7665 (20)	1912 (15)	298 (15)	12.9 (3.2)
C26B	8460 (18)	2465 (12)	1588 (14)	9.3 (2.9)
C27B	8248 (23)	1733 (18)	3656 (19)	14.5 (4.3)
C28B	9154 (26)	2501 (16)	3496 (20)	14.7 (4.7)
C29B	9970 (24)	1927 (18)	4790 (17)	15.2 (3.9)
C30B	11498 (18)	1503 (18)	4690 (13)	12.6 (2.6)
C31B	11648 (16)	2198 (16)	3885 (15)	11.3 (2.7)
C32B	11584 (18)	874 (16)	3774 (18)	14.0 (3.2)

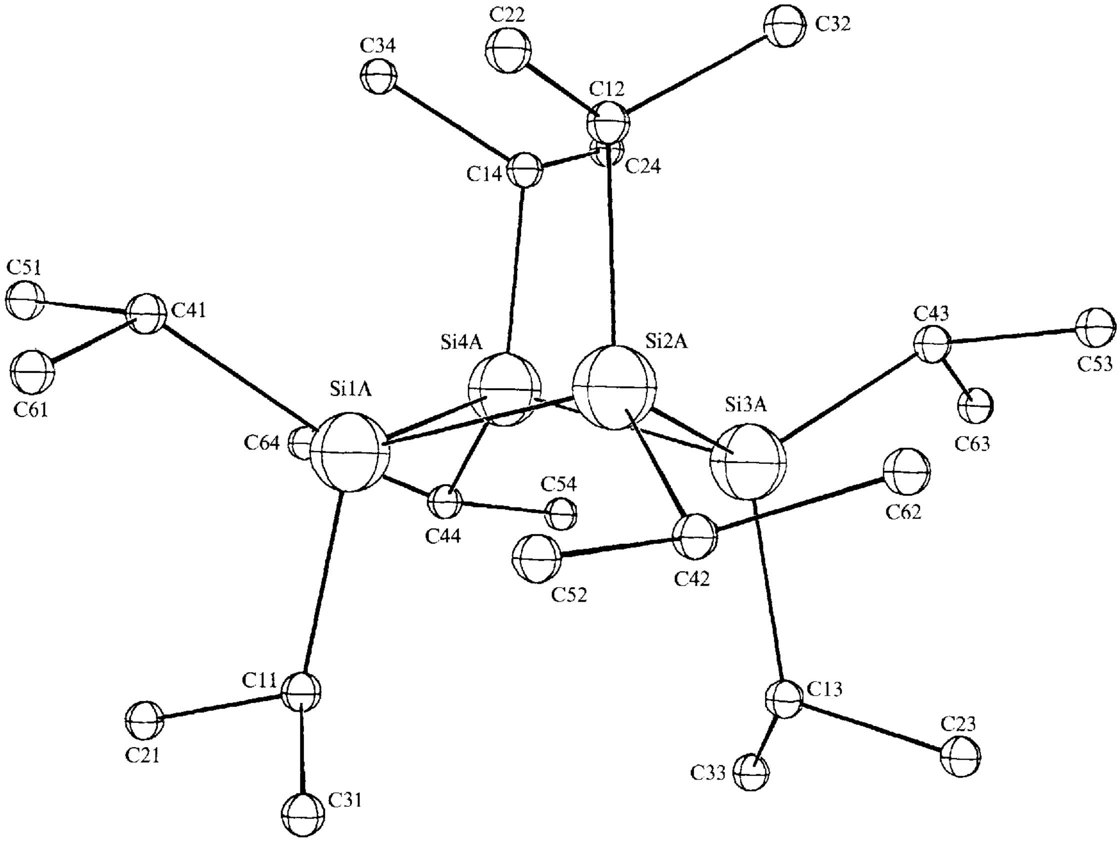

Figure 1 Molecular structure of compound (1) [i-$Pr_2Si]_4$.

system.[20] Lists of anisotropic temperature factors and structure factors are available from supplementary materials.*

RESULTS AND DISCUSSION

Structural features in molecules (1) and (2)

The molecular and crystal structures of compound (1) are shown in Figs 1 and 2 respectively. The molecule has a four-fold rotatory inversion axis ($\bar{4}$-fold axis) and the independent crystallographic unit comprises one silicon atom and two isopropyl groups. The nucleus of the molecule consists of four Si atoms forming a puckered ring and the conformation is very similar to that of [t-BuMeSi]$_4$ reported by West et al., [11] except that eight substituents are all isopropyl groups. Corresponding views of compound (2) are given in Figs 3 and 4. In the asymmetric unit, there are two kinds of crystallographically independent molecules, A and B, which have similar conformations and molecular parameters to each other. The four-membered rings of the two molecules also form puckered Si_4 rings which would have $\bar{4}$-fold axis as shown in compound (1). These features of Si_4 rings were found to be essentially identical in the molecules. Relevant bond distances and angles are given in Table 4 for (1) and in Table 5 for (2) (molecules A and B).

It is of interest to compare the Si—Si bond lengths in (1) (2.374 Å) and in (2) (2.388 Å average of two molecules) (see also Table 6) with those of other cyclotetrasilanes reported. The Si—Si bond lengths of (1) are almost the same as those of [t-BuMeSi]$_4$[11] and $[Ph_2Si]_4$[12] (2.377 Å), and are longer than that of $[Me_2Si]_4$ (2.363 Å).[9] Thus the bond length of (2) is the longest amongst the cyclotetrasilanes yet reported, since the values of

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*From the authors.

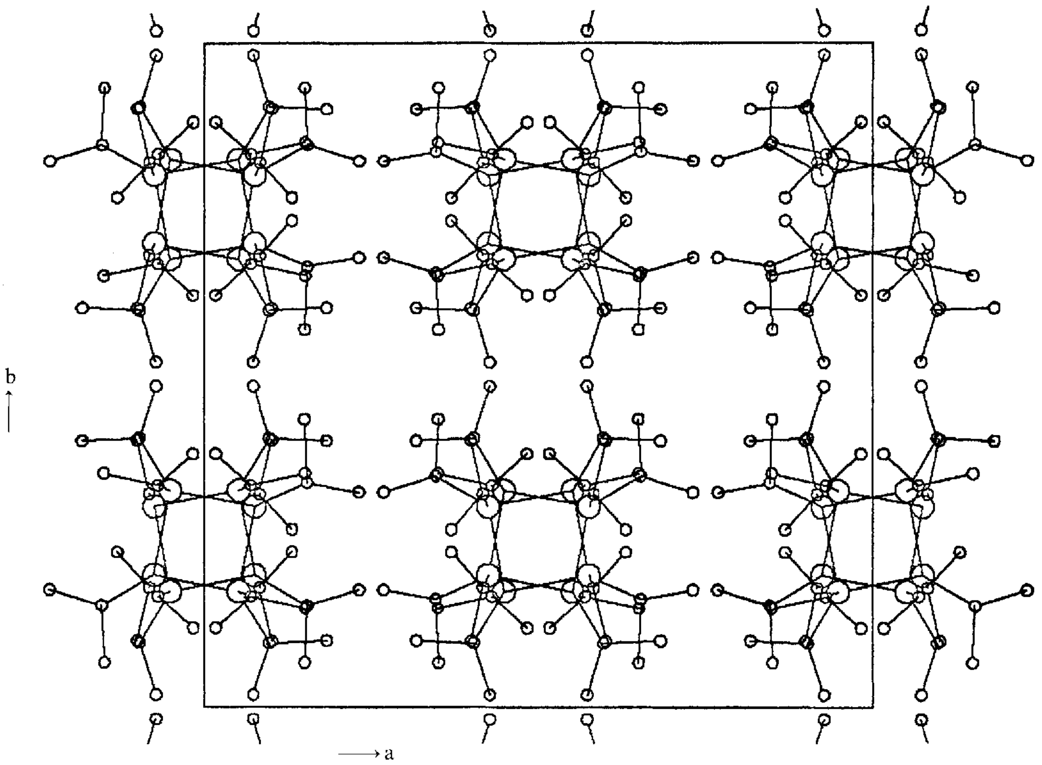

Figure 2 Crystal structure of compound (1) (c-projection). $[i\text{-}Pr_2Si]_4$.

$[(Me_3Si)_2Si]_4$[10] bearing the largest substituents on each ring silicon are not given at this time. The increasing trend in the bond lengths can be related to the increasing congestion due to the substituents on the Si_4 ring silicons in the order, Me/Me $< i\text{-}Pr/i\text{-}Pr \lesssim t\text{-}Bu/Me \approx Ph/Ph <$ Me_3SiCH_2/Me_3SiCH_2. On the other hand, the Si—C bond lengths between the α-carbons and the ring silicons in (1) (1.91 Å) and (2) (1.90 Å) (average values in both) fall into the middle of the range of reported values for the other cyclotetrasilanes (1.81–1.97 Å) (Tables 4 and 5).

The most intriguing feature of the structures in (1) and (2) is the strongly puckered configuration of the Si_4 ring of silicon atoms, as shown in Figs 1 and 2, respectively. The dihedral angle between the two wings of the folded ring is 37.1° in (1) and 36.6° (average for molecules A and B) in (2). Both angles (or puckerings) are very close to that observed in $[t\text{-}BuMeSi]_4$ (36.8°).[11] The Si-Si-Si bond angles in the ring systems of (1) and (2) were shown to be ca. 87.0° (Tables 4 and 5), which is significantly less than 90°, as expected from the large puckering.

The axial and equatorial carbon atoms attached to the ring silicons appear to bend away from the normal configuration which is encountered in a cyclohexasilane, such as dodecamethylcyclohexasilane,[21] so as to minimize the ring strain[22] and the steric repulsions between the substituents on silicons. The C-Si-C angles are ca. 113° in (1) and ca. 109–112° in (2). For (1) and (2) the planes of the Si-C bond pair at each Si atom in the tops of the wings are nearly perpendicular to the corresponding planes.

Si_4 ring structures in cyclotetrasilanes, $[R^1R^2Si]_4$

Previously, Cotton and Frenz studied the molecular structures of various cyclobutane derivatives, including complex fused-cyclobutane systems which have a variety of substitients on the ring carbons.[23] They have shown that the cyclobutanes can be classified into three types of C_4 ring structures: (I) molecules with folded rings with dihedral angles ca. 26±3°, each carbon atom of the ring having fairly close angles to the

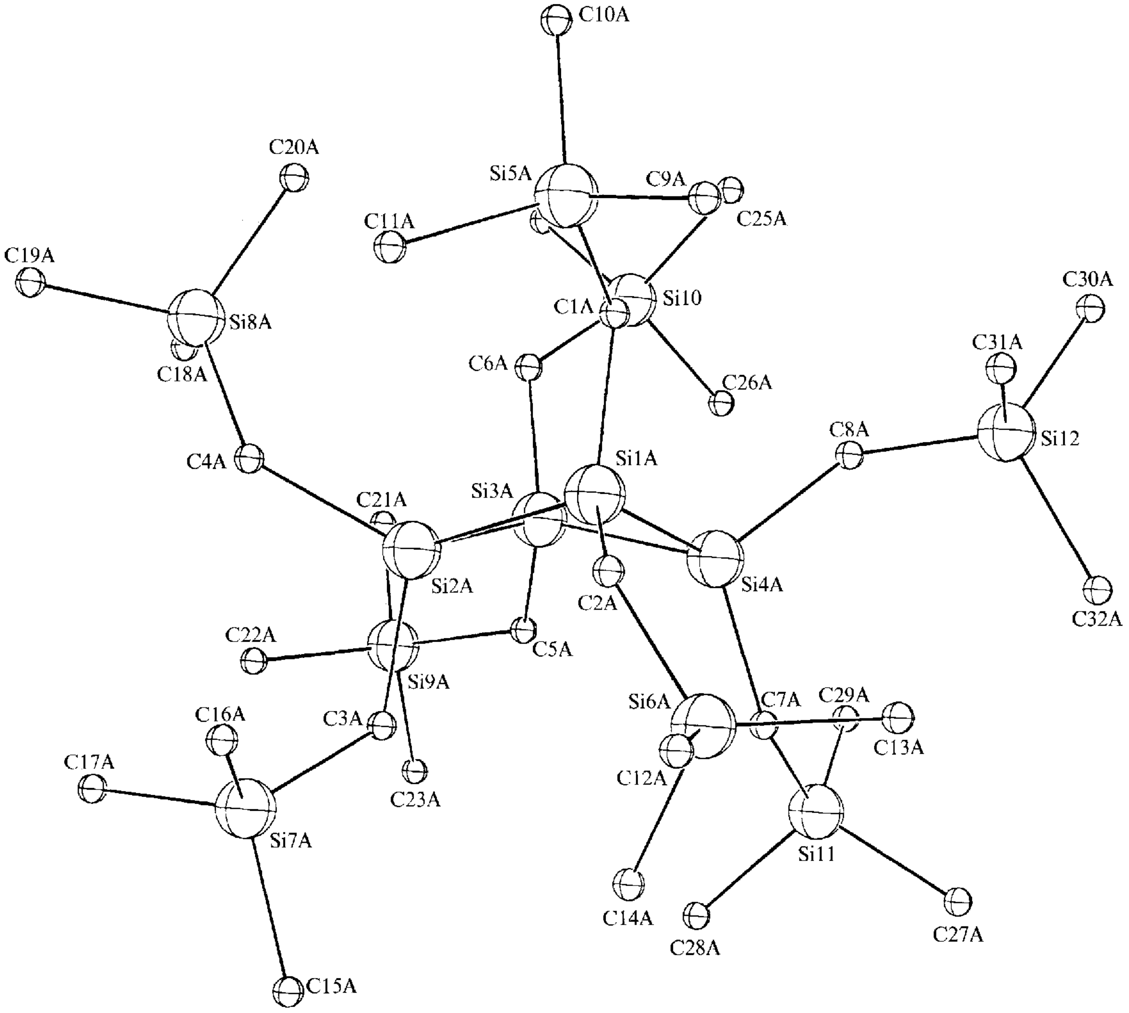

Figure 3 Molecular structure of compound (2) [$(Me_3SiCH_2)_2Si$]$_4$.

Table 4 Structural parameters for [i-Pr_2Si]$_4$ (1)

(a) Interatomic distance (l/Å)			
Si (i)-Si (ii)	2.373 (4)	Si-C1	1.91 (1)
Si-C4	1.91 (1)	C1-C2	1.53 (1)
C4-C5	1.55 (1)	C1-C3	1.50 (2)
C4-C6	1.54 (1)		
(b) Bond angle (φ/°)			
Si (i)-Si (ii)-Si (iv)	87.0 (1)	Si -C1-C2	113.2 (7)
Si (ii)-Si (i)-C1	113.7 (3)	Si -C1-C3	116.2 (8)
Si (iii)-Si (i)-C1	105.1 (3)	Si -C4-C5	115.6 (7)
Si (ii)-Si (i)-C4	114.9 (3)	Si -C4-C6	112.5 (7)
Si (iii)-Si (i)-C4	120.3 (3)	C2-C1-C3	111.4 (10)
C1 -Si -C4	113.3 (5)	C5-C4-C6	110.1 (8)

Symmetry operation code. (i) or no mark: (x, y, z). (ii): $(0.25+y,\ 0.75-x,\ 0.25-z)$. (iii): $0.75-y,\ x-0.25,\ 0.25-z)$. (iv): $(1-x,\ 0.5-y, z)$.

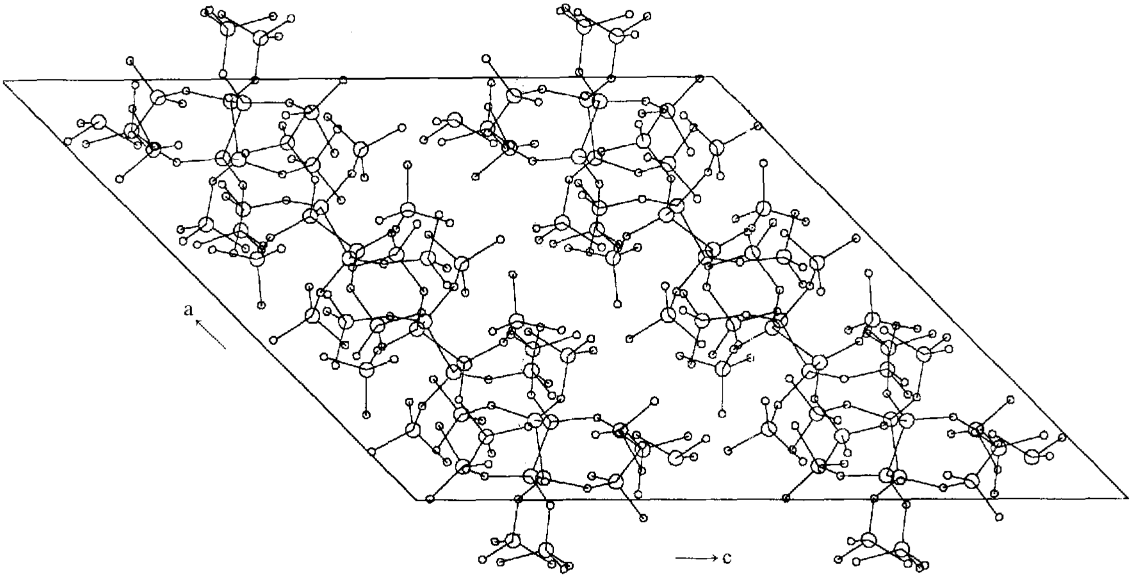

Figure 4 Crystal structures of compound (2) (b-projection). [$(Me_3SiCH_2)_2Si$]$_4$.

Table 5 Structural parameters for [$(Me_3SiCH_2)_2Si$]$_4$ (2)

		(a) Interatomic distance (1/Å)			
	A	B		A	B
Si1-Si2	2.397 (20)	2.385 (12)	Si2-C3	1.90 (2)	1.91 (3)
Si1-Si4	2.384 (12)	2.403 (12)	Si2-C4	1.95 (4)	1.91 (3)
Si2-Si3	2.387 (11)	2.379 (12)	Si3-C5	1.87 (2)	1.85 (4)
Si3-Si4	2.380 (19)	2.390 (8)	Si3-C6	1.87 (3)	1.91 (5)
Si1-C1	1.86 (2)	1.87 (5)	Si4-C7	1.87 (3)	1.91 (5)
Si1-C2	1.92 (4)	1.87 (4)	Si4-C8	1.91 (2)	1.89 (4)
		(b) Bond angle (φ/°)			
	A	B		A	B
Si1-Si2-Si3	87.3 (5)	86.9 (4)	Si2-Si3-C5	115.7 (8)	120.2 (13)
Si1-Si4-Si3	87.8 (5)	86.2 (3)	Si2-Si3-C6	112.1 (9)	111.0 (9)
Si2-Si1-Si4	87.2 (5)	86.3 (4)	Si3-Si2-C3	107.2 (10)	109.0 (10)
Si2-Si3-Si4	87.5 (5)	86.8 (3)	Si3-Si2-C4	122.4 (13)	121.7 (12)
Si1-Si2-C3	108.2 (13)	116.3 (8)	Si3-Si4-C7	114.0 (14)	110.6 (11)
Si1-Si2-C4	119.9 (9)	112.1 (13)	Si3-Si4-C8	111.7 (15)	121.6 (13)
Si1-Si4-C7	114.0 (10)	109.5 (11)	Si4-Si1-C1	104.7 (9)	108.5 (10)
Si1-Si4-C8	116.1 (8)	121.6 (13)	Si4-Si1-C2	125.0 (13)	124.9 (13)
Si2-Si1-C1	117.3 (11)	113.2 (14)	Si4-Si3-C5	112.2 (15)	113.5 (9)
Si2-Si1-C2	117.3 (11)	113.2 (14)	Si4-Si3-C6	115.7 (12)	114.5 (10)
C1-Si1-C2	109.9 (17)	109.9 (18)	C5-Si3-C6	111.7 (16)	109.4 (16)
C3-Si2-C4	109.5 (15)	109.6 (17)	C7-Si4-C8	111.4 (18)	109.7 (17)

A: Molecule A; B: Molecule B

Table 6 Comparison of Si-Si bond lengths in cyclopolysilanes and some related cycles

No.	Cyclopolysilane	Si-Si bond length	(Å) (average)	Ring shape and dihedral angle (°)	Ref.
(1)	[Me_2Si]$_6$	2.332 2.342	2.338		21
(2)	[$PhMeSi$]$_6$	2.356–2.362	2.357		32
(3)	[$(CH_2)_4Si$]$_5$	2.343–2.350	2.347		31
(4)	[$(CH_2)_5Si$]$_5$	2.350–2.366	2.359		31
(5)	[i-Bu_2Si]$_5$	2.352–2.417	2.385		Our work[a]
(6)	[Ph_2Si]$_5$	2.371–2.413	2.396		26
(7)	[Me_2Si]$_4$[b]	2.359 2.367	2.363	Planar (0)	9
(8)	[i-Pr_2Si]$_4$	2.374	2.374	Puckered (37.1)	This work
(9)	[t-$BuMeSi$]$_4$	2.377	2.377	Puckered (36.8)	11
(10)	[Ph_2Si]$_4$	2.370–2.381	2.377	Puckered (12.8)	12
(11)	[$(Me_3SiCH_2)_2Si$]$_4$	2.380–2.403	2.388	Puckered (36.6)	This work
(12)	[$(Me_3Si)_2Si$]$_4$[c]			Planar (0)	10
(13)	[$(t$-$BuCH_2)_2Si$]$_3$	2.367–2.414	2.391		1
(14)	[$(2,6$-$Me_2C_6H_3)_2Si$]$_3$	2.375–2.425	2.407		2
(15)	[t-Bu_2Si]$_3$		2.511		28
(16)	[Ph_2Ge]$_4$	2.458–2.472	2.466	Planar (0)	24
(17)	[$(Me_3SiCH_2)_2Sn$]$_4$	2.829–2.834	2.832	Planar (0)	25

[a] To be published.
[b] X-ray parameter collection was carried out at −186°C.
[c] Crystallographic data are not given.

tetrahedral, (II) molecules of planar ring structure, and (III) molecules with slightly folded rings with intermediate degrees between the two extreme angles, 0° and 26°. They also suggested that the molecule of type I is energetically more preferable than the type III and the most strained is the type II. Thus they concluded that for simple substituted cyclobutane systems the preferred dihedral angle is ca. 26°, unless packing forces require the ring to be planar and that the steric and electronic nature of the substituents has only a limited effect on the puckering of the C_4 ring, except for special cases such as C_4 rings consisting of complex fused ring systems.

In connection with the nature of the cyclobutane derivatives, it is quite interesting to consider the crystal structures of the cyclotetrasilane molecules determined by X-ray analysis. As mentioned above, the ring structures of [t-$BuMeSi$]$_4$,[11] [i-Pr_2Si]$_4$ and [$(Me_3SiCH_2)_2Si$]$_4$ are shown to be folded with dihedral angles of $37 \pm 3°$ (type A), while [Me_2Si]$_4$[9] and [$(Me_3Si)_3Si$]$_4$[10] have been reported to be planar (type B). In addition, the Si_4 ring of [Ph_2Si]$_4$ is slightly folded about the diagonal of the square, the dihedral angle being 12.8° (type C).[12] From observations on the Si_4 ring systems apparently there exist three types of cyclotetrasilane structures, A-C. By analogy with the C_4 ring systems it is likely that the preferred conformation of the Si_4 analogues is the puckered one (type A) with a dihedral angle of ca. 37° and that such cyclotetrasilanes as [Ph_2Si]$_4$, puckered by 12.8°[12] and between the two extreme angles, is a less preferred conformation. The differing degrees of puckering in [Ph_2Si]$_4$ and in the type A cyclotetrasilanes may be due to the differing size (and/or shape) of the substituents and the packing forces in the crystals. The intermediate angle might be due to the result of a compromise between a tendency to pucker and the congestion imposed by the bulky phenyl groups, probably causing a greater ring strain and an enhanced reactivity relative to the fully puckered ones.

It is of interest to discuss the planar structure for the molecules of [Me_2Si]$_4$[9] (No. (7)) and [$(Me_3Si)_2Si$]$_4$ (No. (12)) (Table 6), bearing the smallest and largest substituents respectively. To elucidate the planar shape, knowledge of the structural data of the other tetracyles, [Ph_2Ge]$_4$[24] (No. (16)) and [$(Me_3SiCH_2)_2Sn$]$_4$[25] (No. (17)), might be helpful. In the planar tetracycles, except [$(Me_3Si)_2Si$]$_4$,[10] the steric repulsions between the substituents on the ring metals (M_4) would not be so important a factor because of the rather smaller effective radii of the substituents relative to the M–M distances in each molecule. Thus, since the planar M_4 ring generally appears to have ring strain (type B; see above), the planar structure in these molecules might be attributable to large packing forces with this conformation, the reason for which is not clear at this time. For $[(Me_3Si)_2Si]_4$, however, the planar structure could be explained well in terms of an alternative reason that the remarkable steric crowding due to the very large Me_3Si groups on ring silicons plays an important role and thereby forces the Si_4 ring to be planar. In order to gain an insight about this point further accumulation of structural data on tetracycles (M=Si, Ge and Sn) is apparently necessary.

It is worthwhile to note that variation of the method for making single crystals of cyclotetrasilanes may provide another possibility for producing a crystallographically alternate shape for the molecule. Thus, in the present work, an attempt was made to obtain a single crystal of $[i\text{-}Pr_2Si]_4$ by vacuum sublimation rather than by recrystallization in the usual manner, since a sublimation method has been employed for preparing the crystal of $[Me_2Si]_4$.[9] X-ray diffraction analyses for the single crystals obtained by the two methods showed, however, no difference between both samples in the crystallographic data. Therefore, the molecular structure in the crystals might be independent of the method by which the crystals were prepared, but depends rather upon the nature of the molecule.

Structural features on the cyclic catenation systems, $[R^1R^2Si]_n$ ($n=3$–6)

To date some pertinent structural data by X-ray crystal analyses for a series of cyclopolysilanes, $[R^1R^2Si]_n$ where R^1 and R^2 are alkyls and/or aryls; $n=3$–6, have been accumulated, which permit a survey of the structural features of the cyclic catenation systems, especially of the ring size and bond length. All the compounds thus studied, together with the related ones,[24,25] are summarized in Table 6 which lists the ring size and bond length, and Fig. 3 which shows the relationship between the two sets of structural data in the cyclopolysilanes. Interestingly, it is seen from the distribution of the plots that the smaller the ring size the longer the Si-Si bond length. The increase in the Si-Si bond length going from Si_6, Si_5, Si_4 to Si_3 is probably the result of increasing steric repulsion between the substituents on silicon and thus of ring strain.[18] For different ring systems having the same kind of substituents, however, this trend is not in harmony with the fact that, for example, the Si-Si bond distance of $[Ph_2Si]_5$ (No. (6)) (2.396 Å)[26] is considerably longer than that of $[Ph_2Si]_4$ (No. (10)) (2.377 Å).[12] This is not surprising since the molecular shape and the bond distance indicated are considered to be mainly the result of compromise between steric repulsion and ring strain.[22] Thus, when the same kind (or set) of bulky substituent(s) is attached to different ring systems, as shown in the phenyl substituted systems, it is quite natural to consider that the steric repulsion between the substituents on the larger ring system should be larger than that between those on the smaller ring. This is because of the smaller space around each Si atom in the larger ring system if the Si-Si bonds in the both systems remain of equal length. Then, the steric repulsion in the larger ring molecule would actually force the bonds to elongate and pucker the Si_n ($n \geqq 4$) rings to some extent so as to release and minimize the strain due to repulsion, forming the energetically preferable structure which has larger Si-Si bond distances than those in the smaller ring. However, for the cyclopolysilane systems which bear small substituent(s) such as methyl in the system (Fig. 5, No. (1) and (7), a more detailed study is apparently necessary because only limited data[9,21] is available at the present time.

On the other hand, for a particular ring size the Si-Si bond lengths depend primarily on the steric bulk of the substituents, as indicated in the Si_4 ring series. Similarly, the Si-Si bond distances in the Si_3 ring system were shown to be No. (15)>(14)>(13), the bulk order being $Me_3C > 2,6\text{-}Me_2C_6H_3 > Me_3CCH_2$, which suggests that congestion at the α-atoms attached to the ring silicon evidently determines the effective volumes of the groups. It is of interest to point out that in contrast to the case for the silicon series, the bulk parameter of substituents for carbon compounds, the steric substituent constant [Es(C) value], is estimated to be -1.74 for Me_3CCH_2 and -1.54 for Me_3C group.[27] It is also worthwhile to note that the Si_3 ring of $[t\text{-}Bu_2Si]_3$ (No. (15)), prepared recently by Weidenbruch et al.,[28] would be highly strained and potentially reactive,[29] since it has an unusually long Si-Si bond distance (2.511 Å), caused by very large t-butyl groups, compared with the normal Si-Si bond distances, 2.34 Å. Indeed, we found that our cyclotrisilane, $[(t\text{-}$

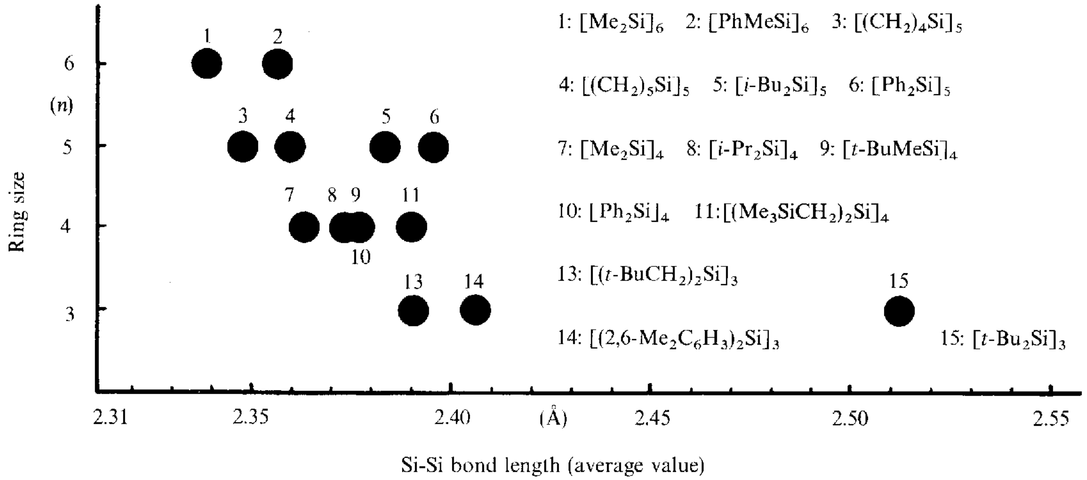

Figure 5 Relationships between ring size (n) and Si-Si bond distance in cyclopolysilanes, $[\text{R}^1\text{R}^2\text{Si}]_n$ ($n = 3$–6) (see Table 6).

$\text{BuCH}_2)_2\text{Si}]_3$,[1,5] is the most reactive towards various reagents relative to other larger cyclopolysilanes, the results of which were described elsewhere.[33]

Finally, it is worthwhile to note that, from the above information and other physico-chemical properties, the cyclopolysilanes discussed above might become useful in applied fields in the forms of various composite materials.

SUMMARY

1. The molecular structures of $[i\text{-Pr}_2\text{Si}]_4$ and $[(\text{Me}_3\text{SiCH}_2)_2\text{Si}]_4$ were found to have a $\bar{4}$-fold axis and strongly puckered configurations of the Si_4 rings with dihedral angles of 37.1° and 36.6°, respectively. In the cyclotetrasilanes $[\text{R}^1\text{R}^2\text{Si}]_4$, it was found that there are three types of the ring structures: the planar, the strongly puckered ($37 \pm 3°$), and another type with intermediate dihedral angles between the two extreme angles. These ring shapes are mainly dependent on factors such as the bulk of the substituents on the silicon atoms (steric repulsion between the substituents) and on ring strain.

2. In the relationship between the ring size and Si-Si bond length in a series of cyclopolysilanes, $[\text{R}^1\text{R}^2\text{Si}]_n$ ($n = 3$–7), it is generally seen that the smaller the ring size, the longer the Si-Si bond length. For a particular ring size, the bulkier the substituent, the longer the Si-Si bond length. Thus the Si-Si bond length serves as a measure for the bulk of substituents on silicon. The increase in Si-Si bond length with decrease in the ring size parallels the increase in ring strain energy which in turn parallels the trend in reactivity for ring-opening reactions.

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