MOLECULAR STRUCTURE OF COMPOUNDS WITH SILICON-SILICON BONDS

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ABSTRACT

The present review provides a comprehensive survey of data on the molecular structure of organosilicon compounds with silicon-silicon bonds, including the derivatives containing the traditional tetrahedral silicon (disilanes, trisilanes, linear and branched polysilanes, cyclic compounds) and disilenes with Si=Si double bond.

INTRODUCTION

Molecules built up from Si-Si bond chains, — oligo- and polysilanes — have come under increased scrutiny because of their unusual electronic, optical and chemical properties. Consequently, the structural information is very useful in understanding of these properties. The results of the structural investigations of the compounds containing Si-Si bond were reviewed in 1989 [1]. During the last 10 years the rapid rise in the creation of new types of polysilane compounds, such as dendritic polysilanes, unique cyclic products (tetrasilatetrahedrane, hexasilaprismane, octasilacubane), strained cyclic allene and acetylene polysilanes can be seen. Exciting progress has been made in the field of new stable disilenes with Si=Si double bond. In the current paper we have summarized the numerous investigations scattered in the literature on the structure of the compounds containing Si-Si and Si=Si bonds.

1. Polysilanes

1.1. Acyclic polysilanes

Within the acyclic polysilanes series the most detailed structural studies have been carried out with various disilanes, applying microwave spectroscopy, electron diffraction and X-ray techniques (Table 1).

The Si-Si bond length varies from 2.24 Å in hexachlorodisilane [47] (according to other data the Si-Si bond length in this compound equals 2.34 Å [46] and 2.324 Å [48]) up to 2.697 Å for hexa(*tert*-butyl)disilane (this is the longest distance between the silicon atoms among all studied polysilanes).

For the most disilanes a remarkable constancy of the Si-Si bond length may be observed. The substitution of one hydrogen atom in disilane H_3SiSiH_3 for a cyano group, fluorine or iodine atom does not induce any substantial change in the Si-Si bond length. By going from iododisilane (2.336 Å) to symmetrical diiododisilane (2.380 Å) and tetraiododisilane (2.389 Å) the length of the Si-Si bond increases insignificantly. According to X-ray diffraction the Si-Si bond in hexaiododisilane is shorter (2.323 Å). Almost the same values were obtained for hexachlorodisilane (2.324 Å) and hexafluorodisilane (2.324 Å) with the aid of electron diffraction.

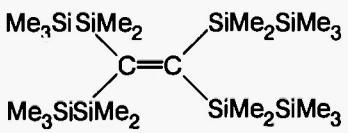
The Si-Si distances in hexamethyldisilane (2.340 Å), pentamethyldisilanyllithium (2.344 Å), 1,1,1-trimethyl-2,2,2-triphenyldisilane (2.355 Å), tetramethyldi(ferrocenyl)disilane (2.340 Å) and in number of tetramethyl-1,2-diaryldisilanes (2.337-2.348 Å) are in a narrow region.

A rather short Si-Si bond has been detected in the 1,1'-bis(silacyclopropane) (2.313 Å) and 1,1'-bis(silacyclopropene) (2.296 Å) derivatives, this fact being apparently due to the decreasing of the cyclic CSiC angles to 49.1° and 42.3°, respectively.

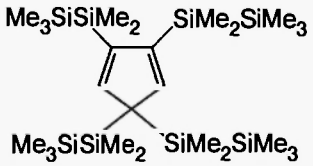
Comparison of the 1,2-di(4-tolyl)disilane (2.329 Å), 1,1,2,2-tetraphenyldisilane (2.344 Å), pentaphenyldisilane (2.357 Å) and hexaphenyldisilane (2.519 Å) structures revealed a lengthening of the Si-Si bond with increasing the number of aryl groups in a molecule, although the last value may be incorrect because it was found for the crystalline mixture $Ph_3SiSiPh_3 \cdot Ph_3PbPbPh_3$. The lengthening of the Si-Si bond was observed for disilanes with sterically demanding substituents, viz hexa(*tert*-butyl)disilane (2.697 Å), 1,1,2,2-tetra(diethylamino)-1,2-di(R)-disilane (R=Me_2CHCMe_2 - 2.539 Å, R= ^{t}Bu - 2.476 Å), 1,2-di(*tert*-butyl)-1,2-di[2,4,6-tn(isopropyl)phenyl]-1-isopropoxydisilane (2.441 Å). As a rule the Si-C distances for bulky groups are also increased.

The calculations did not yield any information concerning the conformation (*gauche* or *anti*) of the 1,1,2,2-tetraphenyldisilane molecule. It is only by means of X-ray diffraction that it became possible [11] to ascertain that the compound exists in an *anti*-conformation, the torsional angles at the Si-Si bond being 50-65°. The 1,1-di(*tert*-butyl)-2,2-dimesityldisilane, 1,1-dimesityl-2,2-di[2,4,6-tri(isopropyl)phenyl]-1,2-dichlorodisilane and 1,2-di(p-R-phenyl)tetramethyl-1,2-diphenyldisilane molecules adopt also an *anti*-conformation.

The molecules of tetrakis(pentamethyldisilanyl)ethylene 1 [54] and tetrakis(pentamethyldisilanyl)cyclopentadiene **2** [55] have four disilanyl groups with an average Si-Si bond length of 2.375 and 2.340 Å, respectively. The lengthening of the Si-C_{sp^2} bonds in compound 1 (1.946Å) and Si-C_{sp^2} bonds in compound **2** (1.920 Å) was observed. The silylethylene 1 is nonplanar with a torsional angle around the C=C double bond of 22.6°, rather close to that in tetrakis(trimethylsilyl)ethylene (29.5°) [56,57].



1



2

The structures of the linear trisilane and octamethyltrisilane were determined by electron diffraction. The Si-Si bond lengths (2.332 and 2.325 Å) do not differ substantially from the values in disilane (2.331 Å) and hexamethyldisilane (2.340 Å) molecules. The Si-H (1.473 Å) and Si-C (1.887 Å) bonds also possess normal length. In other words, it is not possible to make conclusions on any kind of steric strain in these compounds. A slight increase in the bond angle SiSiSi to 118.0° in octamethyltrisilane cannot be considered as a result of steric hindrance owing to the insufficient accuracy of its determination.

The molecular structure of 1,1,1,3,3,3-hexabromotrisilane at 140°C has been defined using gas-phase electron diffraction. Two $SiBr_3$ groups are both staggered relative to the central SiH_2 group to a conformer showing C_2 symmetry, with an experimental twist angle away from C_{2v} symmetry by about 13°. The Si-Si bond length for this compound (2.344 Å) exceeds that in trisilane and octamethyltrisilane.

The structures of other trisilanes have been investigated by means of X-ray diffraction. In octaphenyltrisilane the average Si-Si bond distance (2.394 Å) is greater to some extent than that in 1,1,1,3,3,3-hexaphenyl-2,2-dimethyltrisilane (2.3680 Å).

If the trisilane molecule contains at least one bulky group (^{t}Bu, Mes, 2,4,6-$R_3C_6H_2$, 1,2,3-tri(*tert*-butyl)cyclopropenyl-2) the Si-C and Si-Si distances are longer than normal, but similar to those in the other sterically hindered polysilanes. Two bulky substituents at the central silicon atom of 1,1,1,3,3,3-hexamethyl-2,2-di(R)trisilane molecules cause a compression of the SiSiSi bond angle to 93-97° (Table 2).

Table 1. Geometric parameters of disilanes

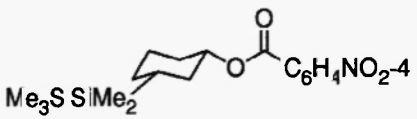
Disilane	Method	r (Si–Si) (Å)	r (Si–R) (Å)	∠SiSiR (°)	Ref.
1	2	3	4	5	6
H_3SiSiH_3	E	2.331 (3)	1.492 (3)	101.3 (4)	[2]
H_3SiSiH_3	C	2.331	1.479	110.4	[3]
H_3SiSiH_2CN	M	2.332 (14)	1.84 (15) Si–C	107.4 (1) SiSiC	[4]
$Me_3SiSiMe_3$	E	2.340 (9)	1.877 (3)	108.4 (4)	[5]
$Me_3SiSiMe_3$	E	2.34 (10)	1.90 (2)	109 (4)	[6]
$Me_3SiSiMe_2Li$	X	2.344 (0)	2.683 (6)		[7]
	X	2.3442 (13)	1.897 (3) 1.873 (3) S'–Me	113.21 (11) 109.4 (2) S'SiMe	[8]
$Me_3S'S'Ph_3$	X	2.355 (1)	1.862 (2) S'–Me 1.886 (1) S'–Ph	109.9 (1) S'SiMe 110.3 (1) S'S'Ph	[9]
4-$MeC_6H_4SiH_2S'H_2C_6H_4Me$-4	X	2.329 (2)	1.863 (2) S'–C	106.5 (9) S'S'H	[10]
$Ph_2HS'S'HPh_2$	X	2.3441	1.873 S'–Ph	109.2 S'SiPh	[11]
$Ph_2SiSiHPh_2$	X	2.357 (1)	1.880 S'–Ph	109.8 (1) S'S'Ph	[12]
(a) $Ph_3S'S'Ph_3$	X	2.519 (4)	1.899 (7)	107.3 (2)	[13]
$[2\text{-}(Me_2NCH_2)C_6H_4]_2SiHS'H[C_6H_4(CH_2NMe_2)]_2$	X	2.384 (2)	1.893 (4) S'–C		[14]
$^tBu(H)_2SiSi(H)_2{}^tBu$	E	2.348 (3)	1.901 (1) S'–C	113.7 (3) S'SiBu^t	[15]
$(^tBu)_3SiSi(^tBu)_3$	X	2.697	1.99		[16]

Table 1 (continued)

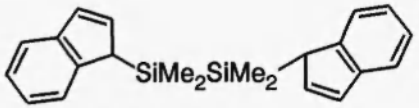
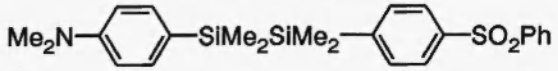
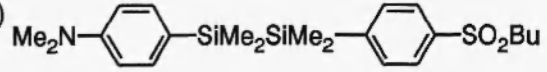
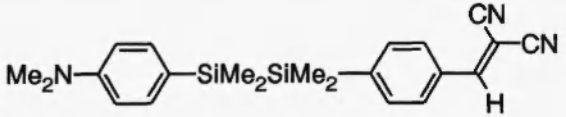
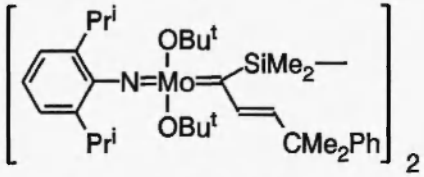
1	2	3	4	5	6
$(^tBu)_2SiHSiHMes_2$	X	2.395 (2)	1.906 (6) Si–^{t}Bu 1.902 (5) Si–Mes	112.6 (2) SiSi^{t}Bu	[17]
$(^tBu)_2(HO)SiSi(OH)(^tBu)_2$	X	2.543 (1)	1.923 (3) Si–Bu^t 1.665 (3) Si–O	103.7 (1) SiSiO	[18]
	X	2.344 (4)	1.851 (8) Si–Me	111.7 (3) SiSiMe	[19]
$MeC{\equiv}C–SiMe_2SiMe_2C{\equiv}CMe$	X	2.327 (1)	1.830 (1) Si–C_{sp}		[20]
	X	2.345 (1)	1.875 (3) Si–Me	104.3 (1)	[21]
(b) 	X	2.337 (4)	1.88 (1) Si–Me	106.0 (3)	[21]
	X	2.348 (5)	1.839 (15) Si–Me	107.8 (5)	[22]
$(C_5H_4SiMe_2SiMe_2C_5H_4)[Mo(CO)_3(CH_2CO_2Et)]_2$	X	2.348 (5)	1.88 (3) Si–Me	108.9	[23]
	X	2.351 (5)			[24]
$(Me_3SiC_5H_3SiMe_2SiMe_2C_5H_3SiMe_3)[Fe(CO)_2I]_2$	X	2.332 (6)	1.865 (11) Si–C_{cp} 1.883 (14)Si–Me	104.7 (4) SiSiC_{cp}	[25]

Table 1 (continued)

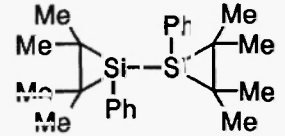
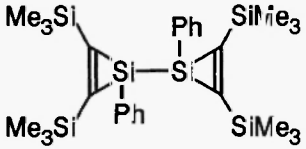
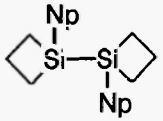
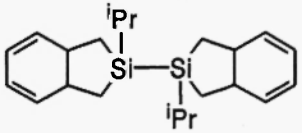
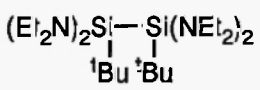
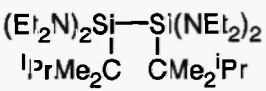
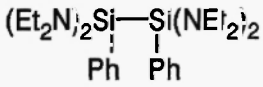
1	2	3	4	5	6
FcSiMe$_2$SiMe$_2$Fc	X	2.340 (1)	1.867 (4)	108.7 (1) SiSiFc	[26]
	X	2.313 (5)	1.879 (5) cyc e		[27]
	X	2.296 (3)	1.83 (1) cyc e		[27]
	X	2.349	1.879 Si–CH$_2$		[28]
	X	2.356 (1)	1.895 (3)	114.5 (1) SiSi^{i}Pr	[29]
	X	2.4764 (9)	1.746 (1) Si–N 1.838 (3) Si–C	111.62 (5) SiSiN	[30]
	X	2.539 (2)	1.749 (4) Si–N 1.962 (6) Si–C	108.6 (2) SiSiC	[30]
	X	2.391 (6)	1.726 (2) Si–N	111.25 (6) SiSiN	[31]
(Me$_2$)N$_3$SiSi(NMe$_2$)$_3$	X	2.369 (1)	1.716 (2)	110.22 (9)	[32]

Table 1 (continued)

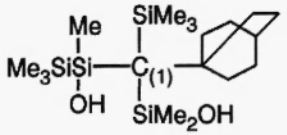
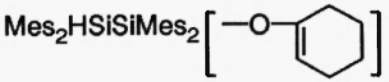
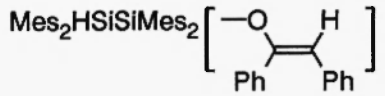
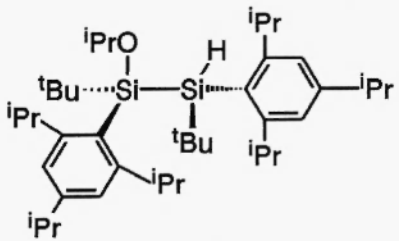
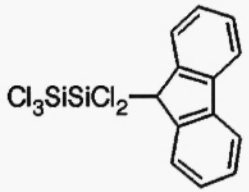
1	2	3	4	5	6
$Mes_2(N)_3S\,S\,Ph_2{}^tBu$	X	2.412 (2)	1.782 (4) Si–N	99.1 (1) SiSiN	[33]
	X	2.38 (2)	1.667 (4) Si–O	124.6 (1) S S $C_{(1)}$	[34]
	X	2.371 (2)	1.654 (3) S –O		[35]
	X	2.404	1.693 Si–O		[36]
	X	2.441	1.639 Si–O		[37]
H_3SiSiH_2F	M	2.332 (5)	1.598 (8) S'–F	109.5 (5) S'SiF	[38]
$[2,4,6\text{-}(^tBu)_3C_6H_2]SiF_2SiHMes_2$	X	2.370 (2)	1.595 (3) S –F 1.922 (3) S.–Mes		[39]
$Br_2HS'S\,HBr_2$	E	2.349 (19)	2 205 (2) Si–Br	107.1 (12) SiSiBr	[40]
$H_3S'SiH_2I$	M	2.336 (7)	2 440 (9) S'–I	106.7 (3) SiSiI	[41]
$IH_2S'S\,H_2I$	E	2.380 (34)	2.429 (13) S –I	107.5 (12) S'SiI	[42]
$I_2HS'S\,HI_2$	E	2.389 (37)	2.440 (9) S'–I	107.2 (10) S'SiI	[42]
$I_3S'Si_3$	X	2.323 (4)	2 426 (2)	107.9 (10)	[43]

Table 1 (continued)

1	2	3	4	5	6
F_3SiSiF_3	E	2.324 (6)	1.569 (2)	100.0 (3)	[44]
F_3SiSiF_3	E	2.317 (6)	1.564 (3)		[45]
$Cl_3SiSiCl_3$	E	2.34 (6)	2.02 (2)	109.5 (10)	[46]
$Cl_3SiSiCl_3$	E	2.24 (6)	2.01 (1)		[47]
$Cl_3SiSiCl_3$	E	2.324 (3)	2.009		[48]
$Cl_3SiSiCl_3$	E	2.32 (6)	2.00 (5)		[49]
$Mes_2ClSiSiCl[C_6H_2(^iPr\text{-}2,4,6)_3]_2$	X	2.396 (2)	2.109 (2) Si–Cl		[50]
$Cl_3SiSiCl_2[W(CO)_2(PMe_3)(C_5Me_5)]$	X	2.350 (3)	2.469 (2) Si–W	122.39 (10) Si Si W	[51]
	X	2.332 (4)	2.062 (3) Si–Cl	108.1 (1) Si Si Cl	[52]
$[2\text{-}(Me_2NCH_2)C_6H_4]_2Si(Li)—Si(Li)[C_6H_4(CH_2NMe_2)\text{-}2]_2 \cdot 3THF$	X	2.380 (2)			[53]

(a) For $Ph_3SiSiPh_3 \cdot Ph_3PbPbPh_3$ mixture

(b) For two independent molecules

E, electron diffraction; M, microwave spectroscopy; C, calculated data; X, X-ray analysis

Table 2. Geometric parameters of trisilanes

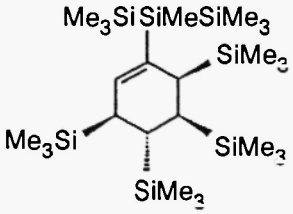
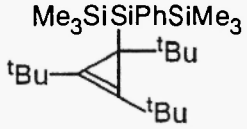
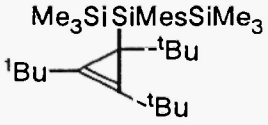
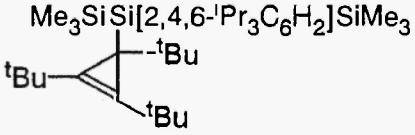
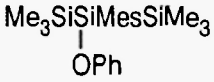
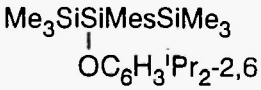
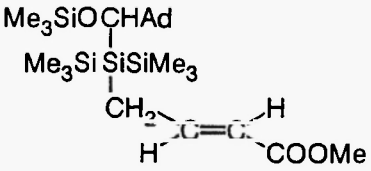
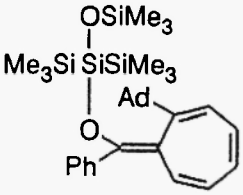
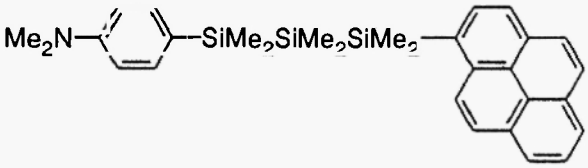
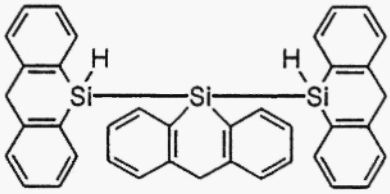
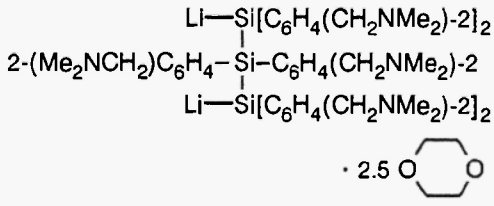
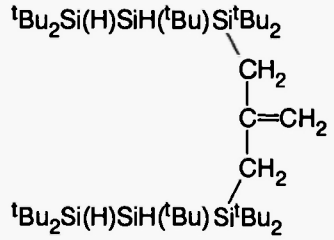
Trisilane	Method	r (Si–Si) (Å)	∠ SiSiSi (°)	Ref.
1	2	3	4	5
$H_3SiSiH_2SiH_3$	E	2.332 (2)	110.2 (4)	[58]
$Br_3SiSiH_2SiBr_3$	E	2.344 (18)	112.9 (19)	[59]
$Me_3SiSiMe_2SiMe_3$	E	2.325 (12)	118.0 (25)	[60]
	X	2.335 (7) 2.361 (8)	111.6 (2)	[61]
$Me_3SiMes_2SiSiMe_3$	X	2.380 (2)	105.2 (1)	[62]
$Me_3SiSiMes[2,4,6\text{-}(^iPr)_3C_6H_2]SiMe_3$	X	2.388 (1) 2.393 (1)	101.0 (1)	[62]
$Me_3SiSi[2,4,6\text{-}(^iPr)_3C_6H_2]_2SiMe_3$	X	2.391 (2) 2.386 (2)	97.5 (1)	[62]
	X	2.396 (2) 2.398 (2)	102.1 (7)	[63]
	X	2.455 (2) 2.426 (2)	93.97 (6)	[63]
	X	2.441 (2) 2.464 (2)	92.60	[64]
	X	2.355 (2) 2.378 (2)	109.7 (1)	[65]
	X	2.371 (1) 2.393 (1)	105.9 (1)	[65]
	X	2.368 (6) 2.370 (7)	111.7 (3)	[66]

Table 2 (continued)

1	2	3	4	5
	X	2.358 (4) 2.350 (4)	112.66 (13)	[67]
	X	2.361 (2) 2.365 (2)	112.81 (6)	[68]
$Me(^tBu)_2SiSi(^tBu)_2Si(^tBu)_2Me$	X	2.593 (1)	118.7 (1)	[69]
$I(^tBu)_2SiSi(^tBu)_2Si(^tBu)_2I$	X	2.581 (1) 2.644 (1)	115.8	[70]
$Ph_3SiSiMe_2SiPh_3$	X	2.3680 (11)	120.75 (7)	[71]
$Ph_3SiSiPh_2SiPh_3$	X	2.382 (1) 2.406 (1)	121.7 (1)	[72]
	X	2.346 (2) 2.332 (2)	112.14 (7)	[73]
	X	2.358 2.342	114	[74]
	X	2.407 (3) 2.401 (3)	136.9 (1)	[53]

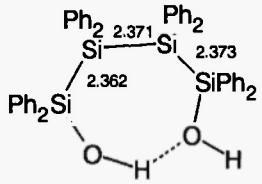
X-Ray crystal structure analysis of 1,2,3,7,8,9-hexasilanonane **3** indicates the existence of all three stereoisomers in the solid state. This is apparent from the disorder in which the R- and S-configurated silicon atoms 2 and 8 take up different positions with an occupation density of 50%. The Si-Si bond lengths vary from 2.373 Å to 2.445 Å [75].



3

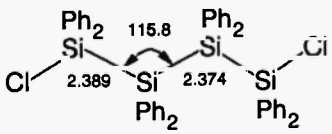
The gas-phase electron diffraction of tetrasilane has been recorded and refinements of *gauche*- and *anti*-conformer mixture of Si_4H_{10} yielded the bond distances $Si_{(1)}$-$Si_{(2)}$ (2.335 Å), $Si_{(2)}$-$Si_{(3)}$ (2.340 Å) and bond angle SiSiSi - 109.6°. The mole fraction of the *gauche*-conformer was 68% [58].

1,4-Dihydroxyoctaphenyltetrasilane **4** according to X-ray data, forms a quasicyclic system due to the intramolecular hydrogen bonding [76,77]. The intramolecular bond is characterized by an O...HO distance of 2.12 Å and O...HO angle of 170.9°, the average Si-Si bond length being 2.369 Å [76]. In addition, the hydrogen atom of the second hydroxyl group enters into intermolecular interaction; thus two molecules of compound **4** form a centrally symmetrical dimer [77].



4

The silyl chains of 1,4-dichlorooctaphenyltetrasilane **5** [78] and 1-carboxyoctaphenyl-tetrasilane **6** [79] are *trans*-planar, which indicates an absence of steric strain in the molecules.The crystalline structure of compound **6** is constructed from the centrally symmetrical dimer associates [79].



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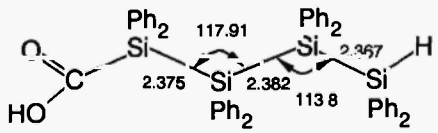
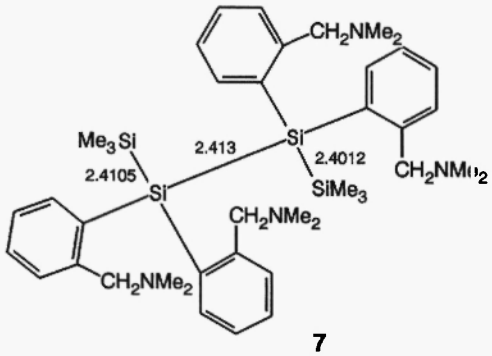


6

For tetrasilane **7** [14] the lengthening of the Si-Si and Si-C_{Ar} bonds reflects the steric influence of bulky substituents. The interaction between amino group of the 1-dimethylaminomethylphenyl substituents and silicon was not detected.



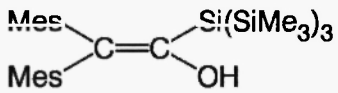
7

Two independent molecules of 1,5-dichlorodecaphenylpentasilane $Cl(SiPh_2)_5Cl$ have different conformation of silyl chains with torsional angles SiSiSiSi 156.9, 157.5° for one and 109.4, 172.0° for other molecule [80]. The pentasilane part of 1,5-diallyldecaphenylpentasilane $CH_2{=}CHCH_2(SiPh_2)_5CH_2CH{=}CH_2$ is characterized by an unusual *trans-gauche* conformation with torsional angles SiSiSiSi 176.6° and 58.3° [79].The Si-Si bond lengths in these pentasilanes lie within 2.367-2.382 and 2.381-2.409 Å ranges, respectively, the terminal Si-Si bonds being shorter than central one.

The shortening of the terminal Si-Si bonds is more pronounced in 1,7-dihydroxytetradecaphenylheptasilane $HO(Ph_2Si)_7OH$. In the crystal the intermolecular hydrogen bonds link the molecules into chains [77].

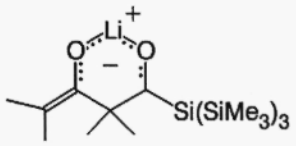
Recently numerous organosilicon derivatives with the simplest branched polysilane $(R_3Si)_3Si$ group have been studied. According to electron diffraction the central silicon atom of tris(silyl)silylmethane $(H_3Si)_3SiMe$ has a tetrahedral geometry with SiSiSi and SiSiC bond angle of 107.7 and 111.1°, respectively. The Si-C and Si-Si bonds in this compound, being 1.883 and 2.332 Å long, are close by length to those found in the most organosilanes and polysilanes [81].

The structure of 2,2-dimesityl-1-tris(trimethylsilyl)silyl-1-hydroxyethene **8** [82] was determined by X-ray diffraction. The diarylvinyl system in the compound **8** is of the propeller-type with a MesC=C torsional angle of 63.3° for the mesityl group *cis* to the silicon and 59.5° for the *trans* one. The largest bond angle around the double C=C bond is found for CCSi (133.8°) and the smallest one is the SiCO angle (104.6°). The MM2* force-field computed Si-C bond length in **8** is *ca.* 0.05 Å shorter than the experimental value (1.94 Å). The steric parameters of the tris(trimethylsilyl)silyl group have been also calculated. The results indicate a similar effective size for the ^{t}Bu (E = -1.54; A = 4.9 kcal·mol^{-1}) and $(Me_3Si)_3Si$ substituents (E = -1.46; A = 4.89 kcal·mol^{-1}) [82].



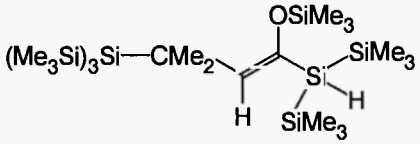
8

The silylacylenolate **9** [83] is tetrameric with four lithium atoms and four oxygen atoms occupying pairwise the corners of a cube. The Si-C(O) bond length in the enolate **9** of 1.976 Å is significantly longer than that in acylsilane and this additional elongation can be attributed to the coordination of the carbonyl group to Li^+. The average Si-Si bond is 2.366 Å.



9

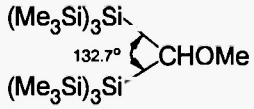
The compound **10** contains two different polysilane fragments with equal Si-Si bond length [84]. The average Si-Si bond lengths for the trisilane part and the tris(trimethylsilyl)silyl group are 2.351 and 2.360 Å, respectively.



10

The crystal structure analysis of tris(trimethylsilyl)silylcarbamylsilane $(Me_3Si)_3SiCONMe_2$ [85] revealed that there are two independent molecules in the unit cell with mean Si-Si distances of 2.348 and 2.351 Å.

Methoxybis[tris(trimethylsilyl)silyl]methane **11** [86] is the first compound containing a carbon atom with two geminal tris(trimethylsilyl)silyl groups. The spatial demand of the two hemispherical groups is expected to cause tremendous steric distortions of the molecular skeleton. The results of the X-ray analysis give a good idea on the steric congestion in the molecule. Two $(Me_3Si)_3Si$ groups force an extreme widening of the SiCSi angle to a value 132.7° and additionally the central Si-C bonds are significantly elongated (1.94-1.95 Å). Consequently, the SiSiSi angles in the $(Me_3Si)_3Si$ groups are reduced, the average angle being 106.0°. The average Si-Si distance is 2.368 Å.



11

The high steric requirements and the electron-releasing properties of the tris(trimethylsilyl)silyl group make it extremely useful as a stabilising ligand for metal complexes. This ligand imparts a number of desirable characteristics on its metal complexes, including high thermal stability. The spatial structure of different metal complexes with the tris(trialkylsilyl)silyl group has been investigated. The studied compounds are the lithium $(Me_3Si)_3SiLi(THF)_3$ [87,88], $(t\text{-}BuMe_2Si)(Me_3Si)_2SiLi.(THF)_3$ [89], $(Me_3Si)_3SiLi(DME)_{1.5}$ [90], $(Me_3Si)_3SiLi[(t\text{-}Bu)_3C_3P_2Li(toluene)]$ [91], sodium, potassium $(Me_3Si)_3SiM$ (M=Li, Na, K) [92], rubidium $[(Me_3Si)_3SiRb]_2$ (toluene), cesium $[(Me_3Si)_3SiCs]_2$ (toluene)$_3$, $[(Me_3Si)_3SiCs]_2$ (THF), $[(Me_3Si)_3SiCs]_2$ (PhPh) (pentane) [92], copper $[(Me_3Si)_3Si]_2Cu_2BrLi$ $(THF)_3$ [93], gold $[(Me_3Si)_3SiAu]$ [dppe) [94], zinc, cadmium, mercury $[(Me_3Si)_3Si]_2M$ (M=Zn, Cd, Hg) [95, 96], boron $(Me_3Si)_3SiB$=N-Bu-t [97], aluminium $(Me_3Si)_3SiAlPh_2$ (THF) [98], gallium $[(Me_3Si)_3SiGa]_4$ [99], $[(Me_3Si)_3SiGaCl]_4$ [100], $[(Me_3Si)_3SiGaMe_2]$ (THF), $[(Me_3Si)_3GaCl_2]$ (THF), $[(Me_3Si)_3SiGa(OEt)_2]_2$, $[(Me_3Si)_3SiGa(OPh)_3]$ (2,2,6,6-tetramethylpiperidino)$_2$.PhOH [101], $(Me_3Si)_3SiGa$(2,2,6,6-tetramethylpiperidino)$_2$ (THF) [102], indium $[(Me_3Si)_3Si]_2MLiCl_2$ (THF) (M=Ga, In) [103], scandium $[(Me_3Si)_3SiScCp_2]$ (THF) [104], germanium $[(Me_3Si)_3SiGeCl]_4.C_6H_6$ [105], $(Me_3Si)_3SiGe(H)C_4Me_4$, $[(Me_3Si)_3SiGeC_4Me_4]$ [Li(12-crown-4) [106], $[(Me_3Si)_3SiGeC_4Me_4Ru(C_5Me_5)]$ [107], tin $\{[(Me_3Si)_3Si]_2Sn\}_2$ [108], $[(Me_3Si)_3Si]_2SnClLi$ $(THF)_3$ [109], lead $[(Me_3Si)_3Si]_2Pb$ [108], titanium $(Me_3Si)_3SiTi(NEt_2)_3$ [110], tantalum $(Me_3Si)_3SiTa{=}CHMMe_3(CH_2MMe_3)$ (M=C, Si) [111], selenium $[(Me_3Si)_3SiSeLi(DMF)]_2$ [112], $\{[(Me_3Si)_3SiSe]_3In\}_2$ (dmpe), $[(Me_3Si)_3SiSe]_3P$ [113], $[(Me_3Si)_3SiSe]_4Zr$, $[(Me_3Si)_3SiSe]_2(\mu$-

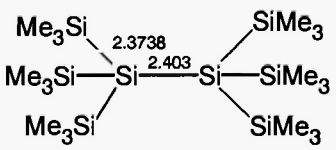
Se)(μ-η^2-dmpm)$_2$] [114], tellurium $(Me_3Si)_3SiTeLi$ (THF) [115], $[(Me_3Si)_3SiTeLi\ (THF)]_2$, $[(Me_3Si)_3SiTe][Li(12\text{-crown-}4)]$ [116], $[(Me_3Si)_3SiTe]_2Mg(THF)_2$, $[(Me_3Si)_3SiTe]_2Ca(THF)_4$ [117], $\{(Me_3Si)_3SiTe]_2Zn\}_2$, $[(Me_3Si)_3SiTe]_2ZnPy_2$, $[(Me_3Si)_3SiTe]_2Cd(bpy)_2$ [118], $[(Me_3Si)_3SiTe]_3Ga$ [113], $[(Me_3Si)_3SiTe]_3La$ [119], $[(Me_3Si)_3SiTe]_2Ti(PMe_3)Cp_2$, $[(Me_3Si)_3SiTe]_2Ti(C_5H_4Me)_2$, $[(Me_3Si)_3SiTe]_2ZrCp_2$, $[(Me_3Si)_3SiTe]Zr(\eta^2\text{-}COMe)Cp_2$ [120], $[(Me_3Si)_3SiTe]_4M$ (M=Zr, Hf) [114], $[(Me_3Si)_3SiTe]_4M$ (M=V, Mo) [121], molybdenum $[(Me_3Si)_3Si](Me_2N)_2Mo{=}Mo(NMe_2)_2[Si(SiMe_3)_3]$ [122], manganese $(Me_3Si)_3SiMn(CO)_5$ [123], rhenium $(Me_3Si)_3SiRe(CO)_5$ [124], iron $\{[(Me_3Si)_3Si]_2FeCl\}$ Et_4N [125] derivatives.

The introduction of organometallic substituents has almost no influence on the Si-Si bond length (2.33-2.35 Å). At the same time the SiSiSi and SiSiM angles are the most affected parameters.

The molecular structure of neopentasilane $(H_3Si)_4Si$ has been determined by electron diffraction analysis [126]. The Si-Si bond length is characterized by a standard value (2.333 Å) similar to those in disilane (2.331 Å) and tris(silyl)silylmethane (2.332 A).

The molecule of tetrakis(trimethylsilyl)silane · THF solvate $(Me_3Si)_4Si.THF$ [87] has almost T_d-symmetry, the average Si-Si distance (2.346 Å) being slightly shorter than in the gas phase determined by electron diffraction [127] and Si K-edge X-ray absorption fine structures (XAFS) spectroscopy (2.364 Å) [128, 129]. In the mixture of tetrakis(trimethylsilyl)silane with tris(trimethylsilyl)silyllithium $[(Me_3Si)_4Si][\ (Me_3Si)_3SiLi(THF)]$ the structures of the two compounds are almost identical to those of the compounds crystallized separately [87].

The structure of dendritic polysilanes **12-19** has been studied by X-ray diffraction. In the molecule of hexakis(trimethylsilyl)disilane **12** [130-132] the effect of six Me_3Si groups leads to the lengthening of the central Si-Si bond to 2.403 Å, although the peripheral Si-Si bond lengths are shorter (2.3738 Å). It should be emphasized that the replacement of six longer Si-Si bonds in compound **12** for the six shorter Si-C [hexakis(tert-butyl)disilane] significantly lengthens the central Si-Si bond (2.697 Å). The steric overcrowding in the hexakis(trimethylsilyl)disilane molecule shows up also in the different dihedral angles ω(SiSiSiSi) of 43° and 77° and in rather short non-bonded C...C distances between methyl groups in the opposite halves of the molecule (3.580 Å).



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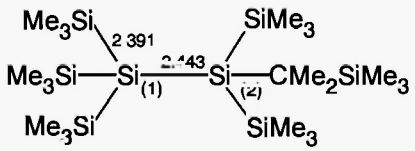
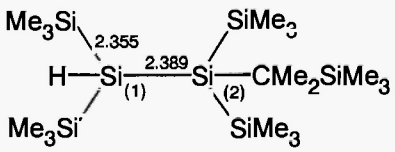
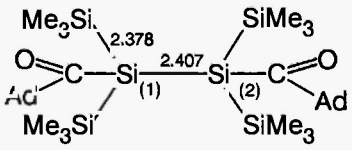


13



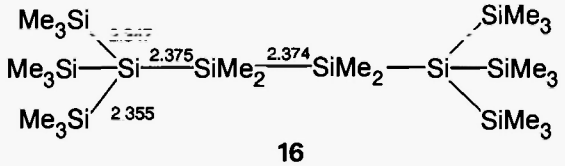
14



15

The substitution of one trimethylsilyl group in hexakis(trimethylsilyl)disilane **12** for the CMe_2SiMe_3 group (compound **13**) [133] leads to further steric hindrance. It results in the elongation of the central Si-Si bond to 2.443 A, in the widening of the $Me_3SiSi_{(2)}SiCMe_2$ angle to 115.9° and in the decreasing of the $Me_3SiSi_{(2)}SiMe_3$ angle to 102.4°. On the other hand in polysilane **14** [133] with a hydrogen atom instead of the Me_3Si group at the $Si_{(1)}$ atom the $Si_{(1)}$-$Si_{(2)}$ bond is 0.054 Å shorter than in compound **13**. The acyl groups in compound **15** are in an *anti* fashion with respect to the central Si-Si bond [134]. All Si-Si bonds, especially the central one (2.407 Å), are longer than the normal values for strain-free disilanes.

Two tris(trimethylsilyl)silyl groups of the central disilane part in polysilane **16** are arranged in the *anti* fashion. The $SiSiMe_2SiMe_2Si$ torsional angle is 180.0°. The internal Me_2Si-$SiMe_2$ (2.374 Å) and $(Me_3Si)_3Si$-$SiMe_2$ (2.375 Å) bonds are similar but longer than terminal Si-$SiMe_3$ bonds (2.345-2.361 Å). The $Me_3SiSiSiMe_2$ angle of 115.3° and $Me_2SiSiMe_2Si$ angle of 117.1° are the major structural deformations of the compound **16** reflecting the steric complexity of the molecule [135, 136].



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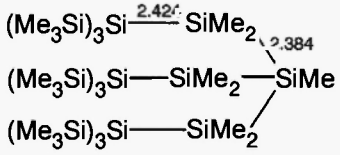
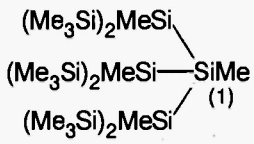


17

A considerable steric interaction exists between three permethylneopentasilyl groups of the branched polysilane **17** [137-139]. As a result three dimethylsilyl groups around the central silicon atom flatten toward the methyl group, as indicated by the enlarged $SiMe_2SiMeSiMe_2$ angles (116.10°) and the diminished $SiMe_2SiCH_3$ angles (101.54°). The most significant distortion revealing the steric interactions is the considerable widening of the $MeSiSiMe_2Si$ angle (130.4°). The average $SiMe_2$-SiMe, $SiMe_2$-Si and Si-$SiMe_3$ bond lengths are 2.384, 2.424 and 2.362 Å, respectively.



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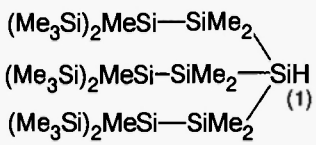


19

The structural parameters of dendrimer **18** [139] indicate only light strain in the molecule. Most of the Si-Si bonds are within 0.01 Å of a normal value of 2.35 Å. Only the three bonds emanating from the core are slightly elongated: $Si_{(1)}$-Si (2.367, 2.374 and 2.375 Å). As in compound **17** the interaction between the three wings around the core is reduced by the flattening of $Si_{(1)}$ tetrahedron toward the methyl group.

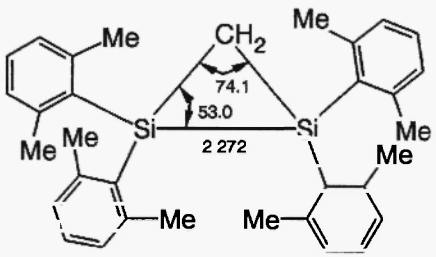
In contrast to **17**, each of the three wings of dendrimer **19** [139] is different. The Si-Si bond lengths were all within the range 2.34-2.37 Å. The average $SiSi_{(1)}Si$ angle of 111.4°, and their sum of 334.3° indicates a little flattening around the central silicon atom.

1.2. Cyclic polysilanes

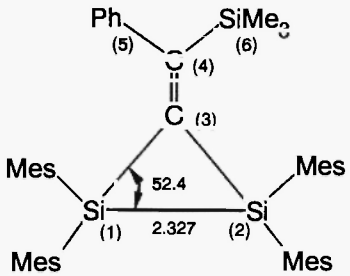
1.2.1. 3-Membered cyclic systems

The most interesting recent work in the field of cyclopolysilane chemistry concerns the nature of the Si-Si bond in small rings. Structural data for several three-membered rings with one or three Si-Si bonds are available in literature: disilacyclopropane, cyclotrisilane, oxadisilirane, thiadisilirane, selenadisilirane, azadisiliridine, arsadisilirane, disilagermirane.

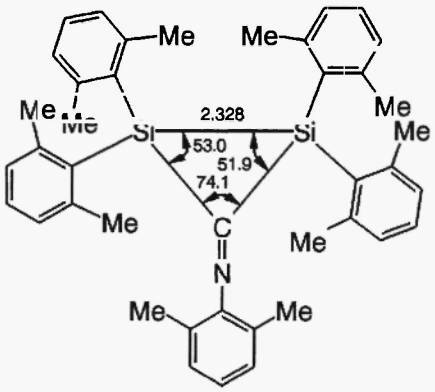
In 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane **20** [140] the Si-Si bond is considerably shortened (2.272 Å), as compared with linear polysilanes, or with cyclotrisilanes **23**. The disilacyclopropane ring in 1,1,2,2-tetramesityl-3-[phenyl(trimethylsilyl)methylene]-1,2-disilacyclopropane **21** [141] and the plane consisting of $Si_{(3)}$, $C_{(4)}$ and $C_{(5)}$ atoms are almost coplanar with a dihedral angle of 7.6°. The two mesityl groups at the atoms $Si_{(1)}$ and $Si_{(2)}$ in **21** are parallel to each other, the Si-Si and Si-C mean bond lengths of the ring are 2.327 Å and 1.907 Å, respectively. The endocyclic angles of disilacyclopropanes **20-22** differ very slightly [140-142].



20

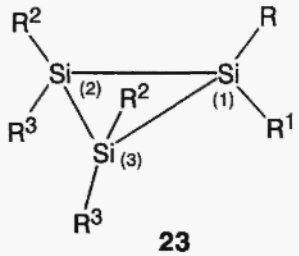


21



22

X-ray diffraction was used for the determination of the structure of the cyclotrisilanes **23**. Some geometric parameters for the simplest cyclotrisilane $(H_2Si)_3$ have been calculated (Table 3). The Si-Si bond in cyclotrisilanes with bulky substituents is considerably longer than in disilacyclopropanes **20-22**, reaching a maximum value (2.511 Å) in hexakis(*tert*-butyl)cyclotrisilane.

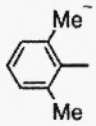
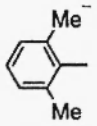
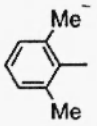
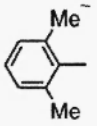
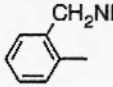
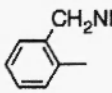
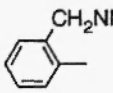
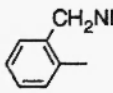
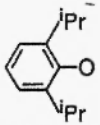
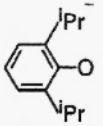


23

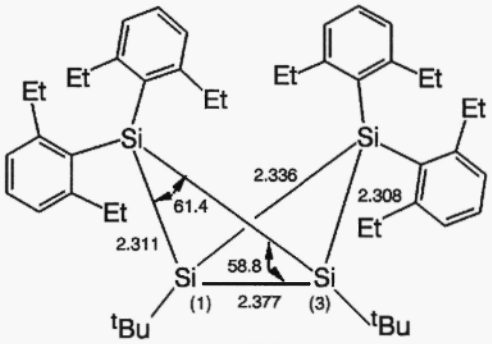
The tetrasilabicyclo[1.1.0]butane system of compound **24** [151] is non-planar. The dihedral angle between two three-membered rings equals 121°. The $Si_{(1)}$-$Si_{(3)}$ bond (2.377 Å) is the longest one in the bicycle, the lengths of the other bonds being close to Si-Si in disilanes. Geometric optimization of the tetrasilabicyclo[1.1.0]butane produced values of 2.304 and 2.370 Å [152] or 2.302 and 2.380 Å [153], the $Si_{(1)}$-$Si_{(3)}$ bond being longer. The calculated dihedral angle is 122.9° [152] (120.0° [153]).

The longest central Si-Si bond length (2.719 Å) has been obtained by the optimization of the pentasila[1.1.1]propellane molecule [154].

Table 3. Geometric parameters of cyclotrisilanes **23**

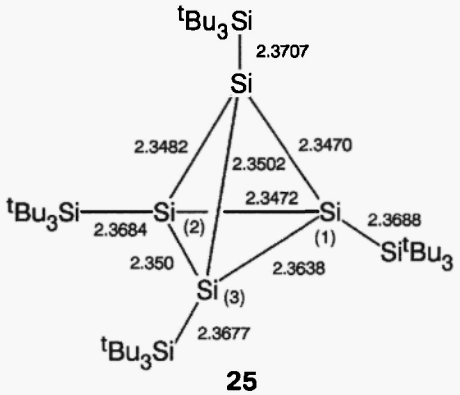
R	R^1	R^2	R^3	$r(Si_{(1)}-Si_{(2)})$ (Å)	$r(Si_{(1)}-Si_{(3)})$ (Å)	$r(Si_{(2)}-Si_{(3)})$ (Å)	$\angle Si_{(1)}$ (°)	$\angle Si_{(2)}$ (°)	$\angle Si_{(3)}$ (°)	Ref.
H	H	H	H	2.330						[143]
H	H	H	H	2.327						[144]
H	H	H	H	2.341						[145]
[a] $^tBuCH_2$	$^tBuCH_2$	$^tBuCH_2$	$^tBuCH_2$	2.386(9)		2.367(8)	59.5(3)	60.3(2)		[146]
				2.414(10)		2.378(10)	59.0(3)	60.5(3)		
^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	2.511(3)						[147]
				2.422	2.425	2.375	58.7	60.7	60.6	[148]
(a) 				2.352(2)	2.368(2)	2.372(3)				[14]
				2.364(2)	2.357(2)	2.356(2)				
^{t}Bu	C_6H_{11}	C_6H_{11}	^{t}Bu	2.422(3)		2.419(4)	59.9(1)			[149]
Mes	^{t}Bu	Mes	^{t}Bu	2.425(2)	2.428(2)	2.431(2)	60.1(1)	60.0(1)	59.9(1)	[150]
^{t}Bu	Mes	Mes	^{t}Bu	2.395(2)	2.413(2)	2.441(2)	61.0(1)	59.8(1)	59.1(1)	[150]
	^{t}Bu	Mes		2.380(1)	2.342(1)	2.407(2)	58.6(1)	60.(1)	61.3(1)	[65]

a) For two independent molecules



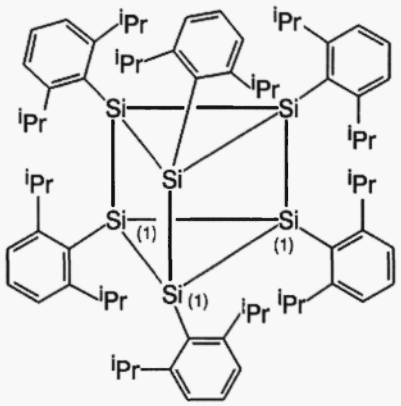
24

Ab initio calculations of tetrasilatetrahedrane yielded a small value for the Si-Si bond length (2.314 Å [145] and 2.3147 Å [155]). The X-ray analysis of the first tetrasilatetrahedrane - tetrakis[tri(*tert*-butyl)silyl]tetrasilatetrahedrane **25** [156,157] in the mixture of two molecules with $(^tBu_3Si)_2 \cdot C_6D_6$ reveals that the average experimental Si-Si distance (2.351 Å) in tetrahedron cage is longer than the calculated one. The exocyclic $(^tBu)_3Si$-Si distances vary from 2.3684 to 2.3707 Å. The central Si_4 cage has an ideal tetrahedron structure (∠SiSiSi = 60°).



25

The unique structure of the first hexasilaprismane - hexakis(2,6-diisopropylphenyl)tetracyclo[2.2.0.$0^{2\,6}$.$0^{3\,5}$]hexasilane **26** [158] has been also determined by X-ray diffraction. The skeleton of hexasilaprismane **26** is slightly distorted from the regular prismane structure made up from two triangular units (Si-Si - 2.380 A, ∠SiSiSi = 60.0°) and three rectangular units (Si-Si - 2.373 Å, ∠SiSiSi - 90.0°). The geometry of the exocyclic bond angles are significantly expanded to 133.5° for SiSiC and 126.9° for $Si_{(1)}SiC$.

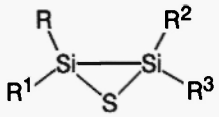


26

A peculiarity in the structure of oxadisiliranes **27** [159-162] consists of a considerable shortening of the Si-Si bonds (2.214-2.229 Å) in comparison with the normal bond length of approximately 2.34 Å in sterically unstrained disilanes. If the Si-Si bond length measured for oxadisiliranes **27** is compared with those in analogously substituted disilanes, it is apparent that the bond is shortened by as much as 0.20 Å and actually closer to that of a Si=Si double bond. Each of the two silicon atoms in **27** has a planar environment in relation to the *ipso* carbon atoms and the other silicon atom. Taken together these data it can be proposed that a significant amount of double-bond character of disilane (structure **28**) is retained in the three-membered ring.

27 **28**

The exceptionally short Si-Si bond distances and the near 360° sum of angles around each silicon atom are also characteristic of thiadisilirane structures **29** [163-165].

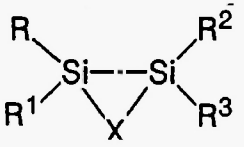


29

By going from 2,2,3,3-tetramesityloxadisilirane to 2,2,3,3-tetramesitylthiadisilirane, 2,2,3,3-tetramesitylselenadisilirane **30** [166] and 2,2,3,3-tetramesityltelluradisilirane **31** [166] the length of the Si-Si bond increases gradually from 2.227 Å to 2.337 Å, as the electrononegativtity of the chalcogen atom decreases. In oxadisilirane **27** ($R=R^1=R^2=R^3$=Mes) the sum of bond angles around each silicon atom is 360.0°. The corresponding values in compounds **29** ($R=R^1=R^2=R^3$=Mes), **30** and **31** are only slightly smaller ranging from 357.5° in **29** to 355.3° in **31**.

30 **31**

In azadisiliridines **32** the Si-Si bond distances are also abnormally short (2.288, 2.232 Å) and the ring nitrogen atom is planar [167,168].

Table 4. Geometric parameters of the three-membered rings  in compounds **27-34**

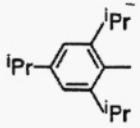
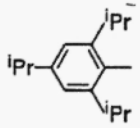
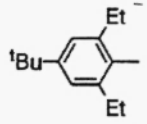
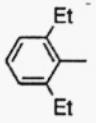
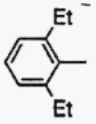
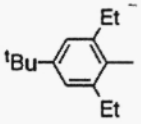
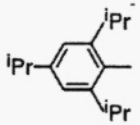
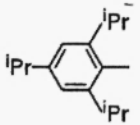
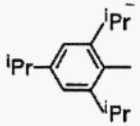
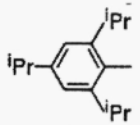
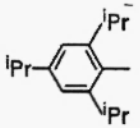
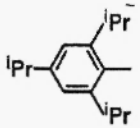
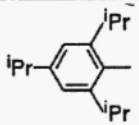
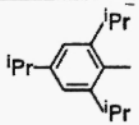
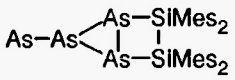
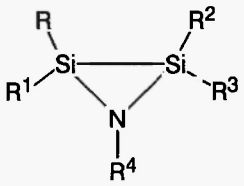
R	R^1	R^2	R^3	X	r(Si-Si) (Å)	r(Si-X) (Å)	∠SiSiX (°)	∠SiXSi (°)	Ref.
1	2	3	4	5	6	7	8	9	10
Mes	Mes	Mes	Mes	O	2.227(2)	1.733		80.0	[159]
Mes	Mes			O	2.229(1)	1.725(5) 1.705(5)	49.8(2) 49.1(2)	81.1(2)	[160]
				O	2.214(2)	1.726(4) 1.748(4)	50.9(1) 50.0(1)	79.2(2)	[161]
				O	2.254(2)	1.717(3) 1.722(3)	49.0(1) 49.1(1)	81.9(1)	[162]
Mes	Mes	Mes	Mes	S	2.289(2)	2.161(2)	58.0(1)	64.0(1)	[163]
^{t}Bu	Mes	Mes	^{t}Bu	S	2.2697(12)	2.1655(8)	58.39(2)	63.21(4)	[164]
^{t}Bu			^{t}Bu	S	2.294(2)	2.166(2) 2.173(2)	58.23(6) 57.93(6)	63.84(6)	[164]

Table 4 (continued)

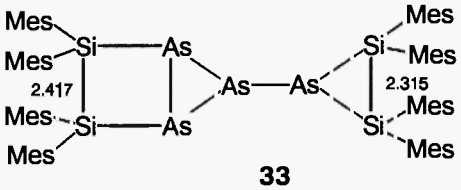
1	2	3	4	5	6	7	8	9	10
^{t}Bu		^{t}Bu		S	2.317(2)	2.159(2) 2.177(2)	58.07(7) 57.30(7)	64.63(6)	[164]
^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	S	2.3049(11)	2.1713(9)		64.11(4)	[165]
Mes	Mes	Mes	Mes	Se	2.303(3)	2.303(2) 2.309(2)	60.2(1) 59.9(1)	59.9(1)	[166]
Mes	Mes	Mes	Mes	Te	2.337(4)	2.524(3) 2.523(3)	62.4(1) 62.4(1)	55.2(1)	[166]
Mes	NHMes	Mes	NHMes	MesN	2.228(1)	1.748(2)	50.4(1)	79.2(1)	[167]
Mes	Mes	Mes	Mes	Me_3SiN	2.232(4)	1.776(5) 1.772(5)	51.9(2) 51.1(2)	78.0(2)	[168]
Mes	Mes	Mes	Mes		2.315(7)	2.404(6) 2.401(6)	61.3(2) 61.1(2)		[169]
^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	$Ge(CH_2SiMe_3)_2$	2.418(5)	2.480(3) 2.458(4)	60.2(1) 61.1(1)	58.6(1)	[170]
Me_3Si	Me_3Si	Me_3Si	Me_3Si	$Ge(SiMe_3)_2$	2.377(14)	2.391(1)			[171]



32

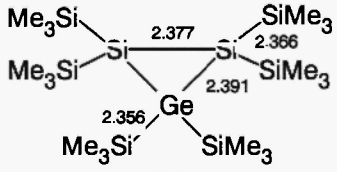
The shortening of the Si-Si bond length in compounds with three-membered rings $(H_2Si)_2X$ (X=O, S, NH) has been confirmed by calculations applying *ab initio* method [172].

The tricyclic structure in compound **33** is quite remarkable: this molecule contains the first example of arsadisilirane and 1,2-diarsadisiletane ring simultaneously. The Si-Si bond distance in three-membered ring (2.315 Å) is smaller than the typical Si-Si bond length and also smaller than in four-membered ring (2.417 Å). The dihedral angle between three-membered $AsSi_2$ and As_3 cycles is 149.7° [169].



33

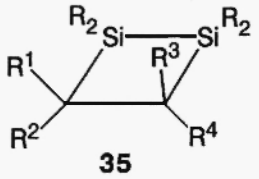
The hexakis(trimethylsilyl)disilagermirane molecule **34** has D_{3h} symmetry. The two exocyclic Ge-Si distances (2.356 A) are shorter than the endocyclic (2.391 A). This is also valid for the Si-Si distances (2.366 and 2.377 Å) [171]. In the molecule of 1,1,2,2-tetra[(*tert*-butyl)methyl]-3,3-di(trimethylsilylmethyl)disilagermirane [170] the Si-Si (2.418 Å) and Si-Ge (2.480 and 2.458 Å) distances are increased due to steric effect. The main geometric parameters of compounds **27-34** are presented in the Table 4.



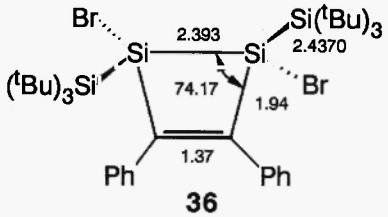
34

1.2.2. 4-Membered cyclic systems

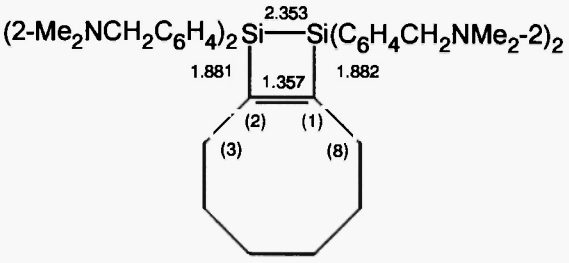
The structure of compounds with 4-membered 1,2-disilacyclobutane, 1,2-disilacyclobutene, trisilacyclobutane, tetrasilacyclobutane rings have been also studied by means of X-ray techniques.



35



36

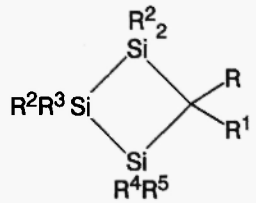


37

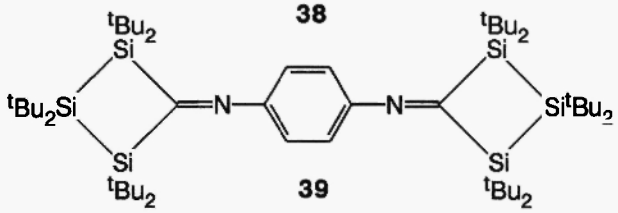
The four-membered ring of 1,2-disilacyclobutane derivatives **35** (Table 5) as a rule has unusually elongated C-C (to 1.647 Å) and Si-C (to 2.008 Å) bonds. The heterocycle of 1,1,2,2-tetrakis(trimethylsilyl)-3,4-di(*tert*-butyl)-3,4-di(trimethylsiloxy)-1,2-disilacyclobutane is almost planar, for other compounds the puckering was observed. The unsaturated 1,2-disilacyclobutenes **36** [157] and **37** [182] have planar rings. The angle between disilacyclobutene ring and plane defined by $C_{(1)}C_{(2)}C_{(3)}C_{(8)}$ atoms in compound **37** is 3.7°. The distances Si-Si, Si-C and C=C in 1,2-disilacyclobutene **36** are longer than in **37**.

The structure of the simplest trisilacyclobutane molecule **38** ($R\text{-}R^5$=H) was studied by *ab initio* quantum mechanical techniques [172]. The planar four-membered ring does not exhibit any specific structural features. The optimized geometric parameters are: r(Si-Si) = 2.363 Å, r(Si-C) = 1.914 Å, r(Si-H) = 1.471-1.472 Å, ∠SiCSi = 101.4°.

The four-membered heterocycle with three silicon atoms in the 1,1,2,2,3-pentakis(trimethylsilyl)-3-triethylgermoxy-4-(1-adamantyl)-1,2,3-trisilacyclobutane molecule is slightly puckered, the dihedral angle between the $Si_{(1)}Si_{(2)}Si_{(3)}$ and $Si_{(1)}CSi_{(3)}$ planes being 14.3°. The endocyclic $Si_{(1)}Si_{(2)}Si_{(3)}$ bond angle of this compound (77.2°) is the smallest observed for the known silacyclobutane structures [183]. The heterocycles of trisilacyclobutanimines **38** (RR^1 = 2,6-$^iPr_2C_6H_3N$=, α-NpN=) [184] and **39** [185] are strictly planar. The Si-Si and Si-C bond lengths are considerably longer (especially for trisilacyclobutanimines with *tert*-butyl groups at the silicon atoms) than the corresponding standard values. The geometric parameters for 1,2,3-trisilacyclobutane rings in compounds **38** are presented in Table 6.



38



39

Table 5. Geometric parameters of 1,2-disilacyclobutanes **35**

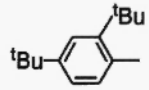
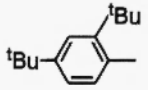
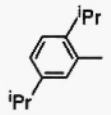
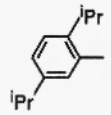
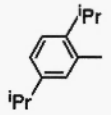
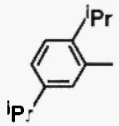
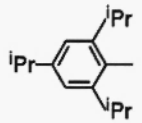
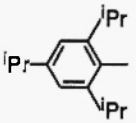
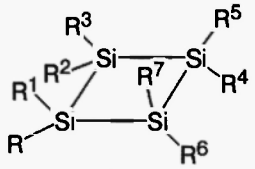
R	R^1	R^2	R^3	R^4	r(Si-Si) (Å)	r(Si-C) (Å)	r(C-C) (Å)	∠S S C (°)	∠CCSi (°)	α(°)	Ref.
Me_3Si	H	Mes	H	Mes	2.358(2)	1.963(5) 1.949(5)	1.613(7)	77.6(2) 79.6(2)	101.4(3) 99.4(3)	8.7	[173]
Me_3Si	H		H		2.358(2)	1.952(5) 1.961(6)	1.605(7)	79.9(2) 76.3(2)	97.6(3) 100.9(3)	26.9	[174]
Me_3Si	H				2.361(2)	1.940(5) 1.950(5)	1.598(7)	76.2(2) 79.3(4)	97.0(4) 102.2(4)	25.2	[175]
Me_3Si	H			H	2.344(3)	1.962(6) 1.962(6)	1.556(8)	75.7(2) 75.2(2)	96.8(4) 97.6(4)	40.6 37.4	[175]
Me_3Si	H			H	2.334(2)	1.973(4)	1.583(8)	76.10(12)	96.7(2)	40.18	[176]
Me_3Si	H	^{t}Bu	H	^{t}Bu	2.353(1)	1.947(3) 1.934(3)	1.577(4)	76.16(9) 76.33(8)	98.43(16) 97.58(17)	35.9	[177]
Me_3Si	^{t}Bu	Me_3SiO	^{t}Bu	Me_3SiO	2.37	2.00	1.66				[178]
Me_3Si					2.333(1)	2.008(3)	1.647(5)	77.3	95.8(3)	39.6	[179]
^{t}Bu	H		H	H	2.402(1)	1.963(3) 1.893(3)	1.561(4)	74.5(1) 74.8(1)	100.8(2) 96.4(2)	39	[180]
Ph	H	$(Me_3Si)_2CH$	H	$(Me_3Si)_2CH$	2.344(9)	1.93(2) 1.94(2)	1.46(3)	75.6(7) 74.5(6)	99.7(13) 101.0(13)		[181]

Table 6. The geometric parameters of 1,2,3-trisilacyclobutanes **38**

R	R^1	R^2	R^3	R^4	R^5	r, (Å)		angles (°)				Ref.
						Si-Si	S-C	∠Si(1)	∠Si(2)	∠Si(3)	∠C	
H	Ad	Me_3Si	Me_3Si	Me_3Si	Et_3GeO	2.391(2)	1.948(5)	89.8(1)	77.2(1)	90.4(1)	100.8(2)	[183]
						2.389(2)	1.924(4)					
2,6-$(^iPr)_2C_6H_3N$=		^{t}Bu	^{t}Bu	^{t}Bu	Bu	2.477(2)	1.955(3)	85.7(1)	84.4(1)	87.4(1)	107(1)	[184]
						2.497(2)	2.010(3)					
α-NpN=		^{t}Bu	H	^{t}Bu	Bu	2.373(1)	1.942(2)	82.9(1)	84.1(1)	84.1(1)	107.0(1)	[184]
						2.405(1)	1.992(2)					

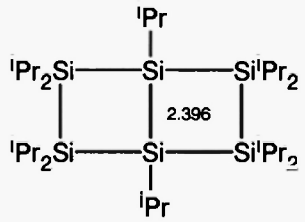
The geometric parameters of the simplest cyclotetrasilane $(H_2Si)_4$, according to *ab initio* calculations, octamethylcyclotetrasilane, studied by electron diffraction and X-ray analysis at 85 K and more complex cyclotetrasilanes **40**, investigated by X-ray techniques, are presented in Table 7.



40

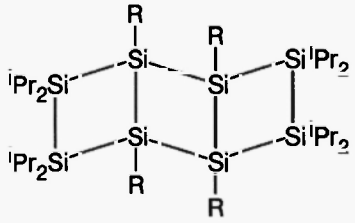
According to X-ray data, the central cyclotetrasilane ring of cyclic compounds **40** is planar only in three compounds - in octamethylcyclotetrasilane at 85 K, 1,1,2,3,3,4-hexa(*tert*-butyl)cyclotetrasilane and octa(trimethylsilyl)cyclotetrasilane. In the octaphenylcyclotetrasilane molecule the ring is bent by 12.8°, in the other compounds presented in Table 7 the angle is even wider, attaining 51.3°. Using electron diffraction, it has been established that the molecule of octamethylcyclotetrasilane has a puckered structure in the gaseous phase, Si-Si bond lengths for solid and gaseous state are equal.

The bicyclic skeleton of deca(isopropyl)hexasilabicyclo[2.2.0]hexane **41** [198] is twisted and characterized by C_s symmetry. The molecule has a *cis*-fused structure. The puckering of each four-membered ring is 21.8°. The central Si-Si bond distance (2.396 Å) is comparable to those found for peripheral Si-Si bonds (average value 2.401 Å).



41

In tricyclic ladder polysilanes **42** [199] the Si_8 framework has a twisted *anti* structure. The Si-Si bond length for compound **42** (R=^{t}Bu) vary from 2.412 to 2.481 Å. These values are fairly long compared with those of isopropyl derivative **42** (R = ^{i}Pr), which range from 2.346 to 2.405 Å. Each of the cyclotetrasilane ring has a folded structure and the dihedral angles are 25.2, 16.6 and 22.1° (R = ^{i}Pr). For the *tert*-butyl derivative **42** (R = ^{t}Bu) three Si_4 rings array in more planar manner.



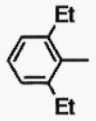
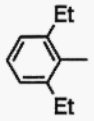
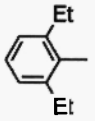
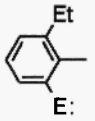
42

During the last several years there is considerable interest in the synthesis of silicon polyhedranes and related compounds, containing four-membered tetrasilane frameworks.

Table 7. Geometric parameters of cyclotetrasilanes **40**

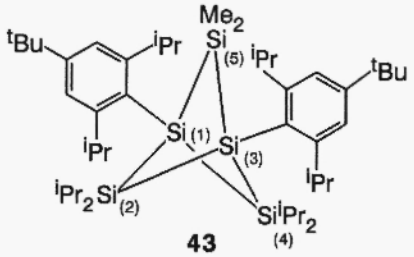
R	R^1	R^2	R^3	R^4	R^5	R^6	R^7	$r_a(Si\text{-}Si)_{av}$ (Å)	$\angle Si\,Si\,Si_{av}$ (°)	α(°)	Ref.
1	2	3	4	5	6	7	8	9	10	11	12
H	H	H	H	H	H	H	H	2.373			[145]
H	H	H	H	H	H	H	H	2.376		31.2	[143]
H	H	H	H	H	H	H	H	2.360		28.7	[186]
[a]Me	Me	Me	Me	Me	Me	Me	Me	2.362(4)	88.1(5)	29.4(40)	[187]
Me	Me	Me	Me	Me	Me	Me	Me	2.363(1)	90.0(1)	0	[188]
^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	2.374(1)	87.0(1)	37.1	[189]
^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	2.409	86.6	38.8	[190]
H	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	2.542(2)	90.4(1)	15.2	[191]
H	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	2.538(4)	89.5(2)	16	[75]
H	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	H	^{t}Bu	^{t}Bu	2.387(1)	90.0(1)	0	[191]
Me	^{t}Bu	^{t}Bu	Me	^{t}Bu	Me	Me	^{t}Bu	2.377(1)	86.99(1)	36.8	[192]
^{i}Pr	^{i}Pr	^{i}Pr	^{i}Pr	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	^{t}BuCH$_2$	2.401(3)	86.7(1)	39.39	[193]
^{t}Bu	c-C$_5$H$_{11}$	^{t}Bu	c-C$_5$H$_{11}$	^{t}Bu	c-C$_6$H$_{11}$	c-C$_6$H$_{11}$	^{t}Bu	2.444(4)	87.5(1)	34	[149]

Table 7 (continued)

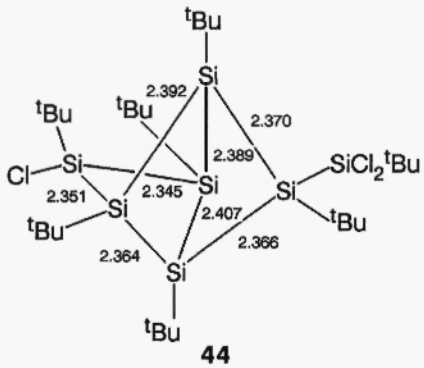
1	2	3	4	5	6	7	8	9	10	11	12
Me_3SiCH_2	Me_3SCH_2	Me_3SCH_2	Me_3SiCH_2	Me_3SCH_2	Me_3SCH_2	Me_3SCH_2	Me_3SiCH_2	2.388(20)	87.0(1)	36.6	[189]
H	$(^tBu)_2SiH$	H	$(^tBu)_3Si$	$(^tBu)_3Si$	H	$(^tBu)_2SiH$	H	2.382(3)	84.11(12)	51.3	[157]
H	$(^tBu)_2SiH$	$(^tBu)_2SiH$	H	H	$(^tBu)_2SiH$	$(^tBu)_3Si$	H	2.418(6)	89.4(2)	16.0	[157]
Me_3Si	Me_3Si	Me_3Si	Me_3Si	Me_3Si	Me_3Si	Me_3Si	Me_3Si			0	[194]
Me	Me_3Si	$(Me_3Si)_2MeSi$	Me	Me_3Si	Me	$(Me_3Si)_2MeSi$	Me				[139]
Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	2.377(1)	89.6(1)	12.8	[195]
^{t}Bu	Ph	^{t}Bu	Ph	Ph	^{t}Bu	^{t}Bu	Ph	2.323(2)	88.3	27.7	[196]
Ph	Bu	^{t}Bu	Ph	^{t}Bu	Ph	Ph	^{t}Bu	2.423(2)	87.6(1)	32.8	[196]
Cl	^{t}Bu	^{t}Bu	Cl	Cl	^{t}Bu	^{t}Bu	Cl	2.375(10)	88.3(3)	26.6	[196]
		^{t}Bu	OH			^{t}Bu	OH	2.409	87.3	36.6	[197]

[a] Electron diffraction

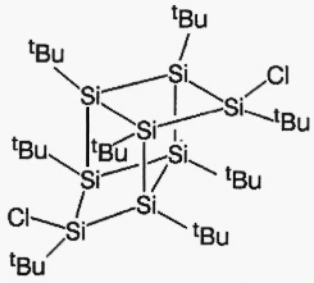
Three cyclotetrasilane rings of bicyclo[1.1.1]pentasilane **43** [200] are bent (the dihedral angle is 60°). The endocyclic SiSiSi angles for the bridging $Si_{(1)}$ and $Si_{(3)}$ atoms are wider (84°) than for $Si_{(2)}$, $Si_{(4)}$, $Si_{(5)}$ (78°). The length of the Si-Si bonds in compound **43** is equal to 2.32-2.38 Å. The distance between two unbonded silicon atoms $Si_{(1)}$ and $S_{(3)}$ is 2.98 Å.



43

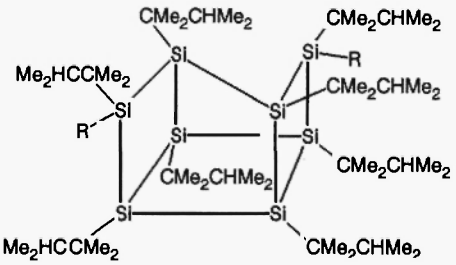


44



45

The structure of compounds **44** and **45** [201] with the tricyclo[2.2.0.$0^{2,5}$]hexasilane and tetracyclo[3.3.0.$0^{2,7}$.$0^{3,6}$]octasilane system, respectively, has been established by X-ray crystallography. In compound **45** two enantiomeric molecules are present in the asymmetric unit with approximately equivalent Si-Si bonds (2.335-2.452 Å).



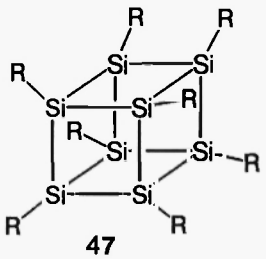
46

The structural features of tetracyclo[3.3.0.$0^{2,7}$.$0^{3,6}$]octasilanes **46** [202, 203] presumably result from the conformational requirement of the octasilane framework as well as the steric hindrance caused by the eight bulky 2,3-dimethyl-2-butyl groups. In compound with R = H the hydrogen atoms occupy *endo,endo* and the bulky 2,3-dimethyl-2-butyl groups *exo,exo* positions (relative to the bridged Si-Si bond). For the chloro derivative **46** [203] the structures of the three possible *endo,endo, exo,exo* and *endo,exo* stereoisomers were determined. The geometric parameters of tetracyclo[3.3.0.$0^{2,7}$.$0^{3,6}$]-octasilanes **46** are presented in Table 8.

Table 8. Geometric parameters of tetracyclo[3.3.0.$0^{2,7}$.$0^{3,6}$]octasilanes **46**

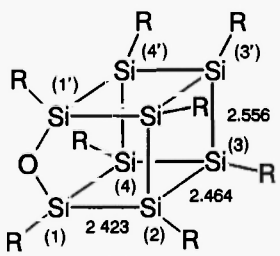
R	Isomer	r(Si-Si) (Å)	∠SiSiSi(°)	∠SiSiC(°)	Dihedral angles of three fused cyclotetrasilane rings	Ref.
H	*endo,endo*	2.342(5)-2.461(5)	79.9(1)-94.2(2)	112.8(4)-134.9(4)	33.0; 45.1	[202]
Cl	*endo,endo*	2.390(3)-2.452(3)	81.2(1)-93.9(1)	113.1(2)-129.5(3)	34.4; 31.7	[203]
Cl	*endo,exo*	2.357(1)-2.471(1)	81.21(3)-93.63(4)	113.96(9)-135.1(1)	31.9;33.7;39.8	[203]
Cl	*exo,exo*	2.351(4)-2.464(4)	82.1(1)-92.4(1)	114.(5)-135.7(6)	41.5;34.6	[203]

The molecular structures of octasilacubanes **47** (R = ^{t}Bu [204, 205], Me_2HCCMe_2 [206], 2,6-$Et_2C_6H_3$ [207]) are slightly distorted from the ideal octasilacubane geometry. The SiSiSi bond angles vary from 89.5 to 90.9°, from 89.2 to 92.6° and from 88.9 to 91.1° for compounds with R = ^{t}Bu, Me_2HCCMe_2 and 2,6-$Et_2C_6H_3$, respectively. The Si-Si bond lengths for octasilacubanes vary in the wide range (2.374-2.400, 2.398-2.447 and 2.384-2.411 Å). *Ab initio* calculations for octasilacubane give value 2.396 for the Si-Si bond length [156].



47

Photo-induced oxidation of octasilacubane **47** (R=Me_2HCCMe_2) with dimethylsulfoxide yields the partial oxidation products **48** and **49** (R=Me_2HCCMe_2) [208]. The insertion of one oxygen atom into the octasilacubane framework causes significant distortions of the Si-Si bonds between 2.423 and 2.556 Å; the longest $Si_{(3)}$-$Si_{(3')}$ bond is among the longest Si-Si bonds in cyclic polysilanes. The elongation of the $Si_{(3)}$-$Si_{(3')}$ distance in compound **48** is responsible for the formation of **49** as the only product out of the four possible isomers. The average Si-Si bond lengths indicate that compounds **49** are less strained than **48** (2.446-2.458 Å). However, one of the bonds is 2.506 Å, showing that there still exists steric congestion.



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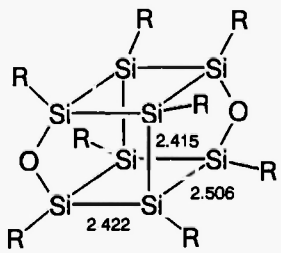
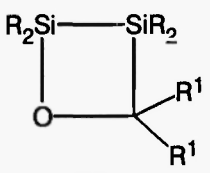


49

The structures of compunds **50-56** with unsymmetrical heterocycles were confirmed by X-ray crystallography. 1,2,3-Oxadisiletanes **50** (R = ^{t}Bu, R^1=Ph [209]; R=Mes, R^1_2= Me_2C= [210])

reveal an almost planar ring, whereas in 1,2,3-thiadisiletane **51** [211] it is highly puckered with a dihedral angle of 45.6° between the SiSiC and SiSC planes.



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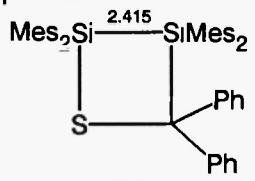

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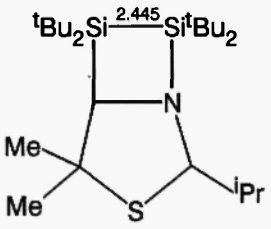

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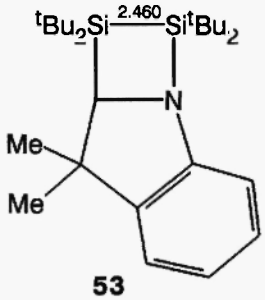

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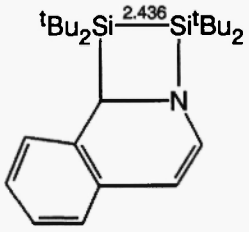

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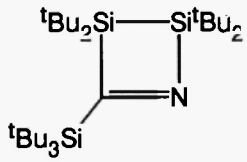

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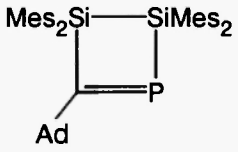
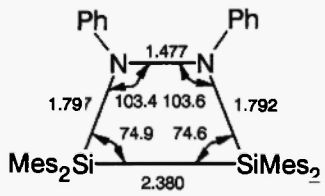


56

In 1,2,3-azadisiletidines **52-54** [212-214], 1,2,3-azadisilete **55** [215] and 1,2,3-phosphadisilete **56** [216] the four atoms of heterocycle are coplanar or almost coplanar. The Si-Si bonds of 2,2,3,3-tetra(*tert*-butyl)-4,4-diphenyl-1,2,3-oxadisiletane [209], 1,2,3-thiadisiletane **51** and 1,2,3-azadisiletidines **52-54** are abnormally long (2.409-2.460 Å). The elongation of the Si-C and Si-X (X=O,S,N) bonds was also observed for four-membered rings (Table 9). The endocyclic bonds of phosphadisilete **56** [216] are elongated to some smaller extent.

The central Si_2N_2 trapezoidal core of 1,2-diaza-3,4-disilacyclobutane **57** [217] deviates from planarity, the SiNNSi torsion angle is 18.20°. The Ph_2N_2 fragment has a *trans* conformation to minimize the lone pair repulsion of the two nitrogen atoms.

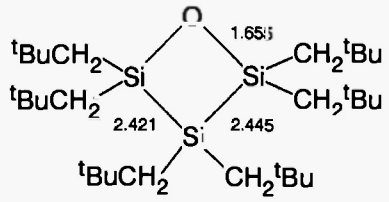


57

Contrary to the octa(*tert*-butylmethyl)cyclotetrasilane [190] the four-membered Si_3O ring of hexa(*tert*-butylmethyl)oxatrisiletane **58** [218] has an almost planar structure. The average Si-Si bond distance (2.433 Å) for heterocyclic compound **58** is longer in comparison with cyclotetrasilane (2.409 Å).

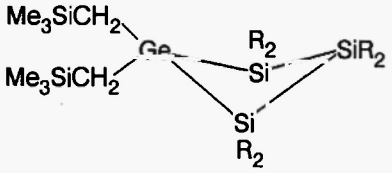
Table 9. Geometric parameters of four-membered heterocycles in compounds **50-56**

Compound	r(Si-Si) (Å)	r(Si-X) (Å)	r(Si-C) (Å)	r(C-X) (Å)	∠SiSiC (°)	∠SiSiX (°)	∠SiXC (°)	∠SiCX (°)	Ref.
50 (R = ^{t}Bu, R^1 = Ph)	2.409(2)	1.681(3)	2.028(4)	1.461(5)	71.6(1)	78.4(1)	112.5(2)	97.5(2)	[209]
50 (R = Mes, R^1_2 = Me_2C=)	2.373(2)	1.693(4)	1.886(5)	1.428(7)	71.1(2)	78.2(1)	106.6(3)	103.5(3)	[210]
51	2.443(2)	2.177(3)	1.994(6)	1.870(6)	81.9(2)	74.5(1)	92.3(2)	93.0(3)	[211]
52	2.445(1)	1.771(1)	1.944(2)	1.487(2)	72.5(1)	76.1(0)	107.0(1)	100.4(1)	[212]
53	2.460(1)	1.745(2)	1.937(3)	1.494(5)	72.4(1)	74.9(1)	108.3(2)	98.7(2)	[213]
54	2.436(4)	1.743(5)	1.944(7)	1.494(3)	73.7(2)	75.6(2)	110.0(4)	98.5(4)	[214]
55		1.798(2)	1.996(3)	1.304(3)	69.5(1)	75.8(1)	109.7(2)	104.8(2)	[215]
56	2.391(1)	2.288(1)	1.903(3)	1.701(3)	85.5(1)	77.6(1)	90.1(1)	108.9(2)	[216]



58

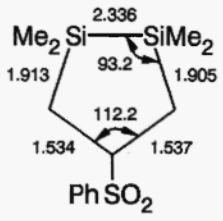
A new four-membered ring system containing one germanium and three silicon atoms was characterized by X-ray analysis. The crystallographic units of both trisilagermacyclobutanes **59** (R=^{i}Pr, ^{t}BuCH$_2$) comprise four molecules. The Si$_3$Ge rings are puckered with dihedral angles of 24° (R=^{i}Pr) and 36° (^{t}BuCH$_2$). The average Si-Si bond distances of 2.386 and 2.393 Å are very close to those of octa(isopropyl)cyclotetrasilane (2.374 Å) and octa(neopentyl)cyclotetrasilane (2.409 Å) and longer than the normal one (2.34 Å). The Si-Ge bond distances are 2.457 Å (R=^{i}Pr) and 2.444 Å (R=^{t}BuCH$_2$), which are considerably longer than those of linear silylgermanes (2.36 Å) and disilagermirane **34** (2.391 Å). Comparison of bond angles shows that the SiGeSi angles (87.1 and 86.4°) are smaller than the SiSiSi angles (90.4 and 88.7°) [219, 220].



59

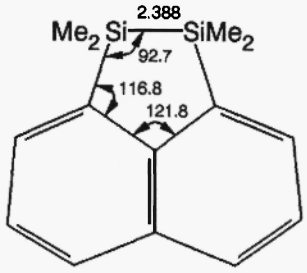
1.2.3. 5-Membered cyclic systems

X-ray analysis was used for structural studies of 1,2-disila-, 1,2,3-trisila- and 1,2,3,4-tetrasilacyclopentanes. The structure of 1,1,2,2-tetramethyl-4-(phenylsulfonyl)-1,2-disilacyclopentane **60** [221] reveals a few bond lengths and bond angle distortions; the most notable of these being the long Si-C bonds (1.905 and 1.913 Å) and small endocyclic SiSiC bond angles of 93.2°. The significant torsional strain that should be present in compound **60** due to the envelope conformation of the five-membered ring enforces a complete eclipsing of the four methyl groups on the adjacent silicon atoms.



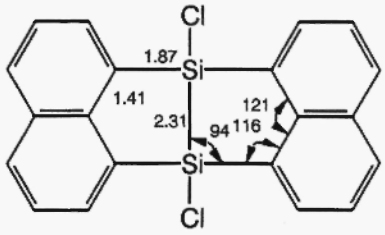
60

The disila analogue of acenaphthene **61** reveals a considerable conformational rigidity. The symmetry of this compound is close to that of the carbon analogue. Whilst the angular distortions of the acenaphthene molecule are distributed over the whole ring, the largest changes in valency angles of 1,2-disilaacenaphthene have been found at the silicon atoms (∠SiSiC=92.7°). The Si-Si bond lengths in compounds **60** [221] and **61** are almost equal [222, 223].



61

The bis(1,8-naphthalene)dichlorodisilane **62** has a "butterfly" conformation. The silicon atoms are practically in one plane with both naphthalene rings, which in turn form a dihedral angle of 109° between themselves [224].



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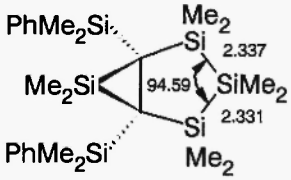

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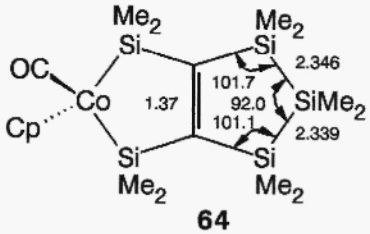

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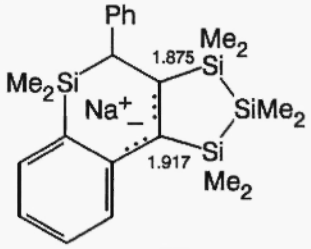
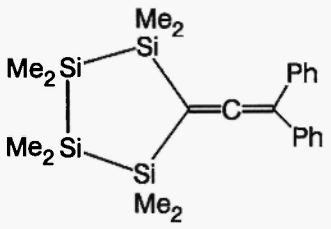


65

According to X-ray analysis the molecules of compounds **63** [225], **64** [226], and **65** [227] contain fused 1,2,3-trisilacyclopentane rings. The notable feature of 1,2,3-trisilacyclopentane fragment is a small bond angle SiSiSi (92-94.59°). X-ray analysis has been applied also for 1,2,3,4-tetrasilacyclopentanes **66** [228] and **67** [226], however, in these cases the geometry of silaheterocycles has not been clearly documented.



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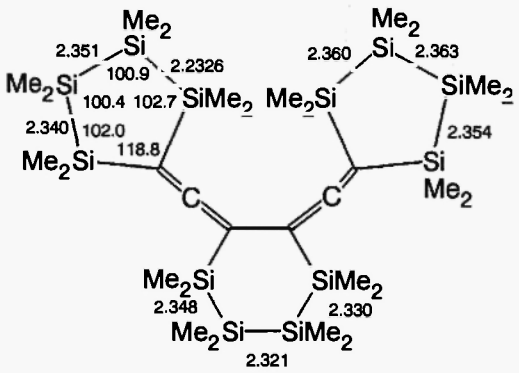
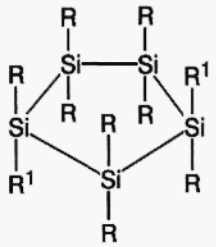


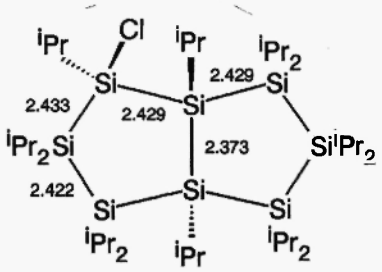
67

The structure of the cyclopentasilane molecule series **68** has been determined by means of calculation [143], by electron diffraction [229] and by X-ray analysis (Table 10).



68

The cyclopentasilane ring of the compounds listed in the Table 10 as a rule possesses a conformation which lies between C_2 (twist) and C_s (envelope). In trans-1,3-difluorooctaphenylcyclopentasilane the silicon ring adopts an envelope conformation. The largest Si-Si bond length (2.395 Å) has been found in decaphenylcyclopentasilane.



69

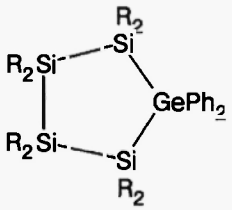
Polysilane framework of *trans*-bicyclo[3.3.0]octasilane **69** has a *trans*-fused structure of cyclopentasilane rings. The cyclopentasilane rings have a conformation intermediate between the envelope and twist forms. The peripheral Si-Si bonds (average 2.428 Å) are longer than the bridgehead Si-Si bond (2,373 Å), probably due to the steric hindrance of the isopropyl groups [235].

Table 10. Geometric parameters of cyclopentasilanes **68**

R	R^1	r(Si-Si) (Å)	∠SiSiS(°)	Ref.
H	H	2.367		[143]
H	H	2.342(3)	104.2(7)	[229]
—$(CH_2)_4$—		2.347(1)	104.5(2)	[230]
—$(CH_2)_5$—		2.359(1)	102.5(2)	[230]
Ph	Ph	2.395(4)	104.5(3)	[231]
Ph	F	2.375(2)	102.64(7)	[232,233]
Br[a]	Br	2.353(6)	105.4(2)	[234]
I	I	2.362(8)	105.3(3)	[234]
I[b]	I	2.366(7)	105.4(2)	[234]

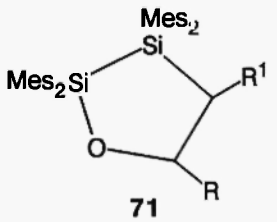
[a] 87 K
[b] 96 K

The five-membered rings of tetrasilagermacyclopentanes **70** (R=^{i}Pr, ^{t}BuCH$_2$) [236] have envelope and half-chair forms, respectively. The average Si-Si distances of two compounds **70** are equal (2.414 Å), but this value is *ca.* 0,024 Å longer than Si-Si distances in related four-membered trisilagermacyclobutanes **59**. The Si-Ge bond lengths for compounds **70** are 2.434 Å (R=^{i}Pr) and 2.449 Å (R=^{t}BuCH$_2$) [236].



70

The five-membered ring of 1-oxa-2,3-disilacyclopentanes **71** (R=H, R^1=Me [237], RR^1=$(CH_2)_4$ [237], R=R^1=Ph [36]) adopts a slightly distorted envelope conformation. All compounds exhibit the elongated Si-Si bonds (2.407-2.480 Å) due to the steric hindrance of four mesityl groups. In addition compound **71** [RR^1=$(CH_2)_4$] has *cis*-fusion of 5- and 6-membered rings with the six-membered ring in a chair conformation. In the molecule of the diphenyl derivative **71** (R=R^1=Ph) two phenyl groups are situated *trans* to each other, occupying pseudoequatorial positions.



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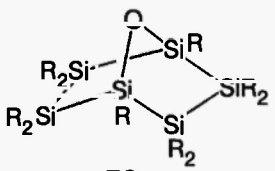


72

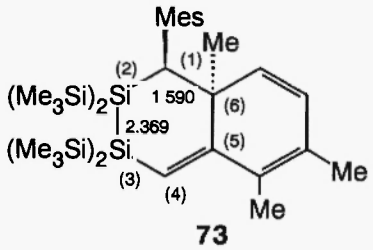
In the molecule of 7-oxahexasilanorbornanes the oxygen atom links two bridgehead silicon atoms. The average Si-Si bond length (2.402 Å) of the decaisopropyl derivative **72** (R=^{i}Pr) [238] is almost the same as this one in deca(isopropyl)hexasilabicyclo[2.2.0]hexane **41** (2.400 Å) [198]. It must be noted that the distance between two bridgehead silicon atoms (2.920 Å) is within

the sum of van der Waals radii. The Si-O bond is longer (1.683 Å) than that in other disiloxanes, and angle SiOSi (120.2°) is small.

According to X-ray analysis two molecules of decamethyl-7-oxahexasilanorbornane **72** (R=Me) [239] are connected by an electrostatic interaction with one molecule of 1,4-dihydroxydecamethylcyclohexasilane in the unit cell. Replacement of all isopropyl groups for the methyl ones decreases the average Si-Si distance (2.3600 Å). At the same time, in permethyl compound **71** the Si-O bond (1.695 and 1.700 Å) is lengthened, and angle SiOSi (116.21°) is narrowed, as compared with the isopropyl derivative [239].

1.2.4. 6-Membered Cyclic Systems

The 1,2-disilacyclohexane fragment of *cis*-4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane [240] is conformationally close to C_2, possessing an almost planar disilane moiety (the torsional angle at the Si-Si bond being 8.9°). The Si-Si bond length (2.318 Å) is considerably shortened, whilst the Si-C bond has usual length (1.861 Å).



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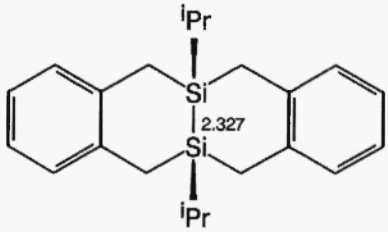
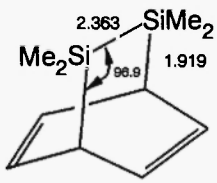


74

The X-ray analysis of (E)-1,2,3,8a-tetrahydro-5,6-dimethyl-1-mesityl-2,2,3,3-tetrakis(trimethylsilyl)-2,3-disilanaphthalene **73** [177, 241] yields an interesting boat conformation of the disilacyclohexene fragment, in which the plane $Si_{(1)}Si_{(2)}C_{(4)}$ is tilted by 16.8° and the plane $C_{(1)}C_{(5)}C_{(6)}$ - by 43.6° with respect to the plane defined by the $C_{(1)}Si_{(2)}C_{(4)}C_{(5)}$ atoms. The disilacyclohexane rings of compound **74** fused with benzene rings assume the boat conformation, and the two benzene rings are oriented in an *endo,exo* manner [29].

7,7,8,8-Tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene **75** [242] - the [2+4]cycloaddition product of tetramethyldisilene with benzene - has several interesting features. The four alkenic carbons are coplanar while the bridged carbons are located above the plane. The Si-Si bond (2.363 Å), parallel to the $C_{(2)}C_{(3)}C_{(5)}C_{(6)}$ plane, are lengthened and the bond angles around the bridged Si atoms are highly contracted (96.3°).



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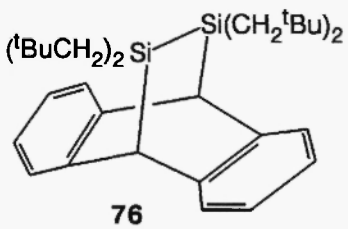
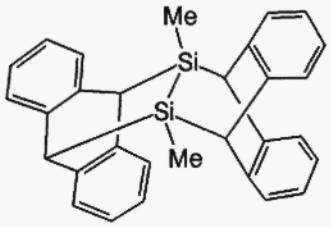


76

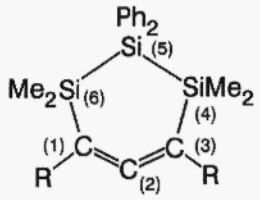
The elongation of the Si-Si bond in dibenzo[b,e]-7,7,8,8-tetra(neopentyl)-7,8-disilabicyclo[2.2.2]octa-2,5-diene **76** [243] in comparison with compound **75** may be a result of greater steric repulsion caused by the bulky neopentyl groups. The endocyclic CSiSi bond angles (96° and 95°) are also highly contracted.

X-ray techniques have been applied for the structural investigation of compound **77**, which may be regarded as a formal adduct of dimethyldisilyne with two anthracene molecules. The length of the Si-Si bond is 2.323 Å, the torsional MeSiSiMe angle being 7.5° [244].



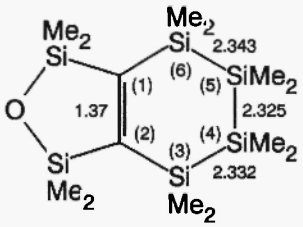
77

Trisilacyclohexa-1,2-dienes **78** (R=Ph [245], Me_3Si [246]) are the most strained cyclic allenes containing silicon atoms. The allene unit is bent from linear geometry to 161 and 166.4° for phenyl and trimethylsilyl derivatives, respectively. The dihedral geometry around the allenic fragments in molecules **78** is also influenced by the ring strains, the torsional angles $Si_{(6)}C_{(1)}C_{(3)}Si_{(4)}$ are strongly contracted [52.2° (R=Ph), 64.6° (R=Me_3Si)] from the normal vertical geometry. The Si-Si bond length is also increased (2.382 and 2.387 Å).



78

In fused tetrasilacyclohexenes **79** and **80** [228, 247] the geometry around the double bond is close to planar, the torsional angles $Si_{(3)}C_{(2)}C_{(1)}Si$ and $Si_{(6)}C_{(1)}C_{(2)}Si$ are 168.0, 174.2 and 172.2, 179.4° for compounds **79** and **80**, respectively.



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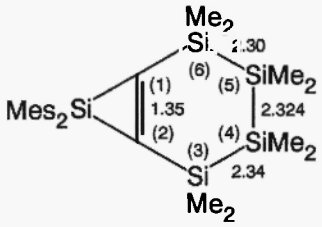

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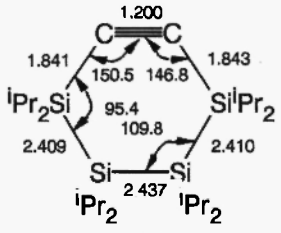


81

Crystal packing of octa(isopropyl)tetrasilacyclohexyne **81** [248] produces a molecular asymmetry, which affords SiC≡C bond angles of 146.8 and 150.5°. The SiC≡C angle of 147.0° calculated for tetrasilacyclohexyne by *ab initio* agrees well with an average experimental value for **81**.

The structure of some representatives of the cyclohexasilane series has been ascertained by means of electron diffraction [249] and X-ray techniques (Table 11). In the dodecamethyl and decamethyldiphenyl derivatives the cyclohexasilane ring has an ideal chair conformation with average torsional angle values of 53.5 and 57.1°, respectively. These values are close to those found for the cyclohexane ring [250]. For 1,2,3,4,5,6-hexamethyl-1,2,3,4,5,6-hexaphenylcyclohexasilane there is a chair conformation of the hexasilane ring; however, a considerable deviation from the ideal geometry with torsion angles varying from 47.9° to 61.8° is observed. The cyclohexasilane ring in the dodecaphenyl derivative has the chair conformation, which, however, is more shallow (torsional angles are 47.2-47.8°) than in the corresponding dodecamethyl compound. The flattening of the six-membered ring is more exaggerated in the hexabenzylcyclohexasilane with an endocyclic SiSiSi angle of 117.01° and with a dihedral SiSiSiSi angle of 33.58°. It was impossible neither to ascertain precisely the structure of the gaseous non-substituted cyclohexasilane [249], nor to determine the conformer ratio, since the experimental data obtained correspond to three different models (100% chair; 63% chair, 37% twist; 62% chair, 25% twist, 13% boat).

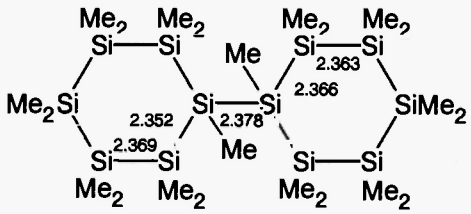
Table 11. Geometric parameters of cyclohexasilanes

Compound	r(Si-Si) (Å)	∠SiSiSi (°)	Ref.
$(H_2Si)_6$	2.342(5)	110.3(4)	[249]
$(Me_2Si)_6$	2.338(4)	111.9(4)	[250]
trans-PhMeSi[$(Me_2Si)_2]_2$SiMePh	2.350(3)	110.6(6)	[251]
$(MePhSiSiMe_2)_3$	2.3466(87)	110.71(32)	[252]
all *trans*-$(PhMeSi)_6$	2.359(2)	111.1(4)	[253]
$(Ph_2Si)_6$	2.394(3)	113.8(1)	[254]
all *trans*-[$PhCH_2(H)Si]_6$	2.332(2)	117.01(7)	[255]
trans-^{i}Pr(Cl)Si[(^{i}Pr$_2$Si)$_2]_2$Si(Ci)^{i}Pr	2.417(3)	114.23(3)	[256]
cis-^{i}Pr(Cl)Si[(^{i}Pr$_2$Si)$_2]_2$Si(Ci)^{i}Pr	2.414(6)	113.79(8)	[256]

X-ray analysis indicates a chair conformation also for the cyclohexasilane rings in compounds **82-84** [257, 258, 259]. In polysilane **82** the Si-Si bond connecting two rings is lengthened to 2.378 Å, other Si-Si distances of cyclohexasilanes **82-84** exhibit rather usual values.

The cyclohexasilane ring in *trans*- and *cis*-bicyclo[4.2.0]octasilanes **85** [235] has different conformations. The *trans*-isomer is characterized by chair form with both chlorine atoms in axial positions. The *cis*-isomer shows an unprecedented cyclohexasilane structure. The 6-membered ring does not adopt the well-known conformations such as the chair, boat, twist-boat and half-chair forms. In this cyclohexasilane ring, the $Si_{(1)}Si_{(2)}Si_{(3)}Si_{(4)}$ atoms construct a partial twist-boat form. Therefore, the cyclohexasilane ring can be regarded as a half-twist-boat form. The Si-Si bond distances of the 1,6-*cis*-compound (average 2.414 Å) are longer than those of 1,6-*trans*- **85** (average 2.402 Å). Especially, the bridgehead Si-Si bond (2.427 Å) is far longer than that of *trans*- (2.388 Å). These structural features reveal that *cis*-bicyclo[4.2.0]octasilane is a highly strained molecule in comparison with *trans*.

The crystal structure of octadecamethylbicycio[4.4.0]decasilane **86** [260] confirms the *trans* geometry of the fused cyclohexasilane rings, which adopt a regular chair conformation. The unit cell contains two crystallographically non-equivalent molecules. The observed average Si-Si bond length is 2.351 Å. The Si-Si bond common for two rings is significantly longer in both molecules (2,369 Å). The two molecules appear to be completely unstrained with SiSiSi angles of 111.0°.



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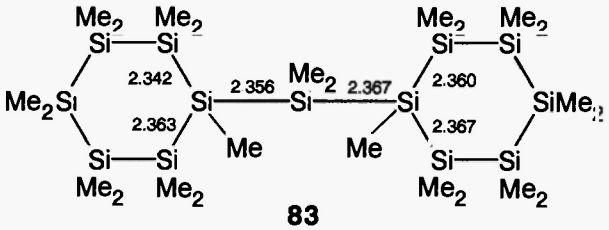

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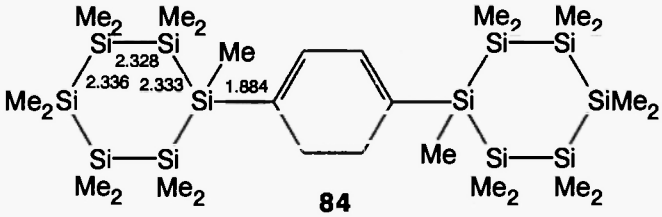
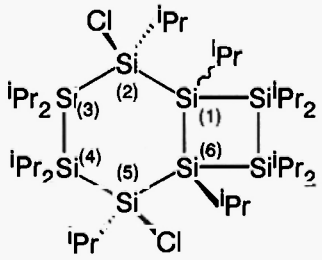


84

X-ray analysis shows that the compound Si_9Me_{16}, obtained in the reaction of dimethyldichlorosilane and methyltrichlorosilane with sodium, is a bicyclic polysilane, namely hexadecamethylbicyclo[3.3.1]nonasilane **87** [261, 262]. Two independent molecules of compound **87** have the six-membered ring $Si_{(1)}Si_{(9)}Si_{(6)}Si_{(7)}Si_{(8)}$ in a classical chair conformation, whilst the second ring shows a conformation which lies between chair and boat owing to the steric repulsion between the methyl groups. This results in the widening of the $Si_{(2)}Si_{(3)}Si_{(4)}$ angle to 120°. The mean Si-Si bond length is 2.343 Å.



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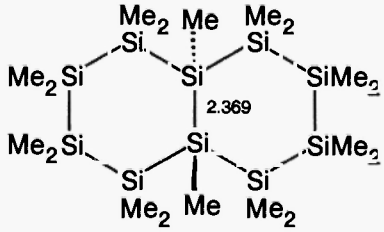
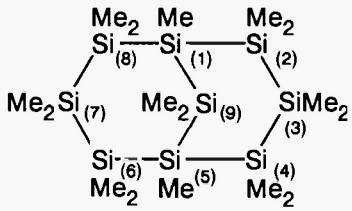
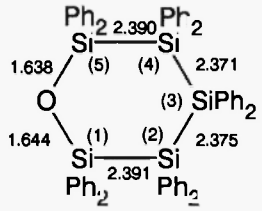


86



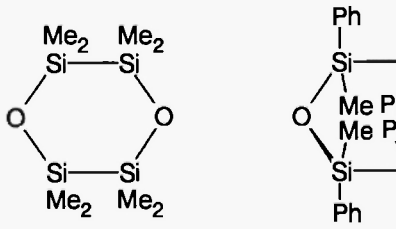
87

Some investigations have been devoted to the molecular structure of polysilane systems containing, in addition to silicon atoms, oxygen atoms in the six-membered ring [263-267]. In decaphenyl-1-oxapentasilacyclohexane **88** [263] the Si_5O ring is in a boat conformation. The O and $Si_{(3)}$ atoms are on one side of the remaining four silicon atoms, which do not form an ideal plane (maximum deviation of 0.08 Å). The Si-Si bond lengths are not equivalent, the $Si_{(1)}$-$Si_{(2)}$ and $Si_{(4)}$-$Si_{(5)}$ bonds being slightly longer than those of $Si_{(2)}$-$Si_{(3)}$ and $Si_{(3)}$-$Si_{(4)}$. The angles at the silicon atoms vary from 106.6° to 109.2°.



88

The geometry of molecules containing the 1,4-dioxa-2,3,5,6-tetrasilacyclohexane ring (**89-92**) has been determined by X-ray diffraction. The Si-Si bond distances in siloxanes **89-92** are 2.35, 2.362, 2.37 and 2.36 Å. As to the conformation of the 1,4-dioxa-2,3,5,6-tetrasilacyclohexane ring, there is a substantial discrepancy, compounds **89** [264] and **92** [267] having boat, and compound **91** [266] chair conformation. The six-membered ring in the mixture of RR- and SS-enantiomers in all-*trans* siloxane **90** [265] shows a sofa conformation.



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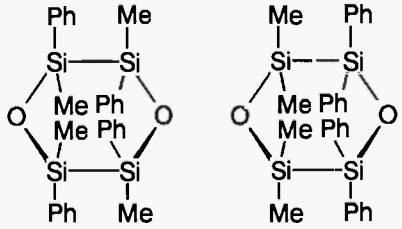

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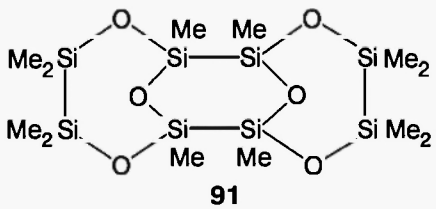

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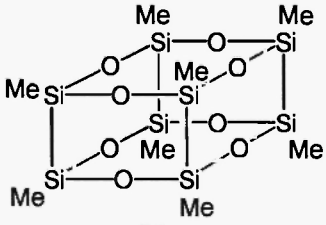
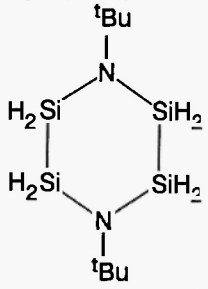


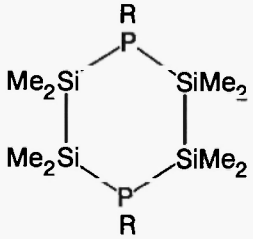
92

The cycle of N,N-di(*tert*-butyl)-2,3,5,6-tetrasilapiperazine **93** [268] has a twist conformation, but the two nitrogen atoms have an almost planar configuration with sums of angles equal to 359.59 and 359.93°. The two Si-Si distances are equal within the limit of standard deviations (2.337 and 2.334 Å) and only slightly longer than in disilane



93

In 2,2,3,3,5,5,6,6-octamethyl-1,4-diphospha-2,3,5,6-tetrasilacyclohexanes **94** (R=H [269], Ph [270]) the Si-Si bond distances are 2.340 (R=H) and 2.345 Å (R=Ph), the ring, unlike in compounds **89** and **93**, adopting a chair conformation. The structures of phosphorus (**94**, R=H) and arsenic **95** analogues are isotypic [269]. The Si-Si bond length of 2.332 Å in the 1,4-diarsa-2,3,5,6-tetrasilacyclohexane ring is slightly different from those in compounds **94**.



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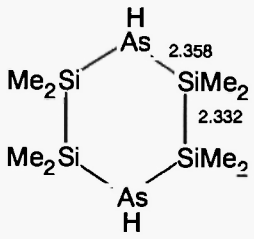

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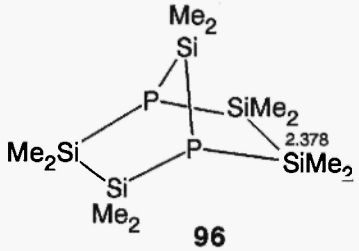

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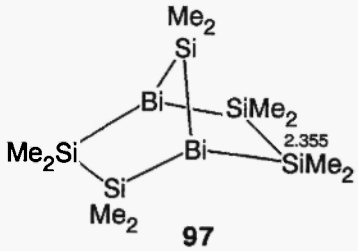
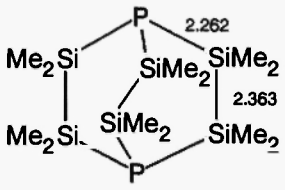


97

The molecules of decamethyl-1,3-diphospha- **96** [270] and decamethyl-1,3-dibismuthapentasilabicyclo[2.2.1]heptane **97** [270, 271] consist of six-membered Si_4M_2 (M=P, Bi) rings in a boat conformation, bridged by a Me_2Si group. The Si-Si bond length in the bismuth compound (2.355 Å) is shorter than in the phosphorus analogue (2.378 Å).

Molecular structures of dodecamethyl-1λ^3,4λ^3-diphospha- (**98**) and dodecamethyl-1λ^3,4λ^3-diarsa-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octanes (**99**) are also isotypic [269]. Whereas, the Si-P and Si-As bond lengths show usual feature, the Si-Si bonds in both derivatives are 0.02-0.03 Å longer than in the less strained cyclic compounds **94** and **95.**



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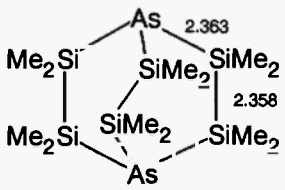
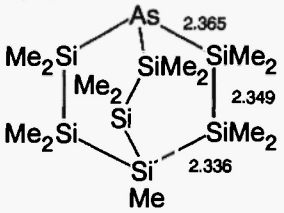


99

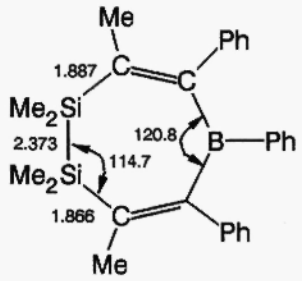
In the crystal the $AsSi_7$ skeleton of tridecamethyl-1-arsa-heptasilabicyclo[2.2.2]octane **100** [270, 272] is composed of three Si_5As six-membered rings that adopt a twisted boat conformation (C_3 symmetry). The average Si-As bond length (2.365 Å) is comparable with these values in compound **99**. The mean Si-Si distance of the bonds adjacent to the As atom (2.349 Å) is longer by 0.013 Å than the mean distance to the bridgehead silicon atom (2.336 Å), reflecting the steric repulsions of the nearly staggered methyl groups.



100

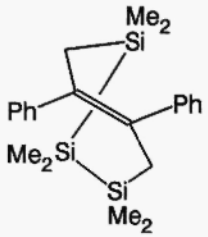
1.2.5. 7-Membered Cyclic Systems

X-ray techniques have been applied to examine the molecular structure of some seven-membered cycles with different polysilane fragments. The seven-membered heterocycle of 1,2-dihydro-1,1,2,2,3,7-hexamethyl-4,5,6-triphenyl-1,2,5-disilaborepine **101** [20] is nonplanar. The boron atom is shifted by 0.66 A out of the best plane of the ring.



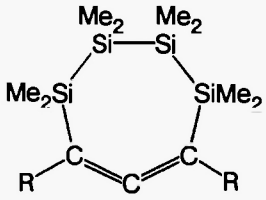
101

Trans-1,2-diphenyl-4,4,5,5,6,6-hexamethyl-4,5,6-trisilacycloheptene-1 **102** [73] has a symmetrical conformation. The most interesting point of the structure is a twisting around the C=C double bond. The torsional angle $C_{(3)}C_{(2)}=C_{(1)}C_{(7)}$ was found to be 147.3°. The bond angles around the ring atoms are almost normal except for the expanded $Si_{(4)}Si_{(5)}Si_{(6)}$ (120.62°). The C=C double bond (1.344 Å) is slightly stretched, the expansion of the C=C bond may be a result of the twisting. Furthermore, two benzene rings incline at 47.3° and 51.1° from the planes of $C_{(1)}C_{(2)}C_{(3)}$ and $C_{(2)}C_{(1)}C_{(7)}$, respectively. The average Si-Si bond length is 2.382 Å.



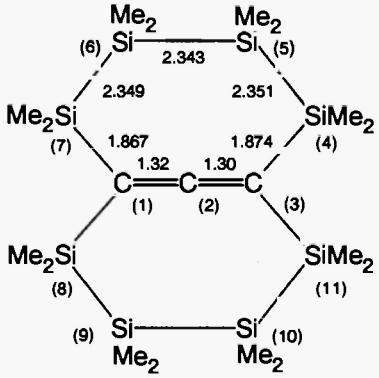
102

The most interesting structural part of the tetrasilacyclohepta-1,2-dienes **103** (R=Ph [245], Me_3Si [246]) is the relationship of the allenic moiety. Contrary to trisilacyclohexa-1,2-dienes **78** the molecules of compounds **103** are almost strain free. The allene unit is bent from linearity to 174° (R=Ph) and 174.4° (R=Me_3Si).



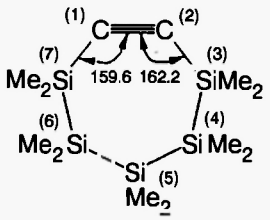
103

The X-ray crystallographic analysis of the bicyclic allene **104** [245, 274] shows the symmetrical conformation, the bond lengths and angles are almost normal. The allene *sp* carbon atom is linear, the torsional angles $Si_{(4)}C_{(3)}C_{(1)}Si_{(8)}$ and $Si_{(8)}C_{(1)}C_{(3)}Si_{(11)}$ are 72.0° and 73.3°, respectively.



104

The Si-Si, Si-C, C=C bond lengths of pentasilacycloheptyne **105** are ranging between 2.340-2.353, 1.80-1.84 and 1.22 Å, respectively. However, there is an interesting alternation in the bond angles around the polysilane chain; the bond angles $C_{(1)}C_{(2)}Si_{(3)}$, $C_{(2)}C_{(1)}Si_{(7)}$, $C_{(1)}Si_{(7)}Si_{(6)}$ and $C_{(2)}Si_{(3)}Si_{(4)}$ are contracted, $Si_{(3)}Si_{(4)}Si_{(5)}$ and $Si_{(5)}Si_{(6)}Si_{(7)}$ are normal, while the bond angle $Si_{(4)}Si_{(5)}Si_{(6)}$ is considerably expanded. The acetylene bond is bent from the linear geometry [275], however, the bending is smaller than in tetrasilacyclohexyne **81**.

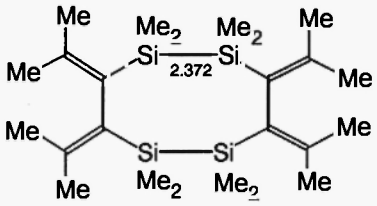


105

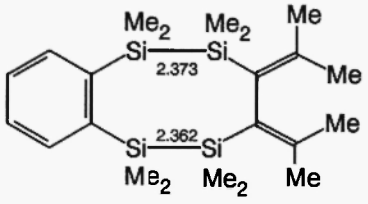
X-ray diffraction has been applied for the structure determination of permethylcycloheptasilane [276]. The cycloheptasilane ring adopts a twist-chair conformation, the average Si-Si and Si-C bond lengths being 2.340 and 1.883 Å, and the average SiSiSi angle (116.2°) being wider than in permethylcyclohexasilane.

1.2.6. 8-Membered Cyclic Systems

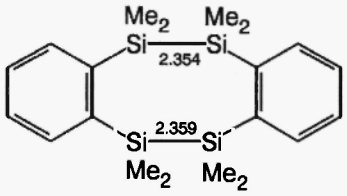
Structural parameters were obtained for compounds **106**-**108**, containing 8-membered rings with two disilane fragments [277, 278].



106



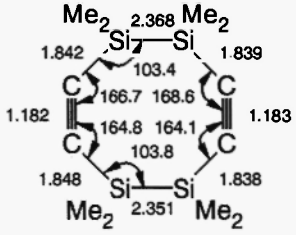
107



108

1,2,5,6-Tetrasilacyclooctane **106** [277, 278] with a chair conformation of the central heterocycle was separated from the 1:1 mixture of two conformational isomers. The average Si-Si bond length in compound **108** [278] with two fused benzo groups is shorter than in the tetrakis(isopropylidene) derivative **106** and in unsymmetrical compound **105** [278].

According to the preliminary results obtained for the molecular structure of 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilaocta-3,7-diyne **109** [279] the acetylene bonds are bent from the linear geometry.

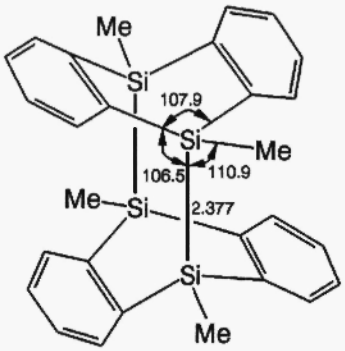


109

The bond and angle values for two (*cis-trans* and all-*trans*) isomers of 1,2,5,6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilaocta-3,7-diyne are essentially the same [280]. The phenyl

groups of the *cis-trans* isomer are located in *trans*-position at each Si-Si bond and in *cis*-position at each Si-C≡C-Si group. The 8-membered ring of this isomer is in a plane within 0.05 Å. The heterocycle of the all-*trans* isomer is twisted and the maximum deviation from a least-squares plane is as large as 0.25 Å.

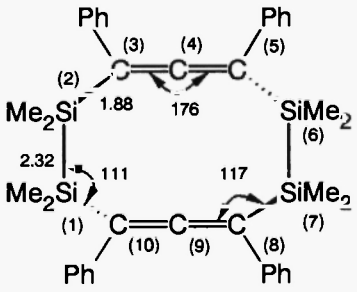
The structure of the anthracene dimer analogue with bridgehead silicon atoms **110** [281] has been reported. The Si-Si bond lengths (2.371, 2.377 Å) are elongated in this compound because of the steric reasons, but the geometry of the silicon atoms is tetrahedral.



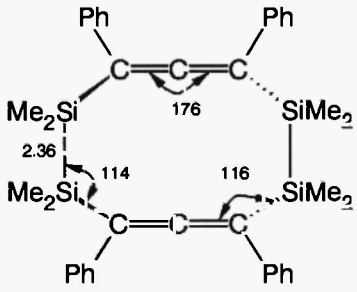
110

1.2.7. Compounds with Larger Rings

The molecular structures of two isomeric 1,2,6,7-tetrasilacyclodeca-3,4,8,9-tetraenes (**111** and **112**) were determined by X-ray diffraction. The same average bent angles (4°) have been found for dl (**111**) and meso-isomers (**112**). The dihedral angles $Si_{(2)}C_{(3)}C_{(5)}Si_{(6)}$ and $Si_{(7)}C_{(8)}C_{(10)}Si_{(1)}$ of these compounds are slightly spread (97-102°) from the normal geometry of the allene [282].

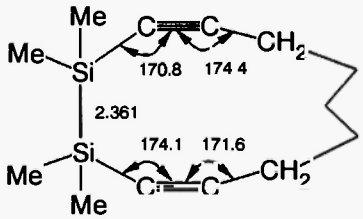


111



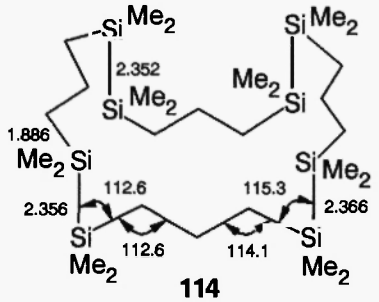
112

In the 11-membered ring of 1,1,2,2-tetramethyl-1,2-disilacycloundeca-3,10-diyne **113** [283] the C≡C triple bonds are slightly bent and the torsional angle $C_{(3)}Si_{(2)}Si_{(1)}C_{(11)}$ between both triple bond systems amounts 19.7°.



113

Permethylcyclopolysilanes with 13- $(Me_3Si)_{13}$ [284] and 16-membered $(Me_2Si)_{16}$ [284] rings have the same average Si-Si bond length (2.355 Å), the mean SiSiSi angles being 115.7° and 111.9°, respectively.

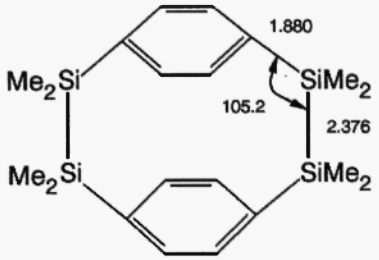


114

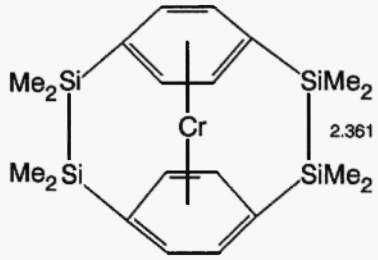
The structure of compound **114** [285] was established by X-ray diffraction, which shows that the four Si-Si moieties of 20-membered ring separated by propylene groups are close to parallel arrangement.

1.2.8. Cyclophane Compounds

Tetrasila[2.2]paracyclophane **115** [286] is the first [2.2]paracyclophane bridged by silicon atoms. This compound is highly symmetric with a center of symmetry. The Si-Si bond lengths (2.376 Å) deviate slightly from the normal values. The silicon atoms of the bridges are displaced from the plane of the aromatic rings toward the cyclophane cavity, the displacements being 15.0°. The distances between aromatic rings are 3.347-3.460 Å.

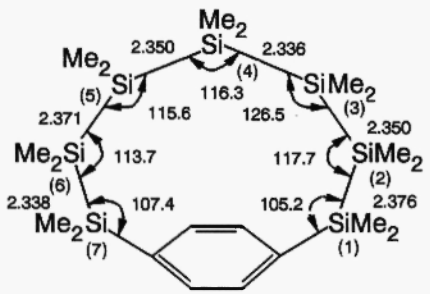


115



116

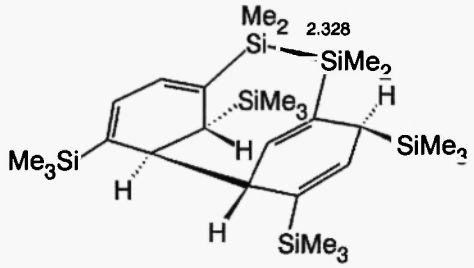
In the chromium complex **116** [287] the Si-Si distance is only insignificantly shorter than in the free ligand **115**, the distances between the aromatic rings are 3.35-3.43 Å. The silicon atoms are also displaced from the plane of the phenyl group and Si-C_{Ph} bonds form angles of 10.1 and 10.9 ° with the C_6H_4-plane.



117

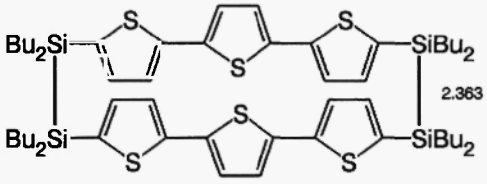
The Si-Si bond lengths of heptasila[7]paracyclophane **117** [288] vary between 2.336 and 2.376 Å. The displacement of the silicon atoms $Si_{(1)}$ and $Si_{(7)}$ from the aromatic plane is 6.5 and 9°, respectively.

The photolysis of 1-trimethylsilyl-4-pentamethyldisilylbenzene in the absence of trapping agent gave 7,7,8,8-tetramethyl-3,10,12,14-tetrakis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.$1^{2,6}$]tetradeca-3,5,6(13),11-tetraene **118** [289]. There are no abnormal bond distances, angles and close intermolecular contacts in this compound.



118

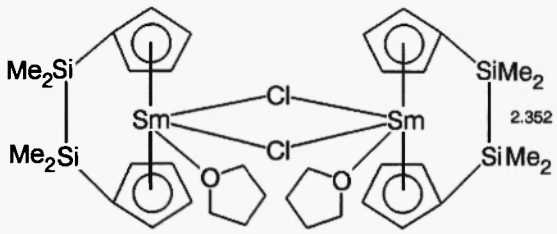
The thiophene rings of octabutyltetrasila[2.2]tertiophenophane **119** [290] are virtually planar and the adjacent rings lie in an antiparallel orientation. The thiophene rings 2 and 2' lie almost face-to-face resulting in a short S...S distance (3,55 Å), whereas in the other thiophene rings the sulfur atoms lie above the middle of the opposite rings. The Si-Si bond length (2.363 Å) is slightly longer than normal Si-Si distances. The conformation of the Si-Si bridges is intermediate between gauche and eclipsed.



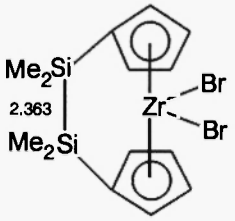
119

Recently several metallocenophanes with disilane or bis(disilane) bridges have been studied crystallographically [291-298].

In the samarium dimer **120** [291, 292] the Si-Si bond length is 2.352 Å, the tetramethyldisilane bridge is twisted (torsion CpSiSiCp angle - 33.46°), the CpSmCp angle is 128.1°. For zirconium complexes **121** [293], **122** [294] and **123** [294] the average Si-Si bonds (2.363, 2.369, 2.362 Å) and CpZrCp angles (129.7, 130.3, 130.8°, respectively) are very similar. The crystal unit of hafnocene **124** [295] contains eight molecules which may be divided into two groups. The main bond angles and distances are approximately the same, but the torsion CpSiSiCp angles are 5.89 and 13.24°.



120



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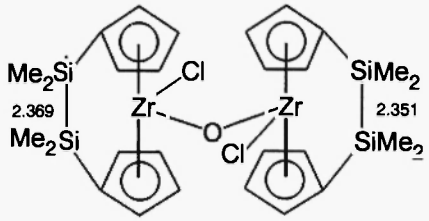

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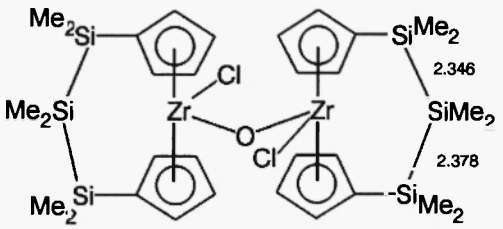
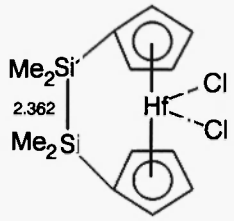
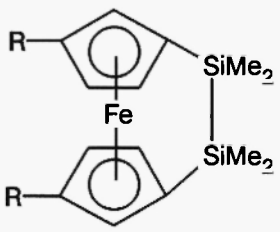


123

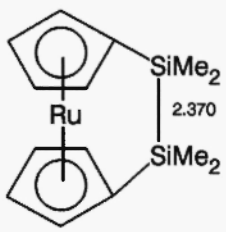


124

The presence of a smaller iron atom in **125** (R=H) [26, 296] leads to subtle rather than dramatic structural differences in comparison to the ruthenium analogue **126** [297]. For example, the tilt angle between the planes of the cyclopentadienyl rings in **126** (7.8°) is only 3.6° greater than that in **125** (R=H, 4.19°). The difference can be further appreciated by comparison of the values of CpMCp angles for these species. However, the values of CpMCp angles are 176.48 and 174.2° for ferrocenophane and ruthenocenophane, respectively. The reason for these relatively small differences between **125** (R=H) and **126** can be traced to the bonds within the bridge structure. In the ruthenium derivative the Si-Si bond (2.370 Å) is significantly elongated in comparison to that in ferrocenophane **125** (R=H) (2.3535 Å). The value in the latter is only slightly greater than that for typical Si-Si bonds.

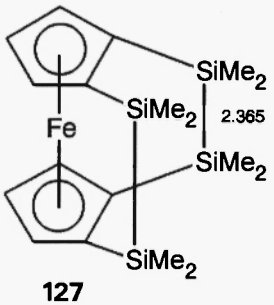


125



126

The elongation of the Si-Si bond in **126** is accompanied by an untwisting of the bridge and an eclipsing of the cyclopentadienyl ligands relative to the situation in **125** (R = H). For example, the bridge in ruthenocenophane is twisted by an angle of only 0.2° with respect to the plane defined by the centroids of the cyclopentadienyl ligands and the metal atom, whereas the corresponding angle in ferrocenophane is 8.4°.



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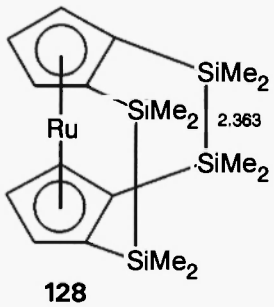
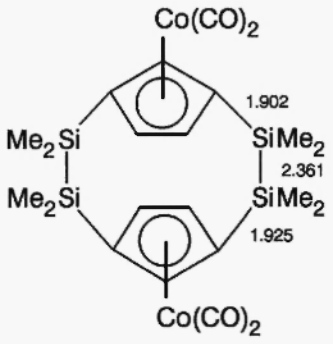


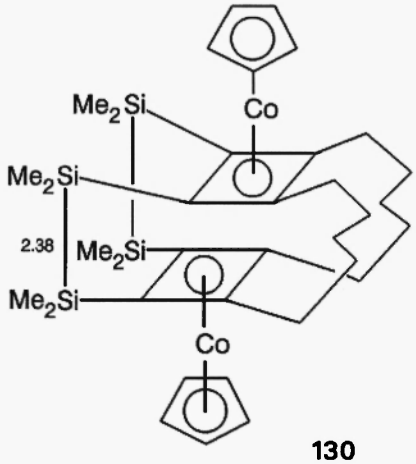
128

The effect of adding another disilane bridge increases the tilt angle from a value of 4.19° in **125** (R=H) to 7.2° in **127** [298] and from 7.8° in **226** to 12.9° in **228** [297]. The Si-Si bond length in the bis(disilane)-bridged ferrocenophane **127** (2.365 Å) is longer than that in **125** (R=H), but very similar to that found in the ruthenium analogue **128** (2.363 Å). The disilane bridges of **127** and **128** are considerably twisted relative to the plane containing the centroids of cyclopentadienyl rings and the metal atom. Thus, the Si-Si bond makes an angle of 16.5° and 15.7° with this plane in compounds **127** and **128**, respectively. It results in a staggering of the cyclopentadienyl ligands in **127** by an angle of 13.0° and in **128** by an angle of 12.5°.

The introduction of trimethylsilyl substituents on the cyclopentadienyl groups of disilane-bridged [2] ferrocenophane (compound **125**, R=Me_3Si) [299] leads to a small increase of the Si-Si bond length (2.349 Å) and of the dihedral angle between the planes of cyclopentadienyl rings (5.9°). A considerable twisting results in a significantly increased staggering of the cyclopentadienyl rings. The stagger angle of 17.7° is much greater than that for the unsubstituted compound **125**.

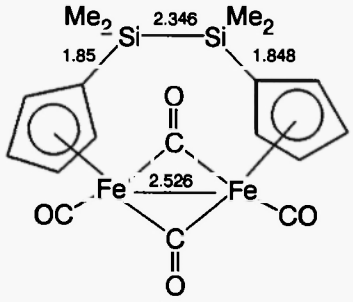


129



130

In complexes **129** [298] and **130** [300] two cobalt atoms lie out of the cyclophane sphere. The Si-Si bond length (2.361 A) in compound **129** is close to that found for the disila-bridged ferrocenophane **127** and ruthenocenophane **128**. The Si-Si distance for the disilane bridges of superphane **130** (2.38 Å) is longer than in 1,1,2,2-tetramethyl-1,2-disilacycloundeca-3,10-diyne **113** [283] - the starting compound for the synthesis of superphane **130**.

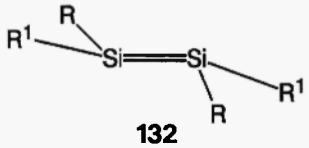


131

The ring-bridged bis(cyclopentadienyl)tetracarbonyldiiron derivative **131** [301, 302] has an unsymmetric configuration. The bond lengths and angles are normal in value, the six-membered ring formed by two silicon, two iron and two bridgehead cyclopentadienyl carbon atoms has a twisted boat conformation.

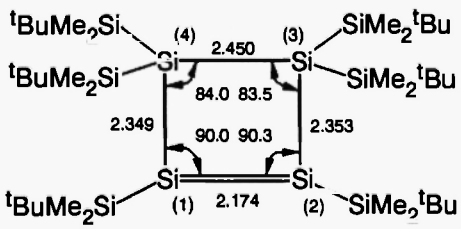
2. Disilenes

Research for the possibility to synthesize the disilenes - silicon analogues of olefines - has been going on for many years. It was considered that they could be formed as intermediate products in various reactions. It proved, however, impossible to separate compounds containing a Si=Si double bond, owing to their unstability. Only in the early 1980s the first stable tetramesityldisilene was obtained, its relative stability being due to the steric effect of the bulky mesityl groups preventing bimolecular condensation. At a somewhat later stage, the molecular structure of this compound was ascertained [303]. Now remarkable progress has been made in the structural studies of disilenes **132** (Table 12).



132

The length of the Si=Si double bond in disilene derivatives **132** lies between 2.138 and 2.251 Å. This is 0.09-0.20 Å shorter than the standard single Si-Si bond length (2.34 Å). The Si=Si distances of (E)- and (Z)-1,2-dimesityl-1,2-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}disilenes (2.228 and 2.195 Å, respectively) are much larger due to the steric repulsion than those of other disilenes having carbon substituents at the silicon atoms. The X-ray structures of tetrakis(trialkylsilyl)disilenes show unusual elongation of the central Si=Si double bond, which is confirmed by *ab initio* calculations [313, 314].



133

The spatial arrangement of the substituents at the Si=Si bond in disilenes indicates the "soft" nature of the Si=Si double bond in comparison with C=C double bond. In most of the disilenes the substituents are twisted along the Si=Si axis and the four atoms (two silicons and two

Table 12. Geometric parameters of disilenes **132**

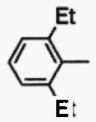
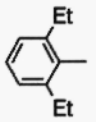
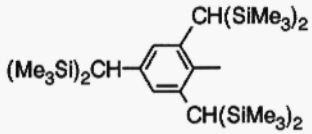
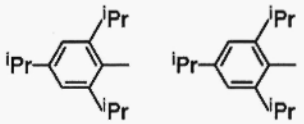
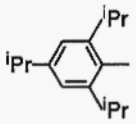
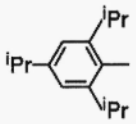
R	R^1	r(Si=Si), (Å)	∠Si=Si R, (°)	∠RSi R, (°)	twist angle, (°)	bent angle, (°)	Ref.
1	2	3	4	5	6	7	8
Mes	Mes	2.1433(2)	126.7(2) 121.2(1) 119.5(1) 115.4(2)	112.1(2) 121.5(2)	3	12 14	[304]
[a]Mes	Mes	2.160(1)	113.9(1) 126.8(1)		6.5	18	[303]
[b]Mes	Mes	2.146			13	0	[305]
Mes	tBu	2.143(1)	123.86(8) 122.77(8)	113.2(1)	0	0	[303]
		2.140(3)	117.6(2)	117.6(2) 124.8(2)	10	0	[306]
Mes	Ad	2.138(2)	123.4(1) 121.2(2)	115.4(2)	0	2.8	[307]
Mes		2.228(3)	120.1(2) 132.2(2) 130.0(2) 115.8(2)	108.8(3) 109.2(3)	8.7(8)	14.6(3) 9.4(3)	[308, 309]

Table 12 (continued)

1	2	3	4	5	6	7	8
[c]Mes		2.195(1)	136.3(3) 134.6(3) 109.5(3) 109.7(3)	113.5(4) 114.5(4)	14(1)	9.8(4) 7.6(4)	[308]
		2.144	120.8 121.6 121.6	117.5	3	0	[310]
	^{i}Bu	2.157(2)			0	0	[311]
	Me_3Si	2.152(3)			0	0	[311]
$^{i}Pr_2MeSi$	$^{i}Pr_2MeSi$	2.228(2) [d]2.370(2)	120.3(1) 124.1(1)	115.3(1)	0	5.4(0)	[312]
$^{t}BuMe_2Si$	$^{t}BuMe_2Si$	2.202(1) [d]2.380(2)	122.9(0) 124.5(0)	112.5(0)	8.9(1)	0.1(0)	[312]
$^{i}Pr_3Si$	$^{i}Pr_3Si$	2.251(1) [d]2.406(2)	126.3(0) 117.5(0)	114.9(0)	0	10.3(0)	[312]

(a) PhMe solvate

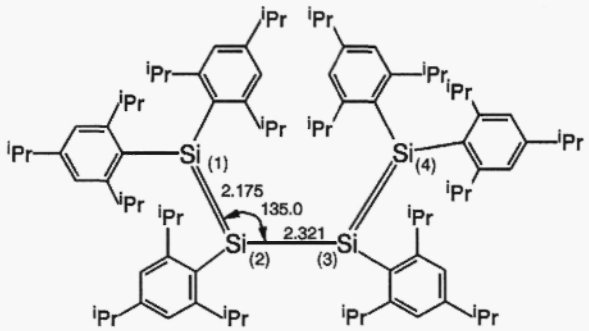
(b) THF solvate

(c) *cis*-isomer

(d) Si-Si bond length

atoms of substituents near one silicon) of fragments $RR^1Si=Si$ are not coplanar. The degree of pyramidalization at the silicon can be gauged by the bent angles formed by RSiR plane and the Si=Si bond axis.

In the first stable cyclic disilene - hexakis(*tert*-butyldimethylsilyl)tetrasilacyclobutene **133** [315] the Si=Si double bond length is 2.174 Å, which is shorter than those of tetrakis(trialkylsilyl)disilenes (2.202-2.251 Å). The four-membered ring is not planar. The angles between $Si_{(1)}Si_{(2)}Si_{(3)}$ and $Si_{(1)}Si_{(4)}Si_{(3)}$ planes and $Si_{(2)}Si_{(3)}Si_{(4)}$ and $Si_{(2)}Si_{(1)}Si_{(4)}$ are 37.1° and 37.0°, respectively. The arrangement around the Si=Si double bond is a slight *trans*-bent. The bent angles at $Si_{(1)}$ and $Si_{(2)}$ are 13.2 and 13.3°. The twist angle determined by the angle between $Si_{(1)}Si_{(4)}Si_{(3)}$ and $Si_{(2)}Si_{(3)}Si_{(4)}$ planes is 12.3°. Steric repulsion between vicinal ^{t}BuMe$_2$Si groups at $Si_{(3)}$ and $Si_{(4)}$ atoms would be the major reason for the folding of the four-membered ring, for the long $Si_{(3)}$-$Si_{(4)}$ (2.450 Å) distance, and also for the deformation around Si=Si double bond.



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The structure of the first compound with the conjugated Si=Si double bonds **134** [316] was confirmed by the X-ray diffraction. The conformation of the tetrasilabuta-1,3-diene approches the *cis*-form; the dihedral angle between the $Si_{(1)}Si_{(2)}Si_{(3)}$ and $Si_{(2)}Si_{(3)}Si_{(4)}$ planes is 51°. The Si=Si double bonds in **134** are about 0.03 Å longer than in the tetra(2,4,6-triisopropylphenyl)disilene. In spite of the presence of the bulky substituents the Si-Si single bond (2.321 Å) is markedly shortened.

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