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Structure and reaction controlled by strong sigma/ pi interactions*

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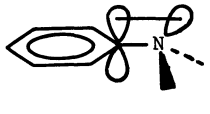
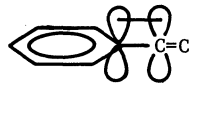
Abstract - The Si-Si bond has an HOMO of energy comparable to the most HOMO's of π systems. Consequently, the Si-Si bond can conjugate efficiently with carbon-carbon double and triple bonds, benzene rings and other π systems. The most Si-Si bonds are stable enough to construct sophisticated structures by themselves and with organic molecules and those systems, like nπ and ππ systems, give interesting opportunities to study structure and reactions governed by σπ conjugation. Herein, the chemistry related to two new such interesting compounds, 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne, 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane and related compounds is described. These are good models of strong σπ mixing and the first hetero-atom bridged [2.2]cyclophanes.

INTRODUCTION

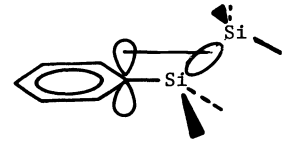
After the discovery of the unique electronic absorption of aryl disilanes (ref. 1), there has been accumulated an intense interest on the electronic properties as well as reactions of organopolysilanes (ref. 2). As a consequence, a concept of the strong σπ mixing (conjugation) between homopolar Si-Si σ bonds and π systems has been developed. A localized Si-Si σ bond of polysilanes such as hexamethyldisilane has a relatively high-lying HOMO, which can match energetically with most π systems. This situation provides an interesting opportunity for studying aryldisilanes as a model of σπ conjugated systems in comparison of well documented nπ and ππ conjugated systems.



nπ



ππ



σπ

We have reported analyses of the electronic structures of aryldisilanes in earlier publications (refs. 3 and 4). For an introductory reference, the author will tabulate ultraviolet (UV), charge-transfer (CT), and photoelectron (PE) spectral data of some Group 14 catenated compounds of the type of $PhMe_2E\text{-}E'Me_3$ (E = Si, Ge; E' = C, Si, Ge, Sn) (ref. 5).

Table 1 shows these spectral data of eight compounds. The CT spectra of tetracyanoethylene (TCNE) complexes with these compounds revealed two bands in which one (band II) had absorption maxima at around 25,000 cm^{-1}, and others had those at lower energies depending on the structures. Noteworthy is the fact that the latter bands had extremely low intensities as noted before for phenylpentamethyldisilane (ref. 4). This means that HOMO of these compounds are composed mainly of σ(E-E') orbitals.

The first ionization potentials of permethyl Group 14 catenates, determined by PE and CT spectra are also tabulated in Table 2.

Such σ(Si-Si)-π conjugation should be exemplified most efficiently if the molecular framework is so fixed that interacting molecular orbitals can overlap in maximum. In this paper, the author will describe the chemistry of such molecules prepared recently in this laboratory.

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* Chemistry of Organosilicon Compounds. 230.

Table 1. Spectral data of $PhMe_2E\text{-}E'Me_3$ (E = Si, Ge; E' = C, Si, Ge, Sn)

Compounds	UV(^1L_a)		CT/cm^{-1}		IP/eV	
	$\tilde{\nu}_{max}/cm^{-1}$	$\varepsilon_{max}/dm^3mol^{-1}cm^{-1}$	I	II	CT	PE
$PhMe_2SiCMe_3$	46300	9260	23300	25400	8.80	8.79
$PhMe_2SiSiMe_3$	43300	10900	20500	25100	8.39	8.35
$PhMe_2SiGeMe_3$	43200	11800	20600	25300	8.40	8.37
$PhMe_2SiSnMe_3$	41400	11700	18900	25300	8.15	----
$PhMe_2GeCMe_3$	46500	8310	22500	25200	8.69	----
$PhMe_2GeSiMe_3$	44300	10300	20600	25300	8.40	8.33
$PhMe_2GeGeMe_3$	44000	10600	20400	25300	8.37	8.29
$PhMe_2GeSnMe_3$	42600	12900	18900	25100	8.15	8.20

Table 2. Ionization potentials of some group 14 catenates

Compounds	IP (eV)	ref	Compounds	IP (eV)	ref
$Me_3SiSiMe_3$	8.69	8	$Me_3SiSnMe_3$	8.32	9
$Me_3GeGeMe_3$	8.6	9	$Me_3GeSnMe_3$	8.33	9
$Me_3SnSnMe_3$	8.20	9	Me_3SiCMe_3	9.29	5
$Me_3SiGeMe_3$	8.65	5*	$Me_3GeGeMe_3$	8.59*	5
				8.55	5

*IP values from CT spectra with TCNE as an acceptor are calculated by the Voigt-Reid type equation, $\tilde{\nu}_{CT}/eV = 0.77_1IP/eV\text{-}3.71_6$, for permethylpolysilanes (ref. 6).

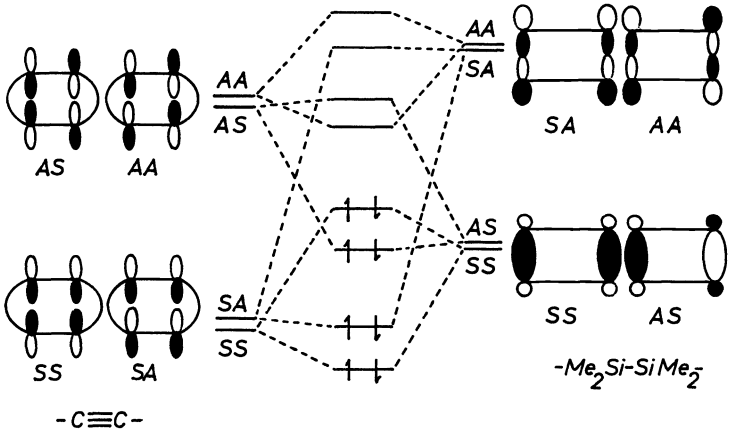


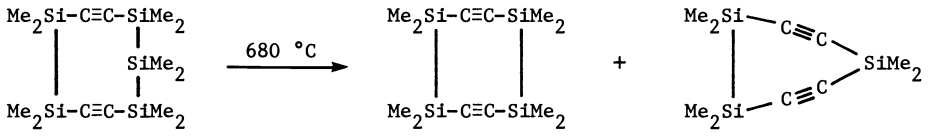
Fig. 1. Qualitative molecular orbital diagram of 1

PREPARATION OF ETHYNLENE POLYSILANYLENE COMPOUNDS (such as octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne and dodecamethyl-3,4,7,8,11,12-hexasilacyclododeca-1,5,9-triyne)

Although several types of cyclic polysilanes having carbon-carbon multiple bonds in the ring are known, no cyclic ethynylene polysilane has been reported. As shown in a qualitative molecular orbital diagram of 3,4,7,8-tetrasilacycloocta-1,5-diyne in Fig. 1, two Si-Si σ orbitals can overlap with one of two π orbitals of each C≡C bond to make up new molecular orbitals with through conjugation. Therefore, it is extremely intriguing to examine the properties of 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (1), which has been prepared recently (ref. 7). On the other hand, neither spatial nor through-bond interaction between two acetylenes has been observed for the corresponding cycloocta-1,5-diyne, the smallest known cyclic diyne (ref. 8).

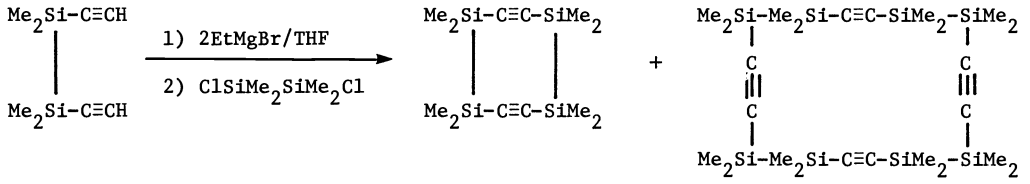
First, we have adopted a ring contraction method for the preparation of 1, since the direct ring closure to 1 was thought to be difficult. Flash vacuum pyrolysis (FVP) of 2 resulted in the formation of 1 as a crystal in 63 % yield, with concomitant extrusion of dimethylsilylene, which was trapped with diethylsilane.

Interestingly, from the pyrolysis products, 3,3,6,6,7,7-hexamethyl-3,6,7-trisilacyclohepta-1,4-diyne (3) was isolated as a white crystal in 3 % yield. Apparently, 1 is the direct precursor to 3, as evidenced by the fact that independent FVP of 1 gave 3 in 6.3 % yield. As far as we know, 3 is the smallest known cyclic diyne. Although unstable in the air, 3 can be purified by sublimation to give correct analyses.



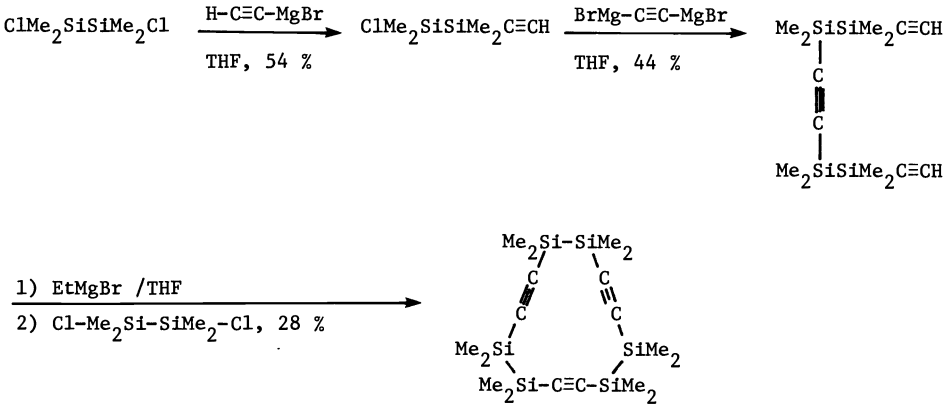
2 1 3

More recently, we have found that the reaction of the Grignard reagent made from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,2-dichlorotetramethyldisilane can indeed afford 1 in 45 % yield.



1 4

Successful preparation of 1 was then extended to the next higher member, dodecamethylhexasilacyclododeca-1,5,9-triyne (5), as shown below (ref. 9).



5

STRUCTURE AND SPECTROSCOPIC PROPERTIES OF ETHYNYLENE POLYSILANYLENES

Now, 1, 5, and 4 are the members of the homologous cyclic ethynylene disilanylenes. Several interesting features can be pointed out from Table 3, which lists physical properties of ethynylene polysilanes, but the most striking fact is an enhanced bathochromic shift in UV spectra for 1. Thus, 1 shows an absorption maximum at 250 nm (ε= 13,400). Two major factors, i.e. ring strain and σ-π conjugation, may be considered to account for the UV shift. However, judging from CNMR data of acetylene units, the ring strain of 1 is not very significant; i.e. only 2.55 ppm shift is observed for CNMR chemical shift of the sp carbon of 1 in comparison with a reference compound, $Me_3Si-C\equiv C-SiMe_2-SiMe_2-C\equiv C-SiMe_3$ (6).

Table 3. Some physical properties of cyclic ethynylene polysilanylenes

Compounds	mp/°C	NMR (δ ppm)			Raman (IR)	UV	(log ε)
		^1H	^{13}C	^{29}Si	(cm^{-1})	(nm)	
1	139	0.25 (s)	-3.07	-33.62	2082.4	242	(sh 4.0)
			119.46			250	(4.13)
2	55-56	0.17 (6H,s)	-7.57	-45.61	2091.5	226.5	(4.21)
		0.23 (12H,s)	-3.46	-35.77	(2080)	236	(sh 4.0)
		0.24 (12H,s)	-2.81	-34.21			
			115.67				
			116.39				
3	64-65	0.34 (12H,s)	-3.13	-26.85	2042.0	243	(sh 3.6)
		0.35 (6H,s)	-1.11	1.57		251	(3.70)
			126.70			260	(sh 2.4)
			132.25				
4	153-155	0.27 (s)	-2.81	-38.34		229	(sh 4.6)
			114.37			234	(sh 4.6)
5	146	0.25 (s)	-3.46	-37.51	2093.2	220	(sh, 4.5)
			113.76			230	(4.31)
6	44-44.5	0.05 (18H,s)	-3.20	-38.17	2097.5	223	(4.03)
		0.24 (12H,s)	111.62	-19.08	(2100)	230	(4.06)

The molecular structure of 1 as determined by X-ray crystallography (Fig. 2) demonstrates rather little distortion in both disilane and acetylene units. Therefore, the enhanced bathochromic shift in the UV spectra of 1 should primarily be caused by the unique electronic structure of 1, in which the HOMO is raised due to extensive σπ mixing.

The carbon-carbon triple bonds of 3 are very much distorted as judged by ^{13}CNMR. Thus ^{13}CNMR chemical shifts of the triple bond appeared with a large low-field shift at 126.70 and 132.25 ppm. These values are rather close to those of 1,2-bis(trimethylsilyl)ethylenes. Therefore, the bond order of the triple bond of 3 decreases considerably. Correspondingly, the C≡C stretching frequencies (Raman) decreased systematically.

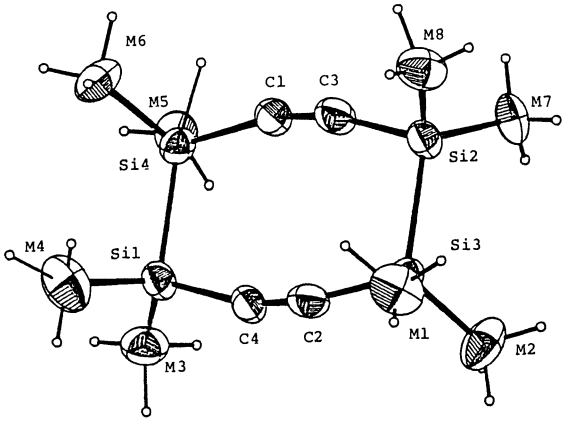


Figure 2. Molecular structure of 1

PHOTOELECTRON SPECTRA OF ETHYNYLENE POLYSILANYLENES

The photoelectron spectra of 1 and 5 have been recorded (ref. 10). The first bands of these spectra were interpreted by the comparison of the orbital energies calculated by the MINDO/3 and MNDO methods. Tables 4 and 5 list these values.

Table 4. Measured and calculated ionization energies of 1 (eV)

Measured Band	MINDO/3	MNDO
8.13	8.14 ($5a_g$)	9.51 ($5a_g$)
9.05	9.62 ($2b_{2g}$)	10.58 ($2b_{2g}$)
9.3	9.75 ($2b_{1u}$)	10.71 ($2b_{1u}$)
9.45	9.96 ($4b_{3u}$)	10.93 ($4b_{3u}$)
10.2	10.83 ($3b_{2u}$)	11.21 ($3b_{2u}$)

Table 5. Measured and calculated ionization energies of 5 (eV)

Measured Band	MINDO/3	MNDO
8.45	8.25 ($5a_1'$)	9.39 ($5a_1'$)
9.5	9.62 (7e')	10.36 (7e')
10.15	9.67 (3e'')	10.64 (3e'')

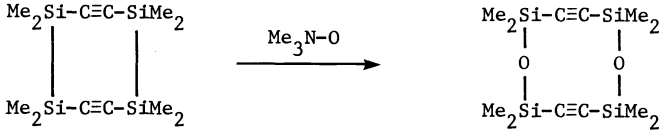
These data demonstrate clearly that the Si-Si bond is idealy situated to interact strongly with triple bonds. A smaller through-space and a larger through-bond interaction for 1 are indicated by the comparison of the orbital sequence of 1 with that of cycloocta-1,5-diyne, where the sequence is b_{2g}, b_{1u}, a_g, and b_{3u}.

Similar strong destabilization of a_1 orbital of 5 is also demonstrated and these are strong indications of the efficient in-plane $\sigma\pi$ interactions of the system.

Morokuma (ref. 11) also has calculated 3,4,7,8-tetrasila-1,5-diyne by the HF method and the 3-21G basis set. The fully optimized geometries agreed excellently with the experimental values for 1. Notable conclusions are: a very small distortion of both acetylene and disilane units is observed and HOMO (MO44, ag) is an antibonding with nearly equal mix of a C≡C π orbital and an Si-Si σ orbital. The corresponding bonding mix is shown in MO39 (ag) and the splitting between these two levels is 3.35 eV. This very large value again demonstrates very efficient $\sigma\pi$ mixing in 1.

REACTIONS OF ETHYNYLENE POLYSILANYLENES

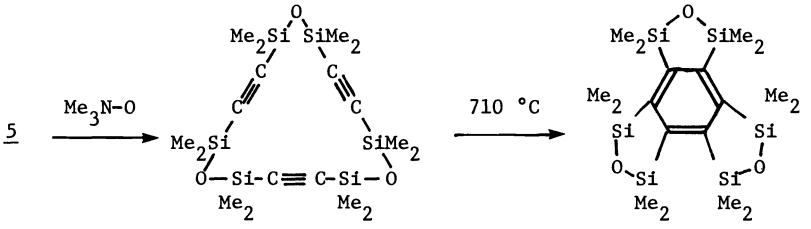
Except for the seven-membered compound (3), cyclic ethynylene polysilanylenes are oxidatively and hydrolytically stable. Thus, 1 is not oxidized by bubbling air in a benzene solution even under photochemical oxidation conditions. Peracids oxidized 1 to a messy mixture, but trimethylamine N-oxide can oxidize the Si-Si bonds of 1 selectively to the corresponding cyclic siloxanes.



1 7

Selective oxidation of three tetramethyldisilanylene units of 1 with trimethylamine N-oxide also gave a 15-membered macrocyclic trioxahexasilatriyne (8) in almost quantitative yield. 8 is thermally stable under usual conditions but isomerizes slowly to the corresponding benzene derivative (9) under rather drastic conditions of 710 °C in 4.9 % yield. This is the first

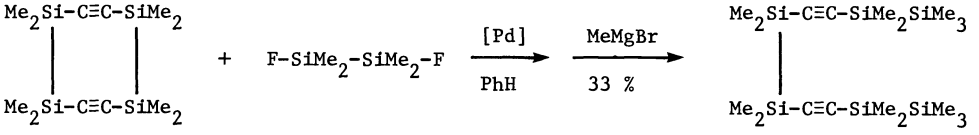
definitive example of intramolecular cyclization of acetylene to benzene in a manner of the [2+2+2] reaction.



8 9

The transition-metal-catalyzed trimerization of the cyclic polysiloxane (8) was also studied extensively. Interestingly, trimerization to the benzene derivative (9) competes to the trimerization to a fulvene derivative (ref. 12). An intermediate vinylydene complex was isolated and the structure was determined by X-ray analysis (ref. 13).

Both silicon-silicon and carbon-carbon triple bonds of 1 are activated and undergo a number of interesting reactions. One notable example is the palladium-catalyzed reaction of the Si-Si bond of 1 with another Si-Si bond.



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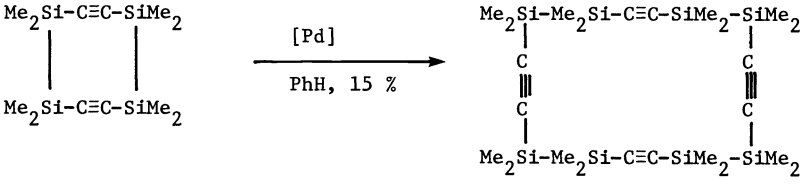
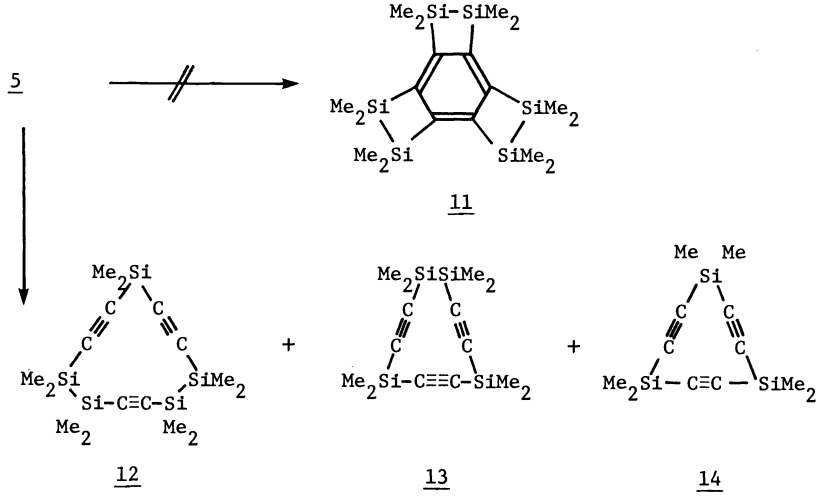


4

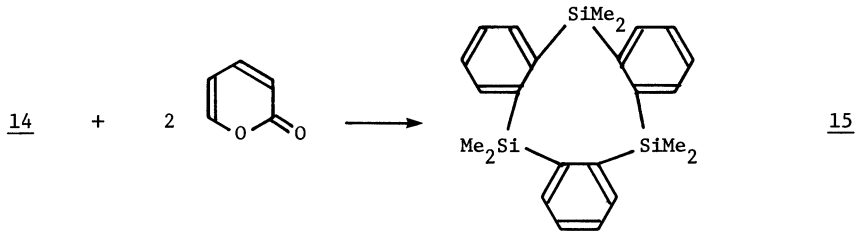
1 reacts with 1,2-difluorotetramethyldisilane in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium to give 10 after methylation. However, in the absence of the difluorodisilane, self-dimerization of 1 occurs to afford 4.



12 13 14

It is well known that 1,5,9-cyclododecatriyne, isomerized thermally to the corresponding tris-cyclobutenabenzene or hexaradialene as a reactive intermediate (ref. 14). However, when 5 was heated at 200-300 °C in the presence of excess diethyl maleate, diphenylacetylene, or acetylene dimethyl dicarboxyate, no product of cycloaddition of the presumed silicon analogue of tris-cyclobutenabenzene (11) with these unsaturated compounds was obtained. Instead, three cyclic triynes, 12, 13, and 14 were obtained by stepwise extrusion of dimethylsilylene. Hexamethyl-3,6,9-trisilacyclonona-1,4,7-triyne (14) is the smallest known cyclic triyne so far isolated. Whereas the pyrolysis of 5 gave three products (12, 13, and 14) in respective moderate yields (8 %, 27 %, and 11 %) at 540 °C, 14 is the single product under more forced conditions of 690 °C in 68 % yield. 14 was stable not only thermally but also oxidatively.

Cycloaddition of 14 with α-pyrone led to a novel tris-bridged cyclophane (15) as a white solid. The chemistry of the corresponding carbon analogue, cyclotriveratrylene (CTV), is of current interest (ref. 15).



The NMR spectra of 6 observed at low temperature indicates the twisted saddle conformation possessing C2 symmetry, and indeed as shown in Figure 1, the molecular structure of 15 determined by X-ray crystallographic analysis of the single crystal indicates a twisted saddle conformation.

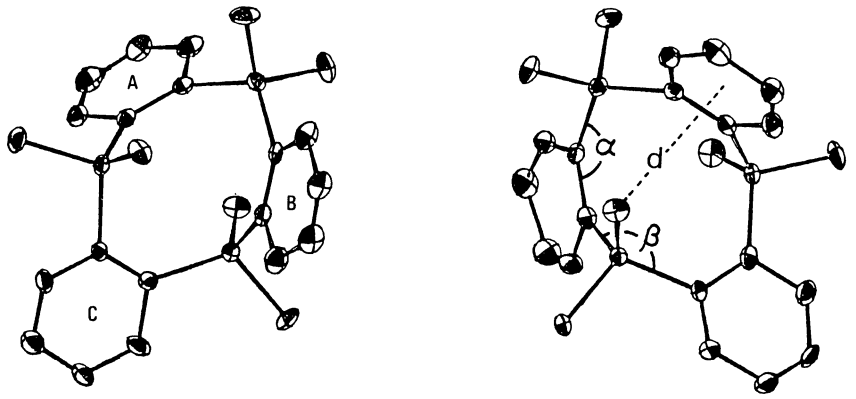


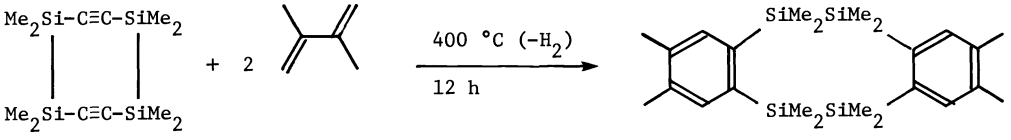
Fig. 3. The ORTEP drawing of two independent molecules of 15.

ORTHO AND META CYCLOPHANES BRIDGED BY POLYSILANES

There is currently intense interest in the chemistry of cyclophanes (ref. 16), in part due to the expected intriguing physical and chemical properties based on through-space and through-bond interactions between separated π systems. Since the first description of di-p-xylene ([2.2]paracyclophane) by Brown and Farthing in 1949, a large number of [2.2]cyclophanes were prepared. However, no cyclophane having Si-Si bond(s) as a bridge, instead of C-C bond(s), has been prepared until quite recently.

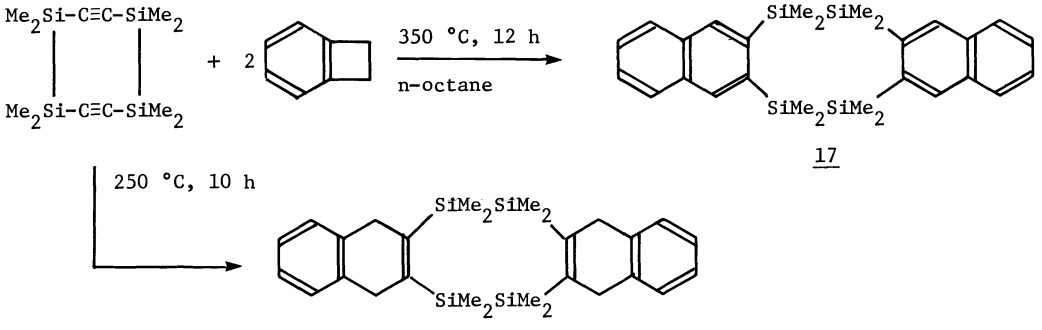
The first disilanylene-bridged cyclophanes were prepared from 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (1) (ref. 17). Thus, the reaction of 1 with 2,3-dimethylbutadiene under a forced condition (400°C, 12 h) afforded 16 in 56 % yield. The Diels-Alder reaction followed by dehydrogenation is a reasonable course to the product. Since the reaction of bis(trimethylsilyl)acetylene with 2,3-dimethylbutadiene under the same condition gave 1,2-dimethyl-5,6-bis(trimethylsilyl)benzene only in 3 % yield, the reactivity of 1 must be enhanced considerably.

A possible intermediate, that may be derived from the Diels-Alder reaction of only one triple bond of 1, must be very reactive due to the internal strain and hence reacts further to give 16. The compound, 16 corresponds to the first 1,2,9,10-tetrasila[2.2]orthocyclophane.



16

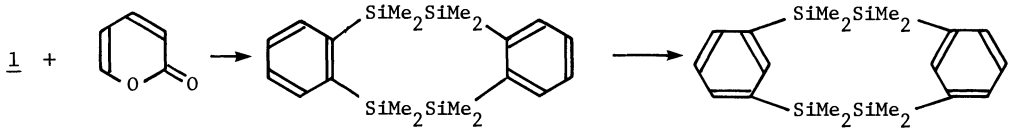
A similar reaction of 1 with benzocyclobutene at 350°C gave an orthocyclonaphtophane (17) in 59 % yield. In this case, an intermediate non-aromatic derivative (18) was also isolated in 56 % yield under different reation conditions.



17

18

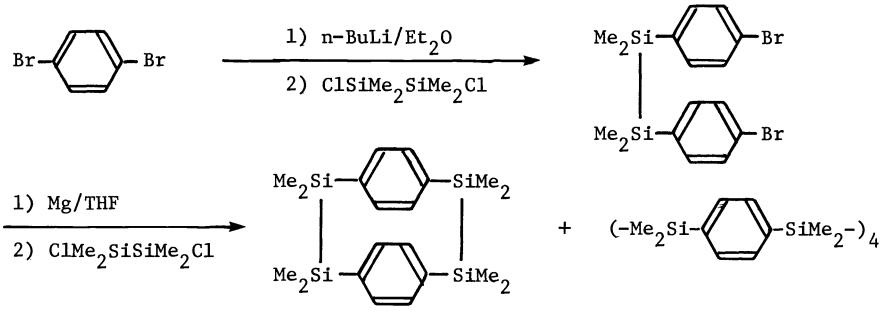
The reaction of 1 with α-pyrone in bromobenzene gave a rearranged [2.2]metacyclophane (19) in 22 % yield, while in the presence of triethylamine [2.2]orthocyclophane (20) was obtained in 93 % yield. It has been reported that a trace amount of acid can catalyzed the isomerization of 1,2-bis(trimethylsilyl)benzene to the meta and para isomers (ref. 17). Indeed, prolonged heating of isolated 20 in bromobenzene at 200°C resulted in the isomerization to 19 in 34 % yield. However, the corresponding [2.2]paracyclophane has not been obtained by the isomerization.



19 20

OCTAMETHYLTETRASILA[2.2]PARACYCLOPHANE

In relation to 3,3,4,4,7,7,8,8-octamethyl-3,4,7,8-tetrasilacyclooctadiyne and related compounds as examples of σπ mixed system, interesting spectroscopic properties due to the strong through-bond interactions should be expected for a [2.2]paracyclophane bridged by two disilane units. Then we have tried to prepare this target molecule (ref. 18). As has been pointed in the previous section, tetrasila[2.2]paracyclophane was not obtained by the isomerization of the corresponding ortho and metacyclophanes.

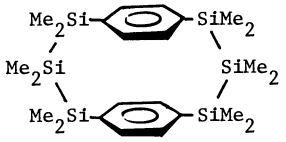


21

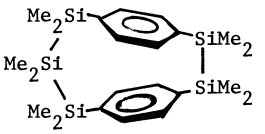
Di(p-bromophenyl)tetramethyldisilane, prepared from p-dibromobenzene and 1,2-dichlorotetramethyldisilane, was converted to the corresponding Grignard reagent which was subsequently subjected to the reaction with 1,2-dichlorotetramethyldisilane under high dilution conditions to give 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]paracyclophane (21) in 1.6 % yield.

We have examined other possible routes to 21 such as those through 1,1,2,2,3,3,10,10,11,11,-12,12-dodecamethyl-1,2,3,10,11,12-hexasila[3.3]paracyclophane (22) and 1,1,2,2,3,3,10,10,11,-11-decamethyl-1,2,3,10,11-pentasila[3.2]paracyclophane (23) by photochemical silylene extrusion, and through a diacetylene compound (24) by a possible Diels-Alder reaction, but only the most direct way shown in Scheme was successful so far, although the yield was very low.

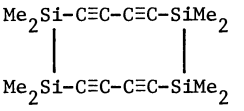
The comparisons of physical and chemical properties of 21 with those of 1,1,2,2,9,9,10,10-octamethyl-1,2,9,10-tetrasila[2.2]meta- (19) and orthophane (20) will be very much intriguing.



22



23



24

The paracyclophane (21) is highly sublimable colorless crystals. The X-ray structure of 21 is shown in Fig. 4. 21 is highly symmetric with a center of symmetry. The Si-Si bond lengths (3.376 A) deviate slightly from the normal values (3.34 A). The 3 and 6 (and 11 and 14) carbon atoms of the aromatic rings are displaced slightly out of the plane of the other four atoms inward. The degree of the displacement was 4.3° which is far smaller than that of the [2.2]paracyclophane (12.6°), indicating a smaller degree of distortion of the benzene rings of 21. However, the silicon atoms of the bridges are displaced appreciably from the aromatic ring toward the cyclophane cavity. The degree of this displacement is 15.0°, larger than that of [2.2]paracyclophane (11.2°). The distances between aromatic rings, 3.347 A for C3-C6 and 3.456-3.460 A for C4-C15 and C5-C16, are close to that observed in graphite (3.40 A) and longer than the mean intramolecular aromatic ring separation of [2.2]paracyclophanes around 3.00 A. Two benzene rings and methyl groups eclipse completely.

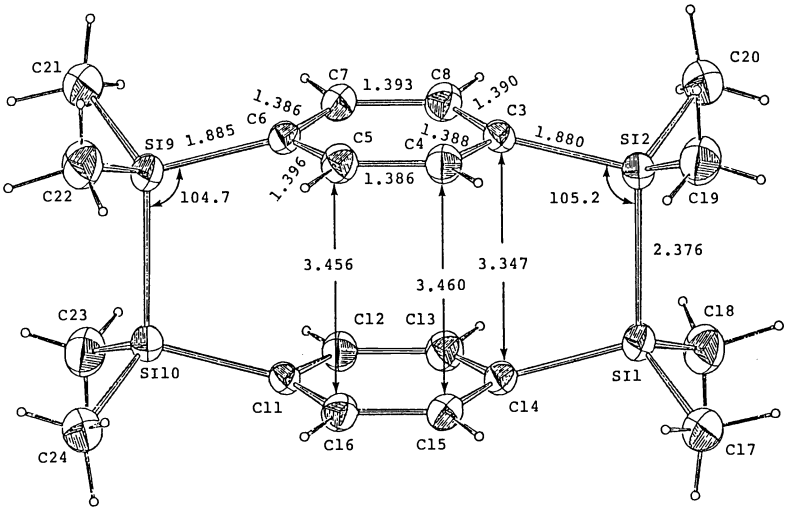


Fig. 4. ORTEP drawing of 21 with pertinent bond lengths and bond angles

These structural data show that 21 is a rather less distorted molecule than [2.2]paracyclophane. However, a dramatic effect of the strong σ(Si-Si)-π interaction was observed in uv spectra as shown in Figure 5.

In uv spectra of phenylpentamethyldisilane, an intramolecular σ(Si-Si)-π charge-transfer band appears around 231 nm (ref. 2). Octamethyltetrasila[2.2]meta- (19) and orthophane (20) show similar absorptions but the band is split into two bands at 223 nm (ε =19,100) and 263 nm (ε = 22,500) in 21. This type of red shift in the uv spectra occurs only in 21 among other polysilaparacyclophanes such as 19 and 21.

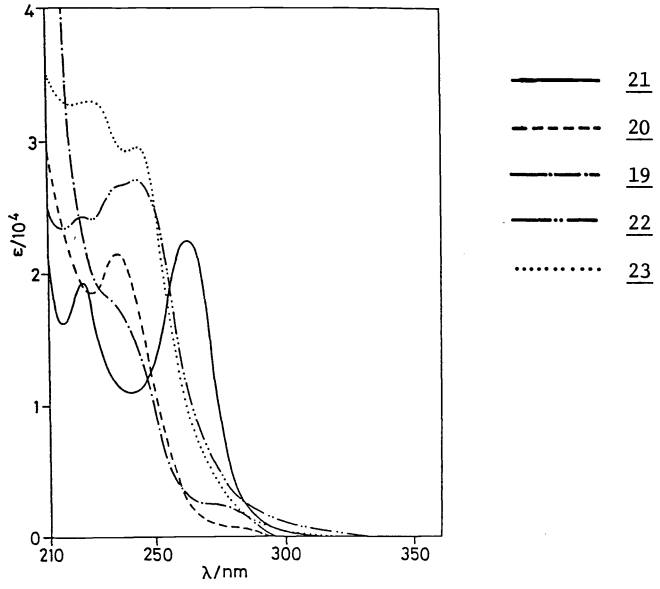


Fig. 5. Electronic spectra of several polysilane-bridged cyclophanes

CONCLUSIONS

The chemistry described in this article is still in progress rapidly in this laboratory. We have prepared some heterophanes bridged by polysilanes such as tetrasilathiophenophane and furanophane, interesting chemistry of which will be reported soon. Rather little is reported in this paper for the reactions of cyclophanes but there will be a large domain which will also be reported in due course.

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