

Redistribution of Linear Tetradecamethylhexasilane with Naphthalene Radical Anion. Using an apparatus and procedure similar to that for the naphthalene radical-anion redistribution of polymer, 40 ml of highly purified tetradecamethylhexasilane²⁰ was added to a dilute naphthalene radical-anion solution which was refluxed for 20 hr. Gas chromatographic analysis showed the presence of the linear compounds Me_2Si_2 , Me_2Si_3 , $\text{Me}_{10}\text{Si}_4$, $\text{Me}_{12}\text{Si}_5$, and $\text{Me}_{14}\text{Si}_6$, along with the cyclics $\text{Me}_{10}\text{Si}_5$, $\text{Me}_{12}\text{Si}_6$, and $\text{Me}_{14}\text{Si}_7$.

(20) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963).

Redistribution of Decamethylcyclopentasilane with Naphthalene Radical Anion. Using an apparatus and procedure similar to that used for the naphthalene radical-anion redistribution of polymer, 0.05 g of pure decamethylcyclopentasilane was added to a dilute naphthalene radical-anion solution in tetrahydrofuran. The reaction was followed by analytical gas chromatography. After 2 hr, the reaction mixture was composed of 10% $\text{Me}_{10}\text{Si}_5$ and 90% $\text{Me}_{12}\text{Si}_6$. No $\text{Me}_{14}\text{Si}_7$ was detected.

Similar reactions and similar results were obtained from the redistribution of dodecamethylcyclohexasilane and also of tetradecamethylcycloheptasilane.

Cyclic Polysilanes. IV.¹ Anion Radicals and Spectroscopic Properties of the Permethylcyclopolysilanes²

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Abstract: Cyclic permethylpolysilanes, $(\text{Me}_2\text{Si})_n$, where $n = 5, 6,$ and 7 , undergo reduction to anion radicals at low temperatures. The compounds with $n = 5$ and 6 give $(\text{Me}_2\text{Si})_5\cdot^-$ and $(\text{Me}_2\text{Si})_6\cdot^-$, respectively, upon electrolytic reduction, but all three compounds give only $(\text{Me}_2\text{Si})_5\cdot^-$ upon reduction with alkali metals. The esr spectra of the anion radicals show that the unpaired electron contacts equally all of the methyl protons and so is delocalized equally over all of the silicon atoms in the ring. The order of electron affinities $(\text{Me}_2\text{Si})_5 > \text{benzene} > (\text{Me}_2\text{Si})_6 > (\text{Me}_2\text{Si})_7$ was established. The ultraviolet, nmr, and infrared spectra of the $(\text{Me}_2\text{Si})_n$ compounds are also described. The compounds have absorption bands in the near-ultraviolet which shift to shorter wavelength as ring size is increased. The proton nmr spectrum for each compound shows only a single line from -95° to room temperature, indicating that conformational equilibration is rapid.

Anion radicals in which unpaired electrons occupy low-lying antibonding π molecular orbitals are well known, but formation of anion radicals by species lacking unsaturation and hence available antibonding π levels is not normally observed. However, the polysilanes,³ and other catenated polymetal compounds,⁴ are exceptional among formally saturated compounds in that they show strong absorption bands in the accessible region of the ultraviolet. This observation suggested that relatively low-energy orbitals are available in the polymetal compounds which might accommodate an additional electron, and in 1965 we reported the reduction of dodecamethylcyclohexasilane, $(\text{Me}_2\text{Si})_6$, to an anion radical.⁵ In this paper, a more complete study of the electrolytic and chemical reduction is reported for the cyclic permethylpolysilanes, $(\text{Me}_2\text{Si})_n$, where $n = 5, 6,$ and 7 , whose syntheses are described in the accompanying paper.¹ The esr and ultraviolet spectra of the resulting anion radicals are discussed, and other spectral properties of the neutral $(\text{Me}_2\text{Si})_n$ compounds, particularly those bearing on the nature of bonding in these species, are also presented.

(1) Previous paper in this series: E. Carberry and R. West, *J. Am. Chem. Soc.*, **91**, 5440 (1969).

(2) Research sponsored by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR-1061-66.

(3) H. Gilman, W. Atwell, and G. L. Schwabke, *J. Organometal. Chem.*, **2**, 369 (1964).

(4) W. Drenth, M. J. Janssen, G. J. M. van der Kerk, and J. A. Vliegthart, *ibid.*, **2**, 265 (1964).

(5) G. R. Husk and R. West, *J. Am. Chem. Soc.*, **87**, 3993 (1965). Recently another report of reduction of cyclopolysilanes to anion radicals has appeared.⁶

Reduction of Decamethylcyclopentasilane. Upon electrolytic reduction at -100 to -120° in complexing ether solvents (normally 3:1 by volume dimethyl ether-1,2-dimethoxyethane), $(\text{Me}_2\text{Si})_5$ was reversibly transformed to an anion radical. The radical was dark blue in color and gave an esr spectrum at low gain consisting of about 15 equally spaced lines at intervals of 0.53 G (Figure 1). These lines fit the binomial intensity pattern expected for the center lines of a 31-line pattern due to splitting by 30 equivalent protons on the 10 methyl groups in $(\text{Me}_2\text{Si})_5\cdot^-$ (Table I). The spectrum therefore indicates that the unpaired electron contacts each proton equally, and so is equally delocalized over each of the five ring atoms, as in a typical aromatic anion radical. In the sense that it is a completely delocalized species which should show a ring current, $(\text{Me}_2\text{Si})_5\cdot^-$ can also be regarded as an aromatic anion radical.

At higher gain and higher resolution, a greater number of lines was observed in the esr spectrum of $(\text{Me}_2\text{Si})_5\cdot^-$, but the pattern was complicated by the appearance of two doublet satellite spectra replicating the central spectrum (Figure 2). The outer doublet, which had a principal splitting of 16.03 G, consisted of about 11 lines with the same spacings, line widths, and relative intensities as the central spectrum. The inner, more intense doublet had a splitting of 6.13 G, and again consisted of about 11 lines with the same spacing and line width as the main spectrum.

The satellite spectra are attributed to splitting by the natural carbon-13 and silicon-29 present in the mole-

(6) V. V. Bakhtiyarov, S. P. Sdodovnikov, O. M. Nefedov, and V. I. Shigorin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1012 (1968).

Table I. Electron Spin Resonance Data for Permethylcyclopolysilane Anion Radicals^a

Parent cyclosilane	Me ₁₂ Si ₆	Me ₁₀ Si ₅	Me ₁₀ Si ₅	Me ₁₂ Si ₆	Me ₁₄ Si ₇
Method of reduction	Elect	Elect	Chem	Chem	Chem
Observed anion radical	(Me ₁₂ Si ₆) ^{•-}	(Me ₁₀ Si ₅) ^{•-}	(Me ₁₀ Si ₅) ^{•-}	(Me ₁₀ Si ₅) ^{•-}	(Me ₁₀ Si ₅) ^{•-}
g value	2.0028	2.0032	2.0032	2.0032	2.0032
Splitting constants, G					
¹ H	0.49	0.53	0.53	0.53	0.53
¹³ C	14.60	16.03	16.06	16.03	16.03
²⁹ Si		6.13	6.13	6.10	6.10
Line widths, G	0.16	0.14	0.12	0.11	0.11
Line intensities ^a					
Center line	100	100	100	100	100
2	94	95	93.5	94.5	94
3	79.5	79	77	78	76
4	59	58	54.5	55.5	57.5
5	42	38	34	38	36
6	24	20	19	22	18
7	14	7.6	9	10	9

^a Calculated for Me₁₀Si₅: 100, 93.5, 78.0, 55.5, 35.0, 20.0, 9.2; Me₁₂Si₆: 100, 94.7, 80.4, 61.4, 41.8, 25.4, 13.8; Me₁₄Si₇: 100, 95.6, 83.3, 66.0, 47.5, 31.0, 18.4. ^b Solvent is 3:1 by volume dimethyl ether-1,2-dimethoxyethane for (Me₂Si)₅^{•-} and 2:1 methyltetrahydrofuran-glyme for (Me₂Si)₅^{•-}.

cules. Each of these isotopes has a spin of 1/2, and would thus produce doublet splittings as observed. The assignment of each doublet to a particular isotope was made on the basis of relative intensities. These de-

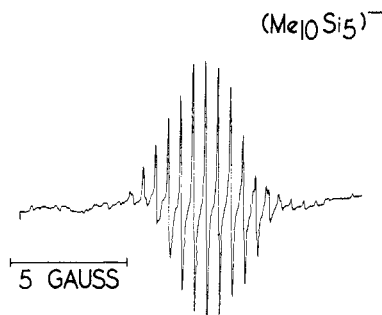


Figure 1. Esr spectrum of decamethylcyclopentasilane anion radical, produced electrolytically in 3:1 methyltetrahydrofuran-glyme at -75°, at low gain showing relative intensity of the center lines.

pend both on the isotopic abundance and on the number of equivalent nuclei in the molecule. For ¹³C each wing of the doublet should have 1.11% × 10/2 or 5.5% of the total intensity, whereas for ²⁹Si the predicted intensity is 4.7% × 5/2 or 11.7%. The expected ratio of ¹³C to ²⁹Si intensities is 0.47, and the observed intensity ratio between the outer and inner doublet was 0.48, so the outer doublet was assigned to ¹³C and the inner one to ²⁹Si.⁷

Assignment of the ²⁹Si splitting is further substantiated by calculations utilizing the method of Hunter and Symons.⁸ Their equation is shown below

$$100a^x/A^x = \rho_x U^x + \rho_y U^x_{yx}$$

where a^x = the coupling constant due to X, A^x = the isotropic one-electron hyperfine constant for X, ρ_x = the spin density on X, U_x = the spin polarization constant for X, and U^x_{yx} = the spin polarization constant due to the adjacent atoms.

Using the isotropic hyperfine constant for ²⁹Si given by Morton⁹ and the values of U^x and U^x_{yx} suggested by

(7) The same conclusion is reached if the two satellite intensities are independently compared with the intensity of the central spectrum, but the errors are greater because of the great differences involved.

(8) T. F. Hunter and M. C. R. Symons, *J. Chem. Soc., A*, 1770 (1967).

Hunter and Symons,¹⁰ and neglecting the effect of the neighboring methyl groups, the total spin density on each silicon atom was calculated to be 0.21. Five silicons would therefore account for all of the unpaired electron density. Since the equation requires only the observed coupling constant and not the number of silicon atoms, this calculation provides additional proof that the radical anion observed was indeed that of the cyclic pentamer.

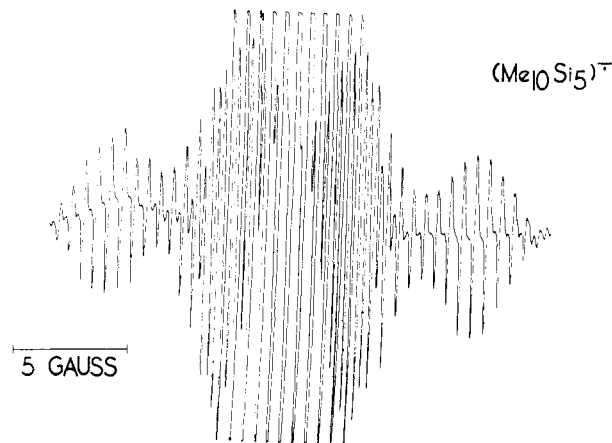


Figure 2. Esr spectrum of electrolytically produced decamethylcyclopentasilane anion radical in 3:1 methyltetrahydrofuran-glyme at -75° at high gain and high resolution, showing satellite doublets due to ¹³C and ²⁹Si.

The fact that the splitting is greater for ¹³C than for ²⁹Si requires discussion. The observed splitting will depend both on the magnetic moment of the nucleus and on the unpaired electron density at the nucleus. The magnetic moment for ¹³C (0.70220) is slightly greater than for ²⁹Si (-0.55177), but this difference alone accounts for only a small part of the difference in hyperfine splitting. It follows that the unpaired electron density at the nucleus is greater for carbon than for silicon in (Me₂Si)₅^{•-}. This is reasonable if the unpaired electron is considered to be in an orbital of essentially π type, made up of combinations of 3d or 4p orbitals from silicon atoms. The spin density at the silicon nuclei would

(9) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964); $A^{Si} = 1208$ G.

(10) $U^{Si} = 3.9$; $U^{Si_{i-1}Si_i} = -0.8$.

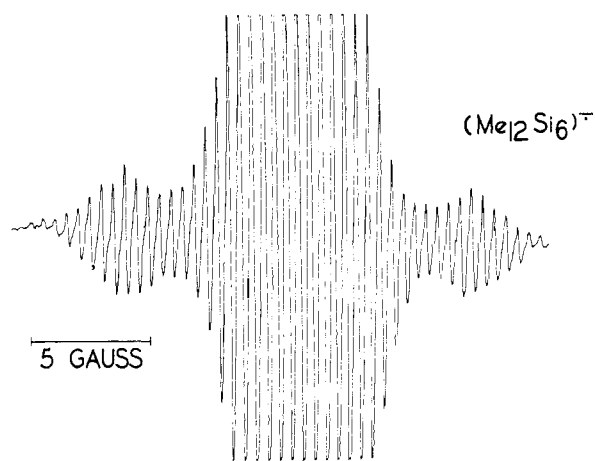


Figure 3. ESR spectrum of dodecamethylcyclohexasilane anion radical generated electrolytically in 3:1 dimethyl ether-glyme at -125° at high gain, showing satellite doublet due to ^{13}C .

be only that due to spin polarization, which could be quite small.

Reduction of Dodecamethylcyclohexasilane and Tetradecamethylcycloheptasilane. Electrolytic reduction of $(\text{Me}_2\text{Si})_6$ below -120° in 3:1 dimethyl ether-glyme gave a yellowish solution with an ESR spectrum generally similar in appearance to that of $(\text{Me}_2\text{Si})_5\cdot^-$, but with significant differences in g value, coupling constants, and line intensities (Table I). At low gain about 19 lines can be observed, with hyperfine splitting $a_{\text{H}} = 0.49$ G compared to 0.53 G for the pentasilane. The lower proton coupling constant is reasonable for $(\text{Me}_2\text{Si})_6\cdot^-$, which should have lower spin density at each silicon atom. At higher gain the spectrum shows satellites due to ^{13}C , with a hyperfine splitting constant of 14.60 G (Figure 3). Satellites due to ^{29}Si were detected as small shoulders in some samples but could never be resolved.

When electrolyte reduction is carried out at temperatures between -120 and -80° , the pentamer anion radical $(\text{Me}_2\text{Si})_5\cdot^-$ is produced as well as $(\text{Me}_2\text{Si})_6\cdot^-$, and the spectrum actually observed is a superposition of lines due to both species. The proportion of $(\text{Me}_2\text{Si})_5\cdot^-$ increases with increasing reduction temperature, and in samples reduced at temperatures above -80° only the pentamer anion radical is observed. However, when samples of $(\text{Me}_2\text{Si})_6\cdot^-$ are prepared electrolytically below -120° and then *allowed to warm* above this temperature, the ESR signal decays *without* formation of $(\text{Me}_2\text{Si})_5\cdot^-$.¹¹ The half-life of $(\text{Me}_2\text{Si})_6\cdot^-$ in tetrahydrofuran was estimated as 5.3 min at -120° and 2.8 min at -110° . The spectrum of $(\text{Me}_2\text{Si})_5\cdot^-$ also undergoes slow decay in solution above -110° , but the half-life for this species is at least an order of magnitude greater than for $(\text{Me}_2\text{Si})_6\cdot^-$.

Many attempts were made to reduce $(\text{Me}_2\text{Si})_7$ to an anion radical electrolytically. All of the solvent systems described in the Experimental Section were tried, at various temperatures from -80 to -130° , but always without success.

(11) The fact that $(\text{Me}_2\text{Si})_5\cdot^-$ is formed when $(\text{Me}_2\text{Si})_6$ is reduced at -120 to -60° , even though $(\text{Me}_2\text{Si})_6\cdot^-$ does not give $(\text{Me}_2\text{Si})_5\cdot^-$ when it decomposes in the same temperature range, suggests that $(\text{Me}_2\text{Si})_6\cdot^-$ decomposes with the formation of *neutral* $(\text{Me}_2\text{Si})_5$. If reduction were still underway $(\text{Me}_2\text{Si})_6$ would preferentially be reduced to its anion radical, $(\text{Me}_2\text{Si})_6\cdot^-$. If reduction were not being carried out, $(\text{Me}_2\text{Si})_5\cdot^-$ could be formed only by the following electron-transfer reaction, which might be slow: $(\text{Me}_2\text{Si})_6\cdot^- + (\text{Me}_2\text{Si})_5 \rightarrow (\text{Me}_2\text{Si})_6 + (\text{Me}_2\text{Si})_5\cdot^-$.

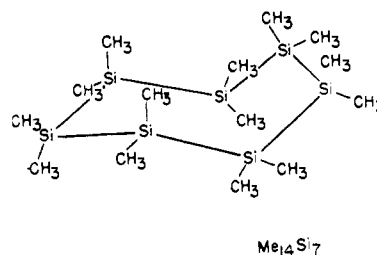
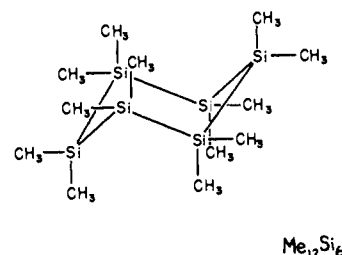
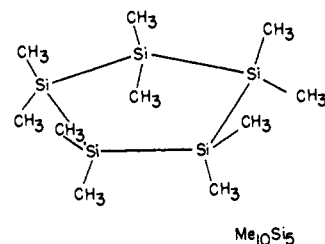


Figure 4. Assumed structures for $(\text{Me}_2\text{Si})_n$ compounds.

All three cyclic compounds underwent reduction to anion radicals upon treatment with alkali metals at low temperature, but the three compounds all produced the *same* anion radical, namely $(\text{Me}_2\text{Si})_5\cdot^-$ (Table I).¹² An earlier communication by Husk and West reported the chemical reduction of $(\text{Me}_2\text{Si})_6$ to an anion radical thought to be $(\text{Me}_2\text{Si})_6\cdot^-$.^{5,13} It is now evident that the spectra obtained were actually those of $(\text{Me}_2\text{Si})_5\cdot^-$.

Relative Stabilities and Chemical Bonding in the Anion Radicals. Rearrangements of polysilanes by chemically produced anion radicals is now known to take place easily,¹⁴ and we have shown that such reactions can be used to convert linear or cyclic polysilanes to an equilibrium mixture of cyclic isomers.¹ At room temperature the mixture consists mostly of $(\text{Me}_2\text{Si})_6$ with only small amounts of the pentamer and heptamer, and at low temperatures it is also probable that $(\text{Me}_2\text{Si})_6$ predominates at equilibrium, for gas chromatographic analysis of chemically reduced samples showed very little pentamer. Our results then indicate that $(\text{Me}_2\text{Si})_5$ is preferentially reduced, and that its anion radical must be more stable than the analogous six-ring radical. Independent experiments verify both conclusions.¹¹ Mixtures of $(\text{Me}_2\text{Si})_5$ and $(\text{Me}_2\text{Si})_6$ give, upon low-temperature *electrolytic* reduction, only the pentamer anion radical.

(12) Linear permethylpolysilanes with six or more silicon atoms also yield $(\text{Me}_2\text{Si})_5\cdot^-$ upon reduction. Experiments on linear silanes will be reported separately.

(13) R. West, *Pure Appl. Chem.*, **13**, 1 (1966).

(14) Unpublished work by K. Shiina and Y. Minoura, cited by M. Kumada in *Advan. Organometal. Chem.*, **6**, 65 (1968).

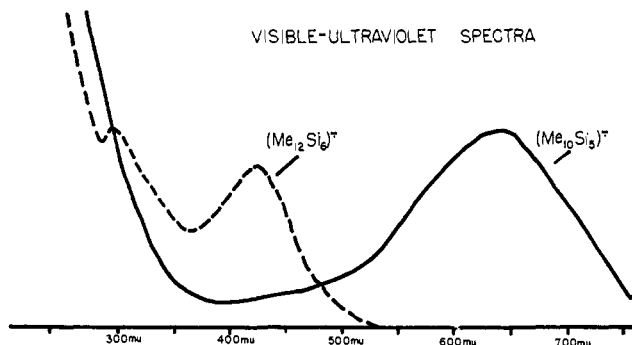


Figure 5. Electronic spectra of permethylcyclopolysilane anion radicals in tetrahydrofuran solution.

The electron affinity of $(\text{Me}_2\text{Si})_5$ is surprisingly high, for it can be preferentially reduced to its anion radical either chemically or electrolytically in the presence of a large excess of benzene. However, if benzene is present with $(\text{Me}_2\text{Si})_6$ only benzene anion radical is produced upon electrolytic reduction.¹⁵ The order of electron affinities is therefore $(\text{Me}_2\text{Si})_5 > \text{benzene} > (\text{Me}_2\text{Si})_6 > (\text{Me}_2\text{Si})_7$. The order of electron affinities for the cyclopolysilanes can be explained in terms of their molecular structures (Figure 4). $(\text{Me}_2\text{Si})_5$ is probably nearly planar so that good overlap of orbitals on adjacent silicon atoms can take place to give a molecular orbital of essentially π type. The deviation from planarity should increase in the six- and seven-membered rings, leading, we believe, to poorer overlap of silicon orbitals and wider spacing of molecular energy levels. The seven-membered ring in particular may be so nonplanar as to behave essentially as a linear polysilane.

The model suggested above is supported by the electronic spectra of the anion radicals $(\text{Me}_2\text{Si})_5\cdot^-$ and $(\text{Me}_2\text{Si})_6\cdot^-$, which show strong absorptions at 645 nm ($16,000 \text{ cm}^{-1}$) and 425 nm ($23,500 \text{ cm}^{-1}$), respectively (Figure 5). These bands are attributed to transitions from the first antibonding level to the next higher level. The fact that this energy is much lower for $(\text{Me}_2\text{Si})_5\cdot^-$ indicates that the excited state levels are closer in energy in this species.

The fact that all the protons in $(\text{Me}_2\text{Si})_6\cdot^-$ interact equally with the unpaired electron indicates that if the anion radical is indeed nonplanar as suggested here, very rapid equilibration must take place between conformers even at -126° , making the protons equivalent on a time-average basis. This is not unreasonable, however, for the barrier to rotation about Si-Si bonds is low in any case and would be lowered further by bond lengthening in the anion radical.^{16, 17}

Quite recently Gohlke has observed the electron-impact-induced anion radical of dodecamethylcyclohexasilane by negative ion mass spectroscopy.¹⁸ This provides evidence for the existence of the radical anion as a stable species in the gas phase. Gohlke similarly attributed the unusual degree of stability to the extensive

(15) The electrolytic production of benzene anion radical at low temperatures has previously been reported by W. M. Tolles and D. W. Moore, *J. Chem. Phys.*, **46**, 2102 (1967).

(16) Of course, the anion radicals need not have the same geometry as the neutral molecules and might well be more nearly planar.

(17) Rapid conformational equilibration in cyclic organosilicon compounds has been observed previously: see, for example, F. R. Jensen and C. H. Bushweller, *Tetrahedron Letters*, 2825 (1968).

(18) R. S. Gohlke, *J. Am. Chem. Soc.*, **90**, 2713 (1968).

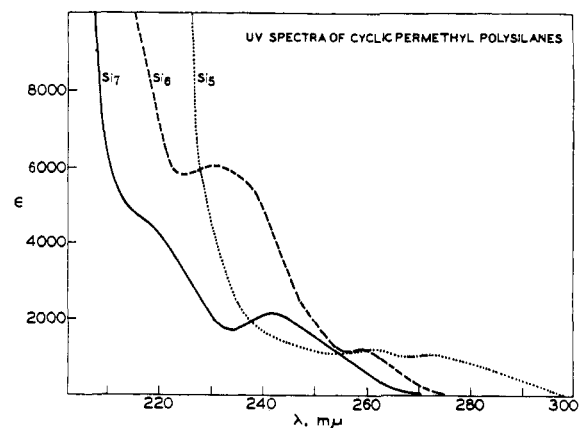


Figure 6. Ultraviolet spectra of permethylcyclopolysilanes in 2,2,4-trimethylpentane solution.

delocalization of the added electron in the 3d orbitals over all the silicon atoms.¹⁸

Ultraviolet Spectra. The cyclic permethylpolysilanes, like their linear analogs, show absorptions above 200 nm in the ultraviolet region. Data for the cyclic compounds are summarized in Table II, and the superimposed spectra are shown in Figure 6. For $(\text{Me}_2\text{Si})_6$, values agreeing well with ours already appear in the literature.^{19, 20}

Table II. Ultraviolet Data for the Permethylcyclopolysilanes

Compound	λ_{max} , nm	ϵ
$\text{Me}_{10}\text{Si}_5$	210	Shoulder
	261	1100
	272	970
$\text{Me}_{12}\text{Si}_6$	230.5	6000
	252.5	1200
$\text{Me}_{14}\text{Si}_7$	217	4500
	242.0	2100

Pitt, Jones, and Ramsey have carried out first-order Hückel molecular orbital calculations for the linear permethylpolysilanes and have shown that in these compounds it is quite likely that the transitions occur from a σ -type orbital of the silicon framework to a π -type molecular orbital over all the silicon atoms. Such a π orbital may be composed primarily of 3d orbitals from each silicon atom or may include some p-orbital contribution.^{21, 22}

The ultraviolet transitions in the cyclic compounds may arise from similar transitions, but there are some important differences. The long-wavelength band of the cyclics undergoes a hypsochromic shift with increasing catenation, just opposite to what is found for the linear polysilanes.³ It is likely this hypsochromic shift

(19) H. Gilman and W. Atwell, *J. Organometal. Chem.*, **4**, 176 (1965). Values reported: 232 nm, ϵ 5800, and 255 nm, ϵ 2000.

(20) P. P. Shorygin, V. A. Petukhov, O. M. Nefedov, S. P. Kolenikov, and V. I. Shiryayev, *Teor. i Eksperim. Khim., Akad. Nauk Ukr. SSR*, **2**, 190 (1966).

(21) C. Pitt, L. I. Jones, and B. J. Ramsey, *J. Am. Chem. Soc.*, **89**, 5471 (1967).

(22) On the other hand, Ramsey has recently treated the permethylpolysilanes according to a model developed for the analogous alkanes.²³ He finds that the cyclic pentamer and hexamer give good agreement but that $(\text{Me}_2\text{Si})_7$ is anomalous: B. G. Ramsey, "Electronic Transitions in Organometallic Compounds," in press.

(23) J. W. Raymond and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

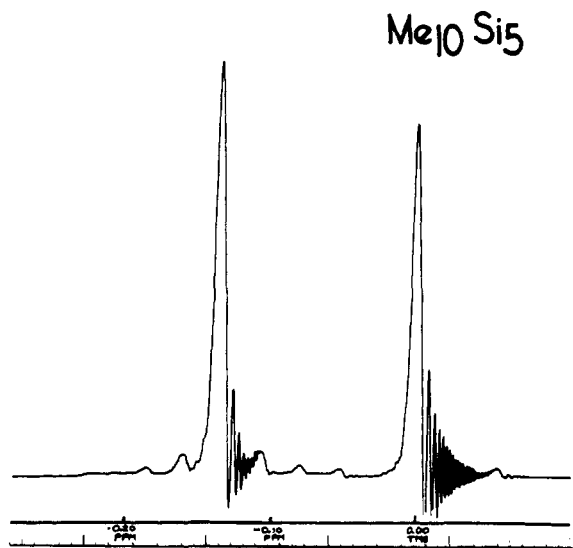


Figure 7. Proton nmr spectrum of decamethylcyclopentasilane, 10% (w/v), in carbon tetrachloride containing tetramethylsilane.

is due to the decreased planarity of the ring as the catenation is increased (Figure 4), as discussed above. This decreased planarity may reduce the effectiveness of d-orbital overlap in the excited state, making the antibonding molecular orbitals higher in energy. Assuming that the ground state is not affected, this would cause the long-wavelength transition in the more planar pentamer to be lowest and that of the heptamer to be greatest in energy.

The intensities of the electronic absorptions for the cyclic compounds, as measured by the extinction coefficients, are about an order of magnitude less than for linear polysilanes having the same number of silicon atoms. The reason why these electronic transitions are more fully allowed in the linear than in the cyclic species is not yet understood.

Proton Nmr Spectra. The proton magnetic resonance spectrum of each of the three cyclic compounds showed only a single resonance at room temperature at nearly the same chemical shift, about 0.13 ppm downfield from tetramethylsilane. The nmr spectra were also determined at -95° (in a 2:1 tetrahydrofuran-glyme mixture) in an attempt to freeze out conformers. However, even at this temperature, all three compounds gave only a singlet, somewhat broadened as a result of the increased solvent viscosity. Thus even at -95° all of the hydrogens in each compound have identical environments on a time-average basis.¹⁷ The spectrum for decamethylcyclopentasilane, which is typical of all the cyclic species, is shown in Figure 7.

Since silicon contains about 4.7% of ^{29}Si which has a nuclear spin of $1/2$, one may expect to see doublet side bands, and in these cyclic compounds it proved possible to measure not only $J(\text{Si}-\text{CH}_3)$ but also $J(\text{Si}-\text{Si}-\text{CH}_3)$, the coupling constant to the β -silicon atom. The proton nmr data for the cyclopolysilanes are summarized in Table III.

Infrared Spectra. The three cyclopermethylopolysilanes give almost identical infrared spectra in the region from 4000 to 600 cm^{-1} (Table IV). A spectrum is shown only for $(\text{Me}_2\text{Si})_6$, in Figure 8. The frequencies can generally be assigned to vibrations of $(\text{CH}_3)_2\text{Si}$ units. The only bands which change with ring size are those

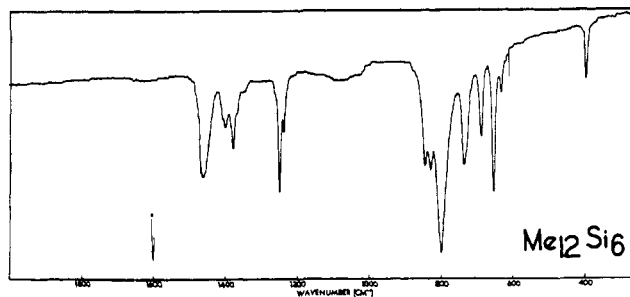


Figure 8. Infrared spectrum of dodecamethylcyclohexasilane, as mull in Nujol.

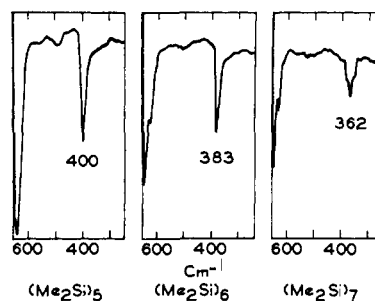


Figure 9. Far-infrared bands for permethylcyclopolysilanes in carbon tetrachloride solution.

near 400 cm^{-1} , shown for the three cyclic compounds in Figure 9. Absorptions near 400 cm^{-1} in hexaphenylsilane have previously been attributed to axial deformations of the silicon atoms.²⁴ Gilman and Schwebke

Table III. Proton Nmr Data for the Permethylcyclopolysilanes

Compound	Chemical shift		Coupling constants, cps		
	Ppm	Cps	$^{29}\text{Si}-\text{CH}_3$	$^{29}\text{Si}-\text{Si}-\text{CH}_3$	$^{13}\text{C}-\text{H}$
$\text{Me}_{10}\text{Si}_5$	-0.135	-8.1	6.3	3.2	121.0
$\text{Me}_{12}\text{Si}_6$	-0.132	-7.9	6.4	3.4	120.0
$\text{Me}_{14}\text{Si}_7$	-0.125	-7.5	6.3	3.2	120

Table IV. Infrared Spectra (cm^{-1}) of the Permethylcyclopolysilanes

$\text{Me}_{10}\text{Si}_5$	$\text{Me}_{12}\text{Si}_6$	$\text{Me}_{14}\text{Si}_7$	Assignment
2950 (s)	2950 (s)	2950 (s)	C-H antisym stretch
2890 (m)	2885 (m)	2890 (m)	C-H sym stretch
2795 (w)	2790 (w)	2790 (w)	
1400 (m)	1400 (m)	1400 (m)	C-H deformation
1250 (s)	1250 (s)	1250 (s)	Si-Me deformation
	1240 (m)	1240 (m)	Si-Me deformation
845 (m)	845 (m)	845 (m)	Si-Me rock
830 (m)	830 (m)	830 (m)	Si-Me rock
800 (vs)	800 (vs)	795 (vs)	Si-Me rock
735 (s)	735 (m)	735 (m)	
690 (m)	690 (m)	690 (m)	Si-Me
655 (s)	655 (s)	655 (s)	Si-Me
	630 (w)	630 (w)	
400 (w)	383 (m)	362 (w)	Si-Si stretch

have also found that the three known perphenylcyclopolysilanes, octaphenylcyclotetrasilane, decaphenylcyclopentasilane, and dodecaphenylcyclohexasilane, have

(24) L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta*, **18**, 21 (1962).

absorptions, often multiplets, centered in this area.²⁵ Thus it is not unlikely that absorption in this region represents a type of Si-Si stretching vibration.

In the permethylcyclopolysilanes, it is seen that this band shifts to lower frequencies as ring size increases. This provides a very rapid and convenient way to identify and distinguish the three cyclic compounds. A study of linear permethylpolysilanes showed that only very weak absorptions occurred in this region. No regular trends were observed.

Experimental Section

The permethylcyclopolysilanes were synthesized as described in ref 1 and were purified by preparative gas chromatography. Samples of the air-sensitive compound $(\text{Me}_2\text{Si})_6$ were freshly collected for each experiment. The purity and identity of the compounds were confirmed by mass spectrometric and infrared spectroscopic analysis. Solvents for esr work were distilled from sodium anthracene anion radical and stored in the presence of the anion radical on the vacuum line.

Formation of Anion Radicals. All samples were made up on a vacuum line. Solvents were distilled into sample cells containing the cyclic polysilane and then degassed several times. Electrolytic reductions were carried out in cells constructed of 4-mm Pyrex tubing with platinum wire electrodes. A glass wool frit was used to separate the electrode compartments. O-Ring flanges were used for connection of the cell to the vacuum line and for the separation of the electrode cell area. A Viton needle valve allowed removal of the cell from the vacuum line for taking spectra. This cell will be described more completely in a separate communication.²⁶ Usually a 3:1 (v:v) mixture of dimethyl ether-1,2-dimethoxyethane (glyme) was used as a solvent, and tetra-*n*-butylammonium perchlorate, 0.05 *M*, was the supporting electrolyte. Electrolysis of each sample was first attempted at 0.2 μA and 3.0 V. The current was increased slowly until an esr signal was observed. Usually a current of 0.4 μA and 6.0 V was satisfactory.

Chemical reduction was carried out in cells consisting of 4-mm quartz tubing, joined to an O-ring vacuum fitting and bearing a side arm in which sodium-potassium alloy was placed. After the sample and solvent were added, the sodium-potassium alloy was distilled as a mirror into the midportion of the quartz tube, which was then sealed off under vacuum. The solution was allowed to contact the alkali metal either in a toluene slush bath (-95°) or in a methylcyclohexane slush (-126°).

Solvent systems studied in both electrolytic and chemical reductions included tetrahydrofuran, tetrahydrofuran-glyme (2:1), methyltetrahydrofuran-glyme (2:1), dimethyl ether, and dimethyl ether-glyme (10:1 and 3:1). Dimethyl ether-glyme (3:1) appeared to be the best solvent for low-temperature work (-120 to -140°) while methyltetrahydrofuran-glyme (2:1) gave the best results in the higher temperature range (-65 to -100°). Data in the table are for 3:1 dimethyl ether-glyme, but the *g* values and splitting constants were essentially unchanged in the other solvents and solvent mixtures.

Esr Spectra. All of the electron spin resonance spectra were determined on a Varian V-4502-13 spectrometer utilizing 100-kc modulation and a Varian V-4557 variable-temperature attachment.

For *g* value calculations, the spectrum of peroxyamine disulfonate anion in water recorded simultaneously using a dual cavity was superimposed for calibration. *g* values are believed accurate to ± 0.00003 G. All coupling constants were determined on an X-Y recorder which was calibrated with tetracene radical cation using values due to Hyde as reported by Carter and Vincow.²⁷ Line-sharpened spectra were obtained by including third derivative character in the first-derivative signal according to a method reported by Glarum.²⁸ This technique significantly decreased the amount of overlapping in the recorded spectra and so allowed accurate determination of the positions of center lines in the satellite spectra. Hyperfine splitting constants are estimated to be accurate to ± 0.01 G for α_{H} , and to ± 0.05 G for $\alpha^{13\text{C}}$ and $\alpha^{29\text{Si}}$.

For $(\text{Me}_2\text{Si})_6^{\cdot-}$, the *g* value and hyperfine splitting constants were obtained in 3:1 dimethyl ether-glyme, in 2:1 tetrahydrofuran-glyme, and in 2:1 methyltetrahydrofuran-glyme. No measurable solvent dependence of the hyperfine splitting constants or *g* value was observed. In methyltetrahydrofuran-glyme, the best resolution was obtained at -75° , but no temperature dependence of *g* value or hyperfine splitting constants was observable over the temperature range -75 to -130° . $(\text{Me}_2\text{Si})_6^{\cdot-}$ could be studied only below about -120° , and was observed in dimethyl ether and dimethyl ether-glyme.

Electronic Spectra. Room-temperature ultraviolet spectra of the neutral compounds were determined using a Cary Model 14 recording spectrometer, scanning the region from 360 to 190 nm. Quartz cells of widths from 1 to 0.05 cm were used with solutions of various known concentrations. Data in Table II are for solutions in Spectrograde 2,2,4-trimethylpentane, but experiments showed that the wavelength maxima are unchanged in dichloromethane, acetonitrile, and methanol. For the low-temperature spectra of the anion radicals, the Cary 14 spectrometer was modified so that a quartz dewar insert attached to a Varian variable-temperature accessory, which was used for temperature control, could be inserted into the sample beam. The solutions, in tetrahydrofuran solvent, were studied in the quartz esr tubes in which they were prepared.

Proton Nmr Spectra. The proton nuclear magnetic resonance spectra were determined on a Varian A-60 or A-60-A, 60-Mc spectrometer using tetramethylsilane as an internal standard. The methyl proton region for each sample was run at 50 cps sweep width. Side bands due to ^{13}C -H were determined at 100- and 250-cps sweep width. Sweep time was 250 sec in all cases. Spectra taken for the measurement of *J* values were calibrated by employing an external frequency modulator to produce side bands of known splittings. All samples run at room temperature were run at 10% (w/v) concentration in carbon tetrachloride. Low-temperature samples were run at 10% (w/v) in a solvent mixture of tetrahydrofuran and 1,2-dimethoxyethane (2:1). The temperatures were calibrated by measuring the splittings between the centers of the doublet and quartet of a methanol sample. The splittings are directly related to the temperature of the sample and have been previously determined.²⁹

Infrared Spectra. Infrared spectra were examined in the region from 4000 to 250 cm^{-1} using both a Beckman IR-10 and a Perkin-Elmer Model 457 spectrometer. Cesium iodide cells were used. Both Nujol mulls and carbon tetrachloride solutions were used to confirm the peak positions in all regions.

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