and toluene (1.7 mL, 16 mmol; 170 μL, 1.6 mmol; 16 μL, 0.15 mmol) was photolyzed in the same manner as described, and the isomer ratios of cresols were analyzed in the same manner as described.

(b) Under Degassed Conditions. An acetonitrile solution (16 mL) of **1** (46.8 mg, 0.152 mmol) and toluene (1.6 μL, 0.015 mmol) or nitrobenzene (1.6 mL, 16 mmol, or 16 μL, 0.16 mmol) in a Pyrex tube was degassed and sealed. Each solution was photolyzed in the same manner as described. The isomer ratios of cresols and nitrophenols were analyzed in the same manner as described.

Acknowledgment. We wish to thank Professor Cheves Walling for many helpful discussions and comments throughout this study. We thank Professor Manfred K. Eberhardt for helpful comments on our first manuscript.

The Permethylcyclosilanes $(Me_2Si)_5$ through $(Me_2Si)_{35}$[1]

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Abstract: The cyclic permethylpolysilanes $(Me_2Si)_n$, where n = 5–35, are all formed when dimethyldichlorosilane (Me_2SiCl_2) is added slowly to sodium–potassium (Na/K) alloy in tetrahydrofuran (THF). NMR, UV, and vibrational spectra are reported for compounds n = 5–19. The ^{13}C NMR and ^1H NMR spectra are explained in terms of methyl–methyl group interactions. Raman and IR spectra are assigned and partially explained on the basis of a standing wave model.

Until recently the synthesis of cyclopolysilanes was limited to the four-, five-, six-, and seven-membered[2] ring compounds. The medium-ring cyclosilanes $(Me_2Si)_8$ and $(Me_2Si)_9$ were reported in 1978.[3] Recently[4] we communicated the synthesis of the larger cyclics $(Me_2Si)_n$, where n = 10–35. These rings apparently form the largest homologous series of cyclic compounds now known, except for the cycloalkanes. Apart from their synthetic interest, these cyclic compounds are of importance because of the unique properties[5] of the five- and six-membered rings, which indicate unusually facile electron delocalization in these molecules. This in turn has generated interest in the study of the permethylated polysilanes in general, as model compounds for the study of eletronic effects in elemental silicon.[10] In this paper we describe the synthesis of the large $(Me_2Si)_n$ rings and present the fundamental spectroscopic properties of all the rings through $(Me_2Si)_{19}$.[11]

Table I. Yield and Mass Spectral Data for Permethylcyclosilanes, $(Me_2Si)_n$

	yield, wt %				
n	a	b	mass calcd	mass obsd	dev, ppm
5	12[a]	17[b]			
6	54	52			
7	3.0	2.6			
8	1.8	1.3	464.1910	464.1908	−0.4
9	1.0	0.76	522.2149	522.2160	2.1
10	0.23	0.15	580.2388	580.2368	−3.4
11	0.26	0.18	638.2626	638.2628	0.3
12	0.23	0.16	696.2865	696.2879	2.0
13	0.21	0.19	754.3104	754.3080	−3.2
14	0.21	0.21	812.3343	812.3332	−1.4
15	0.21	0.22	870.3581	870.3572	−1.1
16	0.18	0.19	928.3820	928.3798	−2.4
17	0.13	0.14	986.4059	986.4077	1.7
18	0.09	0.09	1044.4298	1044.4324	2.5
19	0.05	0.05	1102.4537	1102.4571	3.2
24			1392.5730	1392.5767	2.7

[a] Yields using 10 mol of Me_2SiCl_2. [b] Yields using 2 mol of Me_2SiCl_2.

Experimental Section

Reagent purification and some experimental techniques including safety precautions have been described elsewhere[14,15] and will not be reported here.

Synthesis and Separation of Cyclopolysilanes. Dry THF (1200 mL) and Na/K alloy (185 mL, 4.7 mol) were stirred at reflux in a dried 5-L flask equipped with a high-capacity condenser while Me_2SiCl_2 (244 mL, 2.0 mol) was added dropwise over a period of 8 h. The mixture was then cooled slightly and 1200 mL of hexane was added, after which the excess alloy was gradually destroyed by the *very cautious*, dropwise addition of approximately 100 mL of water. Another 1000 mL of water was then added to dissolve salts. The organic phase was separated, filtered to remove polymer, and washed with small amounts of additional water to

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(1) Paper number 20 in the series "Cyclic Polysilanes". For previous paper in this series see ref 18.

(2) (a) West, R.; Carberry, E. *Science (Washington, D.C.)* **1975**, *189*, 179–186. (b) Hengge, E. In "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements", Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; Chapter 9.

(3) Matsumura, K.; Brough, L. F.; West, R. *J. Chem. Soc., Chem. Commun.* **1978**, 1092–1093.

(4) Brough, L. F.; Matsumura, K.; West, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 955–956. A figure in this communication shows a HPLC trace for a mixture containing all of the $(Me_2Si)_n$ oligomers from n = 5 to 35.

(5) For example they form delocalized anion[6] and cation[7] radicals, yield charge-transfer complexes with π acceptors,[8] and form plastic crystals.[9]

(6) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446–5451.

(7) Bock, H.; Kaim, W.; Kira, M.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 7667–7670.

(8) Traven, V. F.; West, R. *J. Am. Chem. Soc.* **1973**, *95*, 6824–6826. Sakurai, H.; Kira, M.; Uchida, T. *Ibid.* **1973**, *95*, 6826–6827.

(9) Larsen, D. W.; Soltz, B. A.; Stary, F. E.; West, R. *J. Chem. Soc., Chem. Commun.* **1978**, 1093–1094.

(10) Snyder, L. C. "A Quantum Chemist's View of Silicon Chemistry Related to Silicon Surface Reconstruction", paper presented at International Symposium on Atomic, Molecular and Solid State Theory, Flagler Beach, FL, Mar 1978.

(11) UV,[6] IR,[6] Raman,[12] ^{13}C NMR,[13] and ^1H NMR[6] spectra have previously been reported in part for the five-, six- and seven-membered rings.

(12) Hengge, E.; Schuster, H. G.; Peter, W. *J. Organomet. Chem.* **1980**, *186*, C45–C48.

(13) Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1981**, *204*, 295–305.

(14) West, R.; Brough, L. F.; Wojnowski, W. *Inorg. Synth.* **1979**, *19*, 265–268.

(15) Brough, L. F.; Wojnowski, W.; West, R., unpublished work.

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ensure neutrality. Most of the solvent was then removed by distillation through a short Vigreux column. Recrystallization from 95% EtOH/THF (7:1 v/v) followed by sublimation (80 °C (0.05 torr))[16] of the crystalline precipitate removed most of the major product, $(Me_2Si)_6$, from the product mixture. The small amount of higher molecular weight material which did not sublime was combined with the solid obtained after distilling solvent from the mother liquor. Most of the $(Me_2Si)_5$ was then removed by sublimation at 40 °C (0.05 torr).

This experiment was also carried out on a larger scale by using 6 L of THF, 920 mL (24.0 mol) of Na/K alloy, and 1220 mL (10.0 mol) of Me_2SiCl_2. A similar workup and separation procedure was employed.

The residual solid obtained after sublimation of $(Me_2Si)_5$ was then fractionality recrystallized from an excess of boiling 95% EtOH/THF (4:1 v/v). Several fractions were produced following the stepwise removal of solvent, and each was examined by using a Whatman M9 10/50 ODS-2 column. MeOH/THF solvent systems of varying composition were employed in this and all further HPLC work. The most suitable fractions, now highly enriched in medium and large rings, were divided again by using a Waters Prep LC/System 500 HPLC with a Waters PrepPAK-500/C18 column. Following this, the fractions were examined on the Whatman column, and appropriate units were combined so that the resulting product was composed almost entirely of a group of five or six cyclics. Final separation was then carried out on the Whatman column. Yields (Table I) were determined by calibrated gas chromatography for $n = 5$–7 and are accurate to ±5%. For $n = 8$–19 the yields were estimated from HPLC peak areas by using UV detection at 254 nm and correcting for molecular weight and molar absorbance for each compound. Accuracy is ±20%.

The oligomers with $n = 7$–19 were all white, crystalline solids which were stable upon exposure to light and air. However, $(Me_2Si)_{24}$ decomposed to insoluble polymer after several weeks, perhaps via a photolytic pathway (unlike the lower oligomers this compound shows absorption tailing into the near UV). High-resolution, parent peak matches were obtained by mass spectrometry for $n = 8$–19 and also for $n = 24$ with deviations of less than 3.5 ppm (Table I). The cyclosilane structure is assigned to the higher fractions through $n = 35$ on the basis of the HPLC results.[4]

Spectroscopy. ^1H NMR spectra were determined in CCl_4 on a JEOL MH-100 spectrometer. ^{13}C NMR spectra were obtained with a JEOL JNM-FX 60 Fourier transform NMR spectrometer operating at 15.04 MHz and using $CDCl_3$ as solvent. An internal deuterium ($CDCl_3$) lock was employed with broad-band proton decoupling. Chemical shifts (ppm) were measured relative to internal Me_4Si for both ^1H NMR and ^{13}C NMR, positive shifts being downfield. Concentrations varied between 4 and 8%. Spectral reproducibility was typically 0.005 and 0.06 ppm for the ^1H NMR and ^{13}C NMR, respectively.

UV spectra were determined in isooctane with a Cary Model 118 spectrophotometer at a scan rate of 0.5 nm/s. The assignment of peak positions was assisted by taking the first derivative of the overlapping peaks and comparing this with related computer generated spectra.[17] This allowed bands to be accurately resolved which would otherwise appear only as slight shoulders on more intense transitions.

Infrared spectra were examined in the region from 4000 to 275 cm^{-1} by using a Perkin-Elmer 457 spectrometer. Both CsI and KBr cells were used and both CS_2 and isooctane solutions were employed. Nujol mulls were also run for some compounds. Raman spectra were determined with a Spex Ramalog-4 laser spectrometer in the range from 100–3500 cm^{-1} on solid samples contained in glass capillaries.

Low-resolution mass spectral data and parent peak matches were obtained at 70 eV by direct insertion with a source temperature of 200 °C by using a Kratos MS 902C mass spectrometer. Tris(pentadecafluoroheptyl)-s-triazine or tris(perfluorononyl)-s-triazine were used as standards for the higher molecular weight rings, $n > 14$.

Results and Discussion

Yields. The standard[15] synthesis of methylpolysilane rings from Me_2SiCl_2 and Na/K alloy in THF produces an equilibrium mixture[18] of aboout 90% $(Me_2Si)_6$, 9% $(Me_2Si)_5$, and 1% $(Me_2Si)_7$. Most of the $(Me_2Si)_6$ is produced from depolymerization of the polymer which is the initial major product.[15,19] However, if the Me_2SiCl_2 is added to Na/K alloy in THF quite slowly, over 6–10 h, much less polymer is formed. Instead of yielding the equilibrium mixture of products which might be expected, the slow-addition reaction produces a mixture whose composition is at least partly kinetically controlled. The resulting solution contains large as well as medium and small cyclosilane rings. Although the addition time was not optimized for the yields of large rings, much more rapid addition results in polymer formation, while slower addition leads to destruction of the large ring oligomers.

Table II. ^{13}C NMR and ^1H NMR Chemical Shifts for Permethylcyclosilanes, $(Me_2Si)_n$

n	^1H shift, ppm	^{13}C shift, ppm
5	0.135	−6.23
6	0.132	−5.94
7	0.128	−5.23
8	0.144	−4.46
9	0.163	−3.80
10	0.188	−3.15
11	0.186	−3.12
12	0.190	−3.15
13	0.192	−3.08
14	0.200	−3.02
15	0.197	−3.12
16	0.196	−3.26
17	0.196	−3.31
18	0.197	−3.38
19	0.197	−3.41

Weight percent yields for two reactions, which employed 2 and 10 mol of Me_2SiCl_2, are given in Table I. The relative amounts of each of the cyclics decline markedly from $(Me_2Si)_6$ to $(Me_2Si)_{10}$ but then level off. From $(Me_2Si)_{10}$ to $(Me_2Si)_{16}$ the yields (on a weight or Me_2Si equivalent basis) are approximately constant, while for still larger rings the yields again decline.

Any attempt to explain the relative amounts of these compounds must be tentative for several reasons. The mechanism for ring formation in the cyclosilanes is not known, and the larger rings are very minor products in this synthesis compared to $(Me_2Si)_6$ and $(Me_2Si)_5$. The reaction as a whole may be complex and is probably only partially kinetically controlled.[15]

However, similar patterns of yields and of rates of ring closure, with a minimum around $n = 10$, are well-known for cyclization reactions of carbon compounds.[20,21] These results are generally explained as due to a combination of two effects: (1) decreasing probability of ring closure as the chain length increases (an entropy effect) and (2) differences in the intrinsic stability of the rings (an enthalpy effect). The stabilities of the cycloalkanes decline sharply from $n = 6$ to 9 as a result of destabilizing transannular H–H as well as dihedral interactions (nonclassical strain). Ring stability passes through a minimum at $n = 10$ and then increases as the rings become larger and begin to assume linear character.[22]

Related effects may govern the yields found in the Me_2SiCl_2 condensation. Examination of models shows that transannular and dihedral methyl–methyl interactions must be severe in the medium-sized $(Me_2Si)_n$ rings. The decline in yields from $n = 6$ to 10 may therefore result from a combination of entropy and ring strain effects. The sharp change at $n = 10$ suggests that nonclassical strain is abruptly partially relieved at the 11-membered ring. The plateau in yields from $n = 10$ to 16 may result from

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(16) Higher temperatures may destroy some cyclic products.

(17) Giese, A. T.; French, C. S. *Appl. Spectrosc.* **1955**, *9*, 78–96. Cohill, J. E. *Am. Lab. (Fairfield, Conn.)* **1979**, *11*, 79.

(18) Brough, L. F.; West, R. *J. Organomet. Chem.* **1980**, *194*, 139–145.

(19) Carberry, E.; West, R. *J. Am. Chem. Soc.* **1969**, *91*, 5440–5446.

(20) For general discussions of carbocyclic ring forming reactions and ring stabilities see: (a) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; pp 188–203. (b) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; Chapter 4. (c) Sicher, J. "Progress in Stereochemistry"; de la Mare, P. B. D., Klyne, W., Eds.; Butterworths: Washington, D.C., 1962; Chapter 6. (d) Prelog, V. "Perspectives in Organic Chemistry"; Todd, A. Ed.; Interscience: New York, **1956**; pp 96–133.

(21) A careful recent paper has reported rates of cyclization of ω-bromoalkanoate ions to lactones, which show a minimum at $n = 8$ and 9. Galli, C.; Illuminati, G.; Mandolini, L.; Tamborra, P. *J. Am. Chem. Soc.* **1977**, *99*, 2591–2597.

(22) It is important to note that the ease of ring closure is a matter of kinetics and therefore depends on the difference in free energy between the reactant and transition states rather than being simply dependent on the stability of the product rings. Nevertheless, it does not seem unreasonable to expect ease of ring closure to be roughly proportional to ring stability for the series. See ref 20a for a more complete discussion.

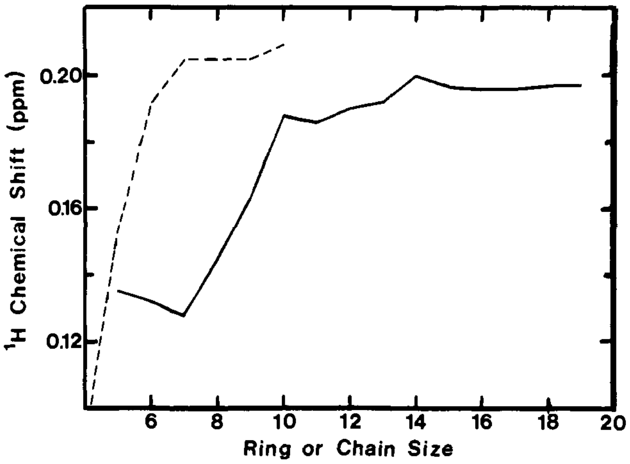

Figure 1. ^1H NMR chemical shifts for the permethylcyclosilanes (solid line) and for the most internal methyl groups in linear permethylpolysilanes (dashed line).

a gradual further decrease in nonclassical strain energy, compensating the gradual increase in entropy requirement for ring closure. Beyond n = 16 the entropy effect apparently predominates, resulting in a continuous slow decline in the yield.

^1H NMR and ^{13}C NMR. All of the compounds show only sharp singlets for both the proton and ^{13}C resonances, indicating that the various proton and carbon environments are averaged by rapid interconversions between conformers. This averaging, observed earlier for $(Me_2Si)_6$ and $(Me_2Si)_7$,[6] is consistent with the known low rotational barriers in disilanes.

Proton chemical shifts for the permethylated cyclopolysilanes are listed in Table II and presented graphically in Figure 1. The dashed line in Figure 1 connects the points due to the chemical shifts of the protons on the most internal methyl groups in the analogous permethylated linear polysilanes.[23] For the linear compounds a downfield shift is observed as chain length increases from 3 to 7, with little change thereafter. This downfield shift is believed to be due mainly to interaction between hydrogens of methyl groups on silicons in a 1,3 relationship on the chain (1,6 H–H interaction). Conformations which bring such methyl groups close to one another are likely for all linear compounds larger than the trisilane. Weaker interactions between methyl hydrogens of 1,4 and 1,5 silicon atoms may also add to the downfield shift.[24]

For the cyclosilanes the proton chemical shift values change little from $n = 5$ to 7 and then increase rapidly from $n = 7$ to 10 and level out thereafter. In the five- to seven-membered rings the cyclic structures may reduce the probability of 1,6 H–H interaction.[25] Models indicate that as ring size increases to $n = 10$ both transannular H–H repulsions and dihedral methyl-methyl interactions become more important, consistent with the observed downfield shift. Beyond $n = 10$ ring-specific nonclassical strain interactions probably decrease. The compounds become more like linear polysilanes, and the chemical shifts may be controlled by the same sorts of 1,6 (1,7 and 1,8) H–H interactions which are believed present in the linear compounds.

The ^{13}C NMR data for cyclic polysilanes is shown as the solid line in Figure 2. Although there are slight differences, the general trends follow those found for the ^1H NMR chemical shifts. It is interesting that the ^1H and ^{13}C chemical shifts level off at $n = 11$, the same ring size where the yields of cyclopolysilanes also stabilize (Table II). Each of these results may be due to a sharp change in nonclassical strain energy at $n = 11$.

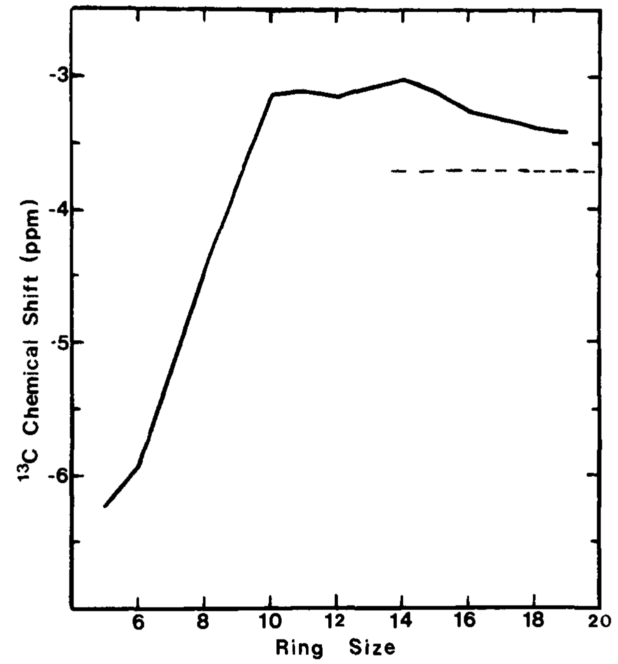

Figure 2. ^{13}C NMR chemical shifts for the permethylcyclosilanes as a function of ring size. The dashed line indicates the predicted chemical shift for the most internal methyl groups in a long chain permethylated polysilane.

Table III. UV Maxima for Permethylcyclosilanes, $(Me_2Si)_n$

n	λ,[a] nm	ϵ	n	λ,[a] nm	ϵ
5^b	275 (sh)	700	13	290 (sh)	7 200
	264 (sh)	800		260	34 200
	220	22 600		242	36 000
	210	24 000		224 (sh)	33 000
6	258 (sh)	1 100		210 (sh)	50 000
	240	5 400	14	294 (sh)	7 000
	232	5 900		277	14 600
	197	43 800		260	43 000
7^b	249	3 000		242	37 800
	239	4 600		215 (sh)	42 000
	220 (sh)	9 200	15	285 (sh)	9 200
	192	62 000		266	48 100
8	246 (sh)	7 600		258	49 000
	235	12 900		234	40 800
	212 (sh)	18 800		215 (sh)	52 400
	193 (sh)	91 500	16	285 (sh)	11 000
9	242	13 750		265	58 800
	230	17 700		248 (sh)	44 900
	208 (sh)	29 000		227 (sh)	46 000
10	285 (sh)	3 400	17	284 (sh)	17 400
	267 (sh)	8 200		264	66 900
	255	29 800		238	43 700
	240	17 000		216	56 000
	222	17 300	18	285 (sh)	23 000
	205	32 600		268	73 500
11	290 (sh)	1 700		249 (sh)	47 900
	268 (sh)	12 000		230 (sh)	46 000
	252	25 000		218 (sh)	57 200
	239	25 400	19	290 (sh)	19 350
	220 (sh)	25 000		268	85 200
	212 (sh)	32 100		245 (sh)	48 900
12	288 (sh)	1 200		220 (sh)	59 800
	266 (sh)	16 400	24	294 (sh)	
	248	33 000		277	
	231	29 200		254 (sh)	
	211 (sh)	39 800		244 (sh)	
				244 (sh)	

[a] In isooctane. [b] Previously reported ϵ values[6] are incorrect.

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(23) West, R.; Kramer, F. A.; Carberry, E.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1967**, *8*, 79–85.

(24) Through-bond electronic effects will be short range and should result in an upfield shift as the series is ascended.[13]

(25) A crystal structure[26] has shown that $(Me_2Si)_6$ exists in a chair conformation with little methyl-methyl interaction. The structure of $Me_9Si_5Me_2SiFe(CO)_2(C_5H_5)$, which contains a sterically isolated Si_5 ring, indicates that the ring is puckered with an average torsional angle of 27°, equivalent to that found in cyclopentane.[27]

(26) Carrell, H. L.; Donohue, J. *Acta. Crystallogr., Sect. B* **1972**, *B28*, 1566–1571.

(27) Drahnak, T.; West, R.; Calabrese, J. *J. Organomet. Chem.* **1980**, *198*, 55–69.

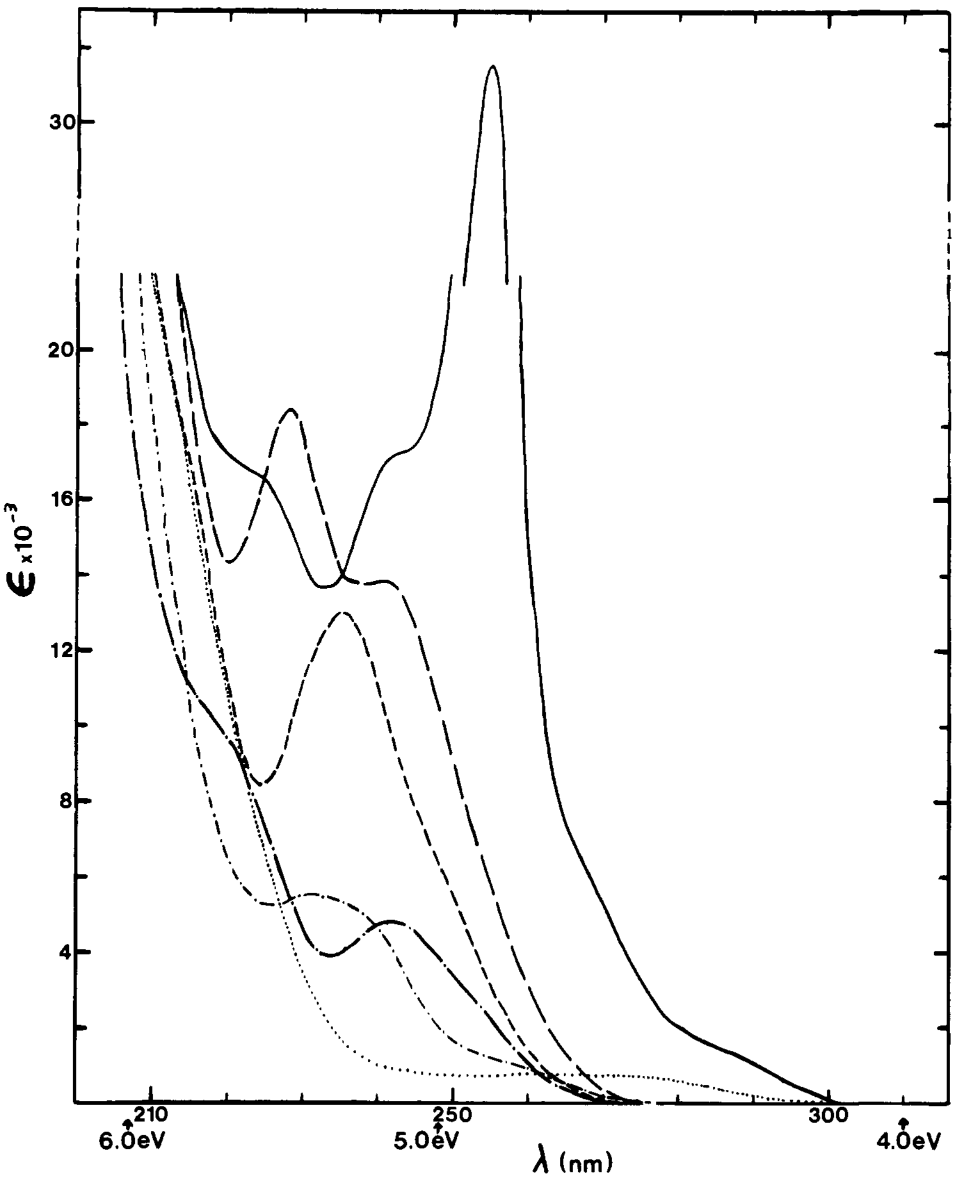

Figure 3. Ultraviolet absorption spectra of permethylcyclosilanes $(Me_2Si)_n$, n = 5–10: ···, 5; -·-, 6; -··-, 7; ---, 8; --, 9; —, 10.

Recent work has demonstrated that the ^{13}C chemical shifts of the linear permethylated polysilanes may be correlated in a manner analogous to the linear alkanes.[13] This leads to a formula[28] which may be used to predict the ^{13}C chemical shift of the most internal methyl carbons in a long chain polysilane. A value of approximately −3.7 ppm (shown as the dashed line in Figure 2) is obtained for a chain of infinite length. The experimental ^{13}C chemical shifts for the cyclosilanes approach this limit in the larger rings, as these rings assume a more linear character.

UV Spectra. Our earlier studies of the spectra of methylcyclosilanes with n = 5–7 showed that the low-energy transitions shift to higher energy with increasing ring size.[6] Results for the medium and large ring cyclosilanes are given in Table III and Figures 3–5. The energy of the longest wavelength transition reaches a maximum at n = 9. A discontinuous change takes place at n = 10; this compound shows a very intense absorption at 255 nm (ϵ = 31 600) and several shoulders at still longer wavelength (Figure 4), the longest at ~285 nm. As ring size increases from n = 11 to 19, further changes in the spectrum are gradual. The most intense band in each spectrum, which appears near 250 nm for n = 11, becomes still stronger and slowly shifts to lower energy reaching 269 nm (ϵ = 85 500) for n = 19 and 277 nm for n = 24. A similar intensification and bathochromic shift with increasing number of Si atoms have been observed for linear polysilanes.[29]

Although the nature of electronic transitions in polysilanes is not yet well understood,[30] the observed trends are understandable if overlap of orbitals contributing to the first excited state is dependent on geometry. The unusually low excited-state energy for n = 5 may be associated with the near planar conformation which this molecule probably adopts.[27] Molecules with n = 6–9 necessarily exist in conformations with larger Si–Si torsional angles, which could result in decreased orbital overlap, leading to increased energy of the first excited state and perhaps also to a reordering of energies of closely lying excited states.

The sharp change in excited state energy at n = 10 corresponds to discontinuities in the yields and NMR chemical shifts found at this point in the cyclosilane series, all of which appear to reflect conformational changes near this ring size. The large-ring cyclopolysilanes behave much like linear polysilanes, which also show monotonic bathochromic shifts and intensification as n increases.[29]

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(28) $\delta_c = B + \sum_i p_i A_i$, where δ_c is the predicted chemical shift, B = 1.9 ppm, p is the number of Me_2Si groups α, β, γ, or δ to the methyl carbon in question, and A_i is a chemical shift parameter where A_α = −4.4 ppm, A_β = 1.2 ppm, A_γ = 0.3 ppm, and A_δ = 0.1 ppm. See ref 13.

(29) Robin, M. D. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974; Vol. 1, pp 305–308.

(30) For discussions see Pitt, C. G. In "Homoatomic Rings, Chains and Macromolecules of Main-Group Elements"; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; Chapter 8. Also ref 29.

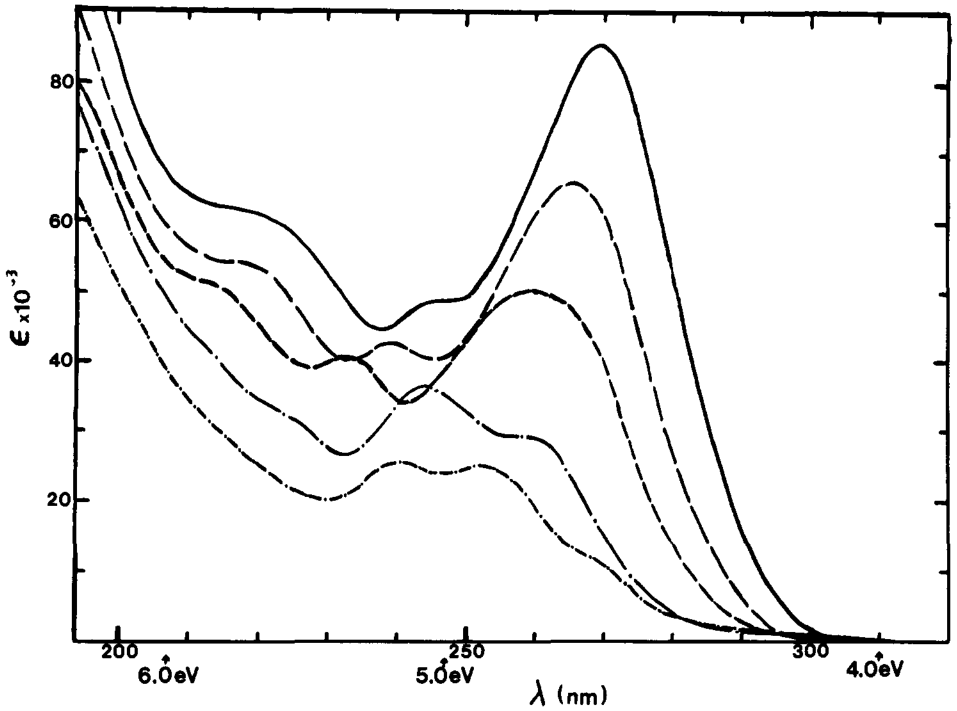

Figure 4. Ultraviolet absorption spectra of permethylcyclosilanes $(Me_2Si)_n$, where n = odd numbers from 11–19: ···, 11; –·–, 13; ---, 15; — — —, 17; —, 19.

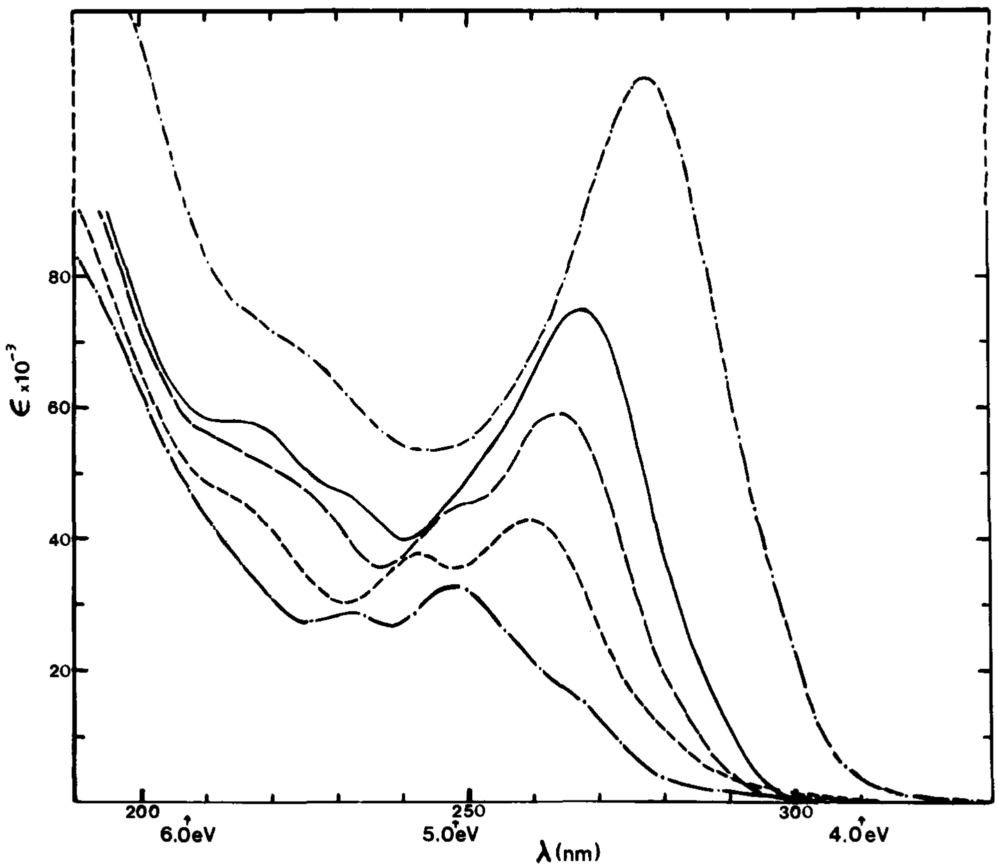

Figure 5. Ultraviolet absorption spectra for permethylcyclosilane $(Me_2Si)_n$, where n = even numbers from 12 to 18 and 24: –·–, 12; --, 14; — — —, 16; —, 18; ---·, 24.

This may reflect the fact that the large rings have conformations available which are similar to those of linear compounds. Similar behavior is also found in the vacuum UV spectra of the cycloalkanes.[31,32]

Vibrational Spectra. The infrared and Raman spectra for $(Me_2Si)_9$, taken as a typical example of the permethylcyclosilanes, are shown in Figure 6 and listed in Table IV. Absorptions occurring above 765 cm^{-1} were assigned by comparing the spectra

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(31) Raymonda, J. W.; Simpson, W. T. *J. Chem. Phys.* **1967**, *47* 430.

(32) Further studies of the electronic spectra and excited states of cyclic silanes are in progress and will be reported separately.

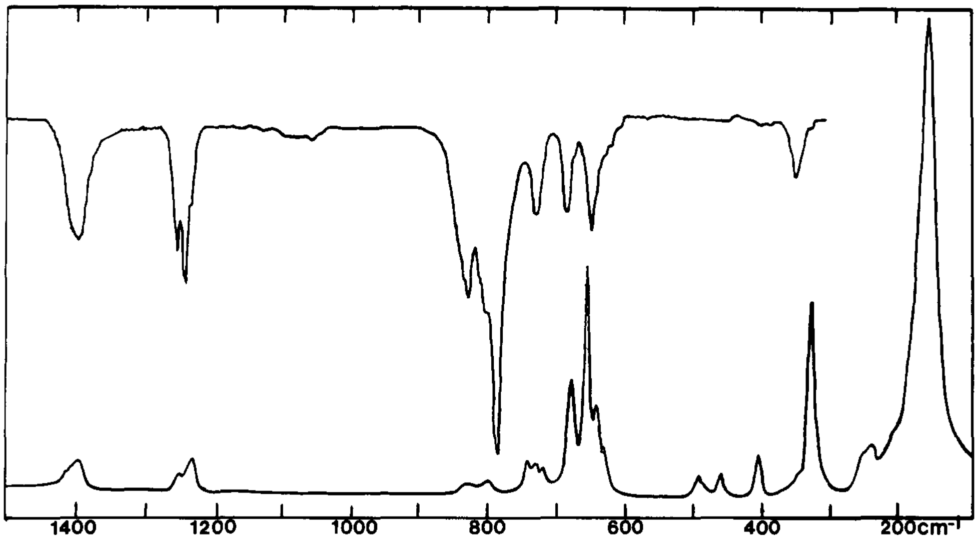

Figure 6. IR (above) and Raman (below) spectra of $(Me_2Si)_9$. IR is a composite of solution and thin-layer spectra.

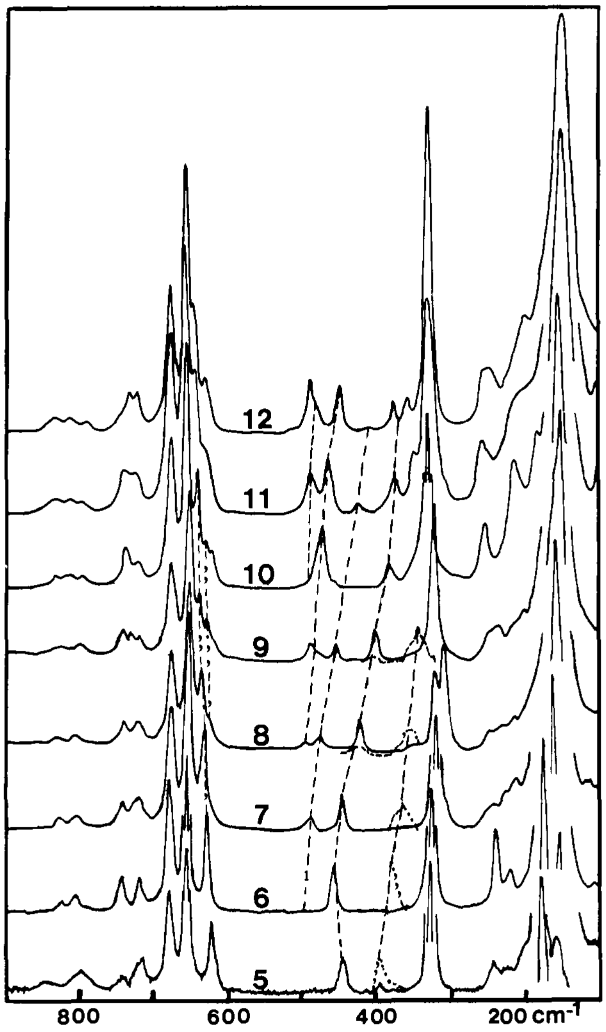

Figure 7. Raman spectra for $(Me_2Si)_5$ through $(Me_2Si)_{12}$ from 100 to 900 cm^{-1}. Peaks appearing as dashed lines represent IR bands. Straight dashed lines connect bands which have the same number of standing wavelengths in the ring. Relative intensities are only approximate from ring to ring and the IR bands for $(Me_2Si)_8$ and $(Me_2Si)_9$ have been enhanced for clarity.

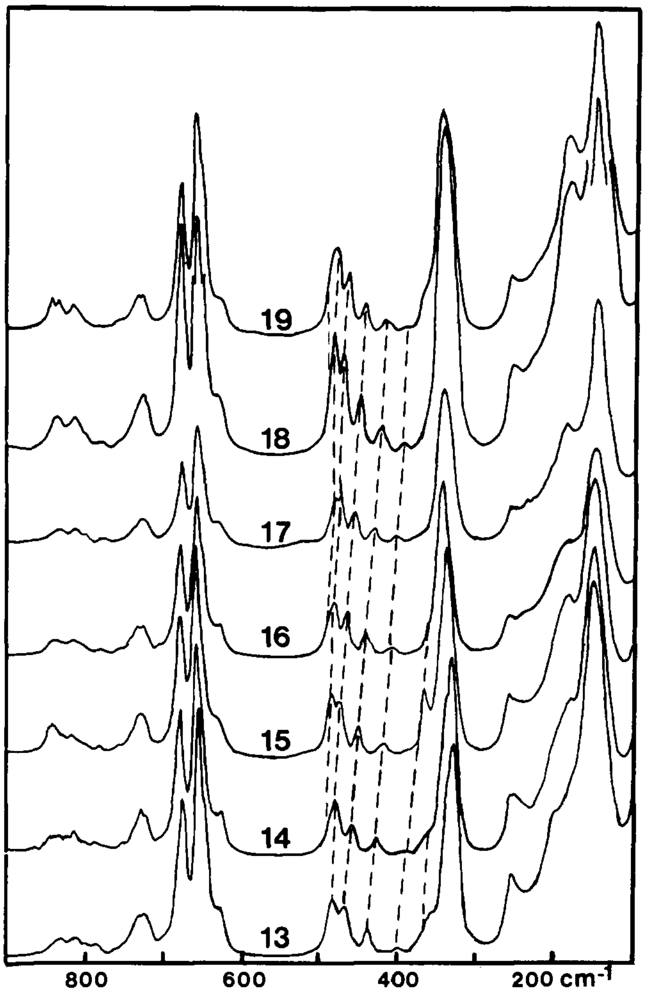

Figure 8. Raman spectra for $(Me_2Si)_{13}$ through $(Me_2Si)_{19}$ from 100 to 900 cm^{-1}. The dashed lines connect bands which have the same number of standing wavelengths in the ring. Relative intensities are only approximate from ring to ring.

with those for dimethylsiloxane oligomers, which have been carefully investigated previously.[33] Assignment of vibrations below 765 cm^{-1} was also aided by previous studies of cyclic phenyl-,[12] methyl-,[6,12] and hydrosilanes.[34] The vibrational spectra for $(Me_2Si)_n$ are almost identical above 900 cm^{-1}. Between 100 and 900 cm^{-1} significant changes are found, especially in the Raman

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(33) Alvik, T.; Dale, J. *Acta Chem. Scand.* **1971**, *25*, 2142–2148.

(34) (a) Höfler, F.; Bauer, G.; Hengge, E. *Spectrochim. Acta, Part A*, **1976**, *32A*, 1435–1441. (b) Hassler, K.; Hengge, E.; Kovar, D. *Ibid.* **1978**, *34A*, 1193–1197.

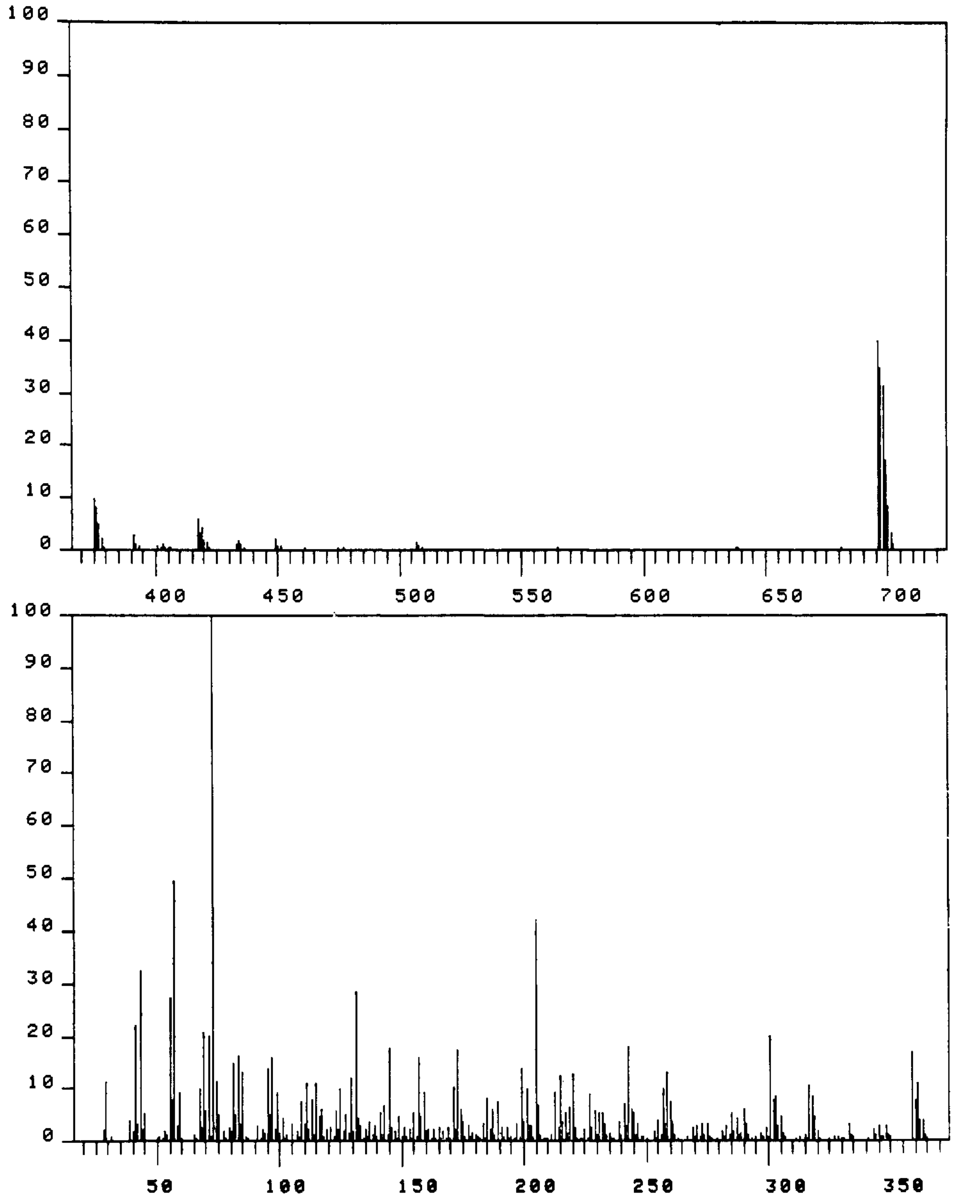

Figure 9. Mass spectrum of $(Me_2Si)_{12}$.

spectra which are shown in Figures 7 and 8.

The absorptions between 300 and 500 cm^{-1} are assigned to Si–Si stretching modes which are known to lie in this frequency range. The strong Raman active vibration between 320 and 350 cm^{-1} is easily assigned as the in-phase, totally symmetric ring breathing mode. The frequency of this vibration decreases slightly from $(Me_2Si)_5$ to $(Me_2Si)_7$. However in larger rings the ring breathing mode shifts to higher frequency and broadens. The broadening is probably due in part to overlap with degenerate modes.

For classification of the Si–Si stretching modes, a standing wave model will be used.[35] The normal vibrations are regarded as a series of waves with a phase difference between motions of adjacent units of $\delta = 2\pi m/n$, where n is the number of silicon atoms in the ring and m can have the values 0, 1, 2, ..., $(n - 1)/2$ for odd n and 0, 1, 2, ..., $n/2$ for even n. Because vibrations of adjacent skeletal atoms are coupled to some extent, modes of different δ will have different frequencies. The total number of vibrations expected is therefore $(n + 2)/2$ for even-membered rings and $(n + 1)/2$ for odd. Each ring will have an in-phase nondegenerate mode corresponding to the totally symmetric stretching vibration. For even-numbered rings, a progression of $(n - 2)/2$ degenerate modes is predicted, headed by the nondegenerate out-of-phase stretching mode ($\delta = \pi$) and ended by the totally symmetric stretch ($\delta = 0$). The next larger odd-membered ring is expected to have the same number of bands, but the out-of-phase vibration is replaced by an additional degenerate mode.

As can be seen from Figures 7 and 8, the Si–Si stretching frequencies for the $(Me_2Si)_n$ series can be correlated fairly well by using the standing-wave model.[35] The vibrations having the same number of standing waves in the ring are connected with dashed lines in the figures. There are a few anomalous features in the spectra: the highest energy degenerate mode in $(Me_2Si)_9$ is split, suggesting that the molecule is frozen into a conformation or occupies a site of low symmetry; similarly at least one of the degenerate modes in $(Me_2Si)_{12}$ appears to be split and one of the degenerate modes is missing for $(Me_2Si)_{10}$. In addition, the weak, degenerate, infrared-active band shown as a dashed line in Figure 7 loses intensity as ring size increases and then disappears at $n = 10$.[36]

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(35) (a) Chapman, A. C.; Paddock, N. L.; Paine, D. H.; Searle, H. T.; Smith, D. R. *J. Chem. Soc.* **1960**, 3608–3614. (b) Chapman, A. C.; Paddock, N. L. *Ibid.* **1962**, 635–645.

(36) The totally symmetric stretching vibration also appears to be split in $(Me_2Si)_8$ and in some of the larger molecules. This splitting might be the result of Fermi resonance with first overtone of the strong Raman line near 160 cm^{-1}.

(37) Sheppard, N.; Simpson, D. M. *Q. Rev., Chem. Soc.* **1953**, *7*, 19–55.

Table IV. Vibrational Spectra of $(Me_2Si)_9$ (cm^{-1})

IR	Raman	assignt
2940 (s)	2945 (s)	asym C-H stretch
2685 (m)	2886 (vs)	sym C-H stretch
2795 (w, br)	2800 (w, br)	[a]
1400 (m, br)	1398 (w, br)	asym CH_3 deformation
1258 (m)		sym CH_3 deformation, umbrella opening
1245 (s)	1252 (w, br)	
1235 (sh)	1232 (w, br)	
830 (s)	829 (w)	sym and asym CH_3 rocking both in and out of plane
800 (s)	800 (w)	
782[b] (vs)		
	742 (w)	asym Si-C stretch
730 (m)	730 (w)	
	720 (w)	
685 (m)	678 (m)	sym Si-C stretch
650 (m)[c]	655 (m)	
[d]	641 (w)	
	629 (w)	
	490 (w)	Si-Si ring stretch
	484 (w, sh)	
	458 (w)	
	405 (w)	
395 (vw)		
	326 (m)	in-phase Si-Si ring breathing ring deformation and SiC_2 deformation?
	248 (w, sh)	
	239 (w)	
	208 (w)	
	157 (vs)	

[a] Overtone or combination frequencies enhanced through interaction with the neighboring C-H stretching bands. See ref 37.
[b] Gradually shifts from 800 cm^{-1} in $(Me_2Si)_5$ to 765 cm^{-1} in $(Me_2Si)_{19}$; a new peak appears at 805 cm^{-1} from $(Me_2Si)_{10}$ on.
[c] Peak at 650 cm^{-1} for $(Me_2Si)_5$ through $(Me_2Si)_9$, 655 for $(Me_2Si)_{10}$ and $(Me_2Si)_{11}$, and 660 for $(Me_2Si)_{12}$ through $(Me_2Si)_{19}$.
[d] Peak at 630 cm^{-1} for $(Me_2Si)_6$ through $(Me_2Si)_8$, 640 for $(Me_2Si)_{10}$ through $(Me_2Si)_{13}$, and 635 for $(Me_2Si)_{14}$ through $(Me_2Si)_{19}$.

The molecule $(Me_2Si)_6$ is known to have D_{3d} symmetry from a crystal structure investigation.[26] This allows a more rigorous analysis of the Si-Si stretching region to be made by using group theory, leading to the following assignments: 329 cm^{-1} A_{1g}(R), 387 cm^{-1} E_u(IR), 460 cm^{-1} E_g(R). The out-of-plase A_{1u} mode which should lie in the neighborhood of 495 cm^{-1} is predicted to be quiet, and in agreement with theory it is not observed. In the larger rings this mode is difficult to observe due to low intensity and overlap with the nearest degenerate vibration.

Modes assigned as Si-C stretching appear between 600-700 cm^{-1} and 700-750 cm^{-1}. The lower frequency bands are assigned to the symmetric stretching modes by analogy with previous work for dimethylsiloxane[33] and phosphonitrile[35] oligomers. Although assignments are difficult to make because of severe overlap as the ring size increases, the symmetric Si-C stretching modes can also be partially correlated by using the standing-wave model. As shown in Figure 7, in agreement with prediction the eight- and ten-membered rings each add one vibration, while the seven- and nine-membered rings have the same number of modes as the six- and eight-membered rings, respectively.

Mass Spectra. A limited number of mass spectral studies have been published for polysilanes. The mass spectra of $(Me_2Si)_n$ where $n = 5-7$, have been determined and analyzed by Gilman and his students.[38] The mass spectrum for $(Me_2Si)_{12}$ is shown in Figure 9 as an example typical of the methylcyclosilanes. Although the mass spectra of these compounds have not yet been carefully studied, several general features stand out. First, good agreement is found between the calculated isotope ratios for the parent clusters and those observed. In all of the rings the parent peaks are quite intense; in many of the rings their total sum exceeds the base peak which is generally $Me_3Si^{+\cdot}$. Moreover, as ring size increases, a noticeable gap appears and then grows between the parent cluster and the next group of peaks of greater than miniscule intensity. In $(Me_2Si)_{12}$ for example only a few very weak peaks appear above m/e 450. Finally, the relative importance of the parent cluster appears to increase moderately with increasing ring size from $(Me_2Si)_8$ through $(Me_2Si)_{13}$.

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Supplementary Material Available: A listing of IR and Raman data (Table V) for the permethylcyclosilanes $(Me_2Si)_n$, $n = 5-19$ (5 pages). Ordering information is given on any current masthead page.

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(38) Kinstle, Y. H.; Haiduc, I.; Gilman, H. *Inorg. Chim. Acta* **1969**, *3*, 373-377.