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^{29}Si AND ^{13}C NMR SPECTRA OF PERMETHYLPOLYSILANES

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Summary

^{29}Si, ^{13}C and ^{1}H NMR spectra are reported for the series of linear permethylpolysilanes Me(SiMe$_2$)$_n$Me where n = 1 to 6, for the cyclic permethylpolysilanes (Me$_2$Si)$_n$ where n = 5 to 8, and for a few related compounds. For linear polysilanes the ^{29}Si and ^{13}C chemical shifts can be accurately calculated from simple additivity relationships based on the number of silicon atoms in α, β, γ and δ positions. Adjacent (α) silicon atoms lead to upfield shifts in the ^{29}Si and ^{13}C resonances, whereas more remote silicon atoms lead to downfield shifts. The ^{29}Si chemical shifts of the polysilane chains are linearly related to the ^{13}C shifts of the carbon atoms attached to the silicon. The ^{29}Si and ^{13}C resonances of the cyclic silanes deviate from this relationship. Ring current effects arising from σ delocalization are suggested as an explanation for the deviations. Proton-coupled ^{29}Si NMR spectra are reported for Me$_3$SiSiMe$_3$ and for (Me$_2$Si)$_n$, n = 5 to 7.

The chemistry of the permethylpolysilanes has developed considerably since their initial discovery in 1949 [1]. Various recent studies have shown that although the polysilanes are structural analogs of the saturated hydrocarbons many of their physical and chemical properties resemble those of unsaturated hydrocarbons [2,3]. The polysilanes are currently being investigated as models for evaluating the physical properties of elemental silicon.

A thorough investigation of the ^{1}H NMR chemical shifts and coupling constants of a variety of the permethylpolysilanes has already appeared [4]. However, because the methyl protons are relatively far from the molecular framework, the ^{1}H chemical shifts are not expected to be very sensitive to electronic effects at the backbone of the molecule. We therefore undertook an examination of the ^{29}Si and ^{13}C NMR spectra for a number of linear and cyclic permethylpolysilanes. For completeness the ^{1}H NMR spectra were redetermined using modern equipment.

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Experimental

NMR spectra

^{29}Si NMR spectra were obtained employing a Varian XL-100-15 NMR spectrometer on benzene-d_6 solutions, usually about 4 M, in a 12 mm NMR tube. Except for the proton-coupled spectra, broadband proton decoupling was routinely employed to enhance signal strength by eliminating the multiplets arising from spin—spin coupling. The nuclear Overhauser enhancement which normally accompanies decoupling was cancelled by employing a gyrocode gating technique so that signal intensities could be used for spectral analysis [5].

The ^{13}C NMR spectra were run on the JEOL FX-60 NMR spectrometer in 5 mm tubes and using the same samples as those used for ^{29}Si wherever possible. These samples were also used for obtaining the ^{1}H NMR spectra on either the XL-100 or the JEOL MH-100 NMR spectrometers.

In all cases TMS was added as an internal standard and all chemical shifts are given in ppm units relative to TMS with downfield shifts assigned positive values.

Synthesis of cyclic polysilanes

The cyclic compounds were obtained from coupling Me_2SiCl_2 with Na/K or Li as described in recent publications [6,7]. The rings were separated by HPLC using a 1/2" × 50 cm Partisil M9 ODS-2 (octadecylsilane reverse-phase) column with an 80% MeOH/20% THF mobile phase at a flow rate of 6 ml/min. The cyclic compounds were characterized by their UV, ^{1}H NMR and IR spectra which were identical to those previously reported [2—4].

Linear polysilanes

These compounds were obtained by chlorination of the five- and six-membered rings to produce the dichloropolysilanes, $Cl(SiMe_2)_nCl$ (n = 2 to 6) [8], which were then methylated using methyllithium in ether [9]. All compounds were characterized by their ^{1}H NMR and UV spectra which were identical to those previously reported [2,4].

Results and discussion

Chemical shifts

The ^{29}Si and ^{13}C NMR chemical shifts for permethylpolysilanes are compiled in Table 1 [10,11]. One of the more striking features of the data is the large ^{29}Si chemical shift range, extending from 0.0 ppm for TMS to —135.2 ppm for the central Si atom in the tetrakis(trimethylsilyl)silane. This range is substantially greater than the 43.9 ppm range observed in the ^{13}C NMR spectra of the saturated hydrocarbons. Chemical shifts are expected to be larger for silicon than for carbon because the paramagnetic shielding term, which dominates the chemical shifts for these nuclei, depends on the inverse cube of the distance from the valence orbitals to the nucleus [12,13]. This effect accounts well for the approximate threefold increase in chemical shift range for ^{29}Si over ^{13}C *.

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* The chemical shift ranges observed for ^{29}Si in methylpolysilanes and for ^{13}C in hydrocarbons lead to a ratio δ(Si)/δ(C) 1.44, a value which seems very reasonable for the ratio of the nucleus-valence orbital distances for the two atoms.

TABLE 1

^{29}Si AND ^{13}C CHEMICAL SHIFTS (ppm) FOR SOME LINEAR AND CYCLIC PERMETHYLPOLYSILANES

Compound	$\delta(^{29}Si)$				$\delta(^{13}C)$			
	Si(1)	Si(2)	Si(3)	Si(4)	C(1)	C(2)	C(3)	C(4)
Si_2Me_6 [a]	—19.6				—2.4			
Si_3Me_8 [a]	—16.0	—48.5			—1.4	—6.9		
Si_4Me_{10}	—15.1	—44.7			—1.1	—5.7		
Si_5Me_{12}	—15.0	—43.4	—40.7	—1.	—1.1	—5.5	—4.4	
Si_6Me_{14}	—14.9	—43.1	—39.2		—1.1	—5.4	—4.1	
$(Me_3Si)_4Si$ [b]	—15.9	—135.2						
$(SiMe_2)_5$			—42.1				—6.3	
$(SiMe_2)_6$			—41.9				—6.0	
$(SiMe_2)_7$			—41.7				—5.2	
$(SiMe_2)_8$			—39.9				—4.5	
$Me_3SiSi_5Me_9$ [c]	—10.0	—83.0	—35.9	—40.7	0.8	—12.0	—3.6 + —5.3	—5.9 + —6.2

[a] Values taken from ref. 10. [b] Values taken from ref. 11. [c] The $SiMe_3$ group is taken as Si(1) and the following silicons are numbered sequentially around the ring.

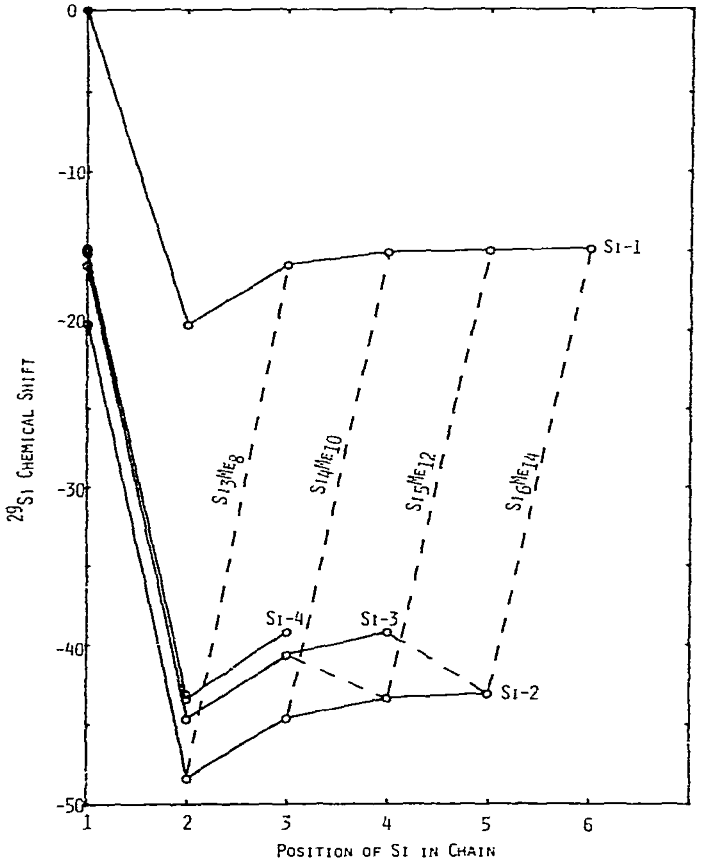

Fig. 1. Plot of ^{29}Si chemical shifts versus silicon positions in the chain. Solid lines connect shifts for silicons having the same position. Dashed lines connect shifts belonging to the same polysilane.

TABLE 2

LINEAR REGRESSION ANALYSIS OF ^{29}Si CHEMICAL SHIFT PARAMETERS IN THE LINEAR PERMETHYLPOLYSILANES

No. of observations: 11
Variables: 4
Standard deviation in predicted ^{29}Si chemical shift: ±0.22 ppm
Correlation constant R: 0.9999
Constant term B: 8.5 ppm

Silicon position 1	A_l in ppm [a]
α	-28.5 ± 0.10
β	$+3.9 \pm 0.05$
γ	$+1.2 \pm 0.09$
δ	$+0.2 \pm 0.01$

[a] A negative sign means an upfield shift.

Although the total ^{29}Si chemical shift range is quite broad, for the linear polysilanes particular types of silicons lie within much narrower regions. The terminal Me_3Si groups fall between -10 and -20 ppm, while the internal Me_2Si groups vary between -39 and -49 ppm. A plot of ^{29}Si chemical shift versus the position of the silicon in the chain (Fig. 1) shows that changes in the chemical shift occur in a very regular manner. The ^{29}Si chemical shifts can be described by eq. 1 similar to the one used by Grant and Paul to describe the ^{13}C chemical shifts of the linear alkanes [14]. Eq. 1 relates the chemical shift of the kth

$$\delta(\mathrm{Si})(k) = B + \sum_{l} A_l n_{kl} \qquad (1)$$

silicon atom to an additive chemical shift parameter for the lth atom, A_l, times the number of silicon atoms in the lth position relative to the kth silicon atom. B is a constant. A regression analysis of the ^{29}Si chemical shifts of the linear polysilanes yields the additive parameters shown in Table 2. The standard deviation of 0.22 ppm is remarkably small compared to the overall chemical shift range observed for the series, and is in fact not much larger than the 0.05 ppm experimental error estimated for $\delta(\mathrm{Si})$ of these compounds.

Similarities in the ^{29}Si and ^{13}C chemical shifts of the linear polysilanes are obvious when these values are plotted against each other (Fig. 2). This similarity suggests that the ^{13}C chemical shifts can also be represented by a linear equation like eq. 1, but in which $\delta(\mathrm{Si})(k)$ is replaced by a term for the chemical shift of the carbon attached to the kth silicon, $\delta(\mathrm{C})(k)$, and A_l becomes the additive parameter for the carbons attached to the silicon atoms in the lth position. A regression analysis of the ^{13}C chemical shifts yields additivity parameters (Table 3) which are also in excellent agreement with the experimental values (standard deviation 0.12 ppm).

All the ^{29}Si shifts displayed in Fig. 2 can be related to the ^{13}C shifts by the relationship shown in eq. 2, in which

$$\delta(^{29}\mathrm{Si}) = 3.08\ \delta(^{13}\mathrm{C}) + 0.95 n_{\mathrm{C}} - 14.2 n_{\mathrm{Si}} \qquad (2)$$

the ^{29}Si shift of interest is related to the ^{13}C shift of the attached methyls by

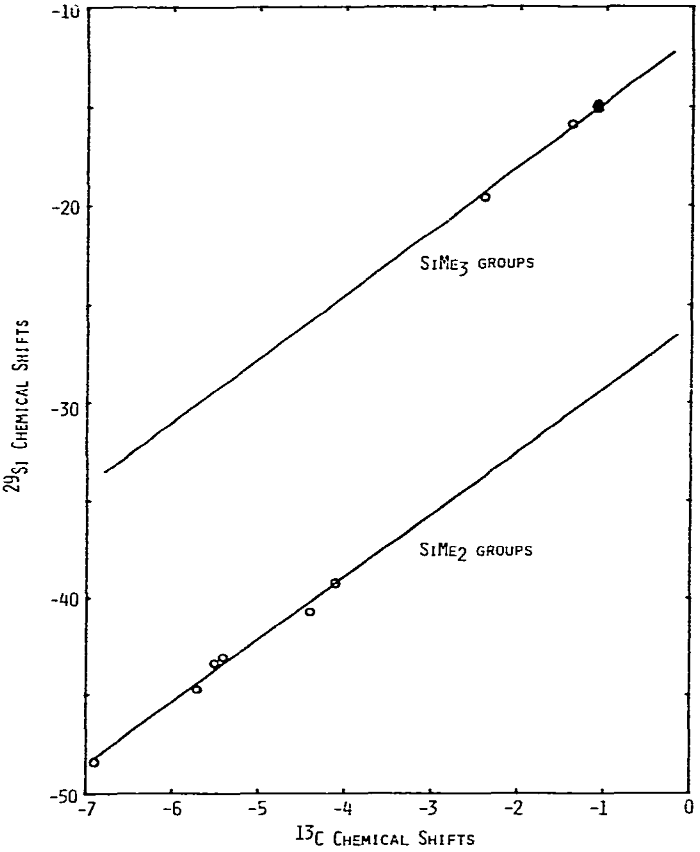

Fig. 2. Plot of ^{29}Si chemical shifts versus ^{13}C chemical shifts of the attached methyl groups in the permethylpolysilanes.

TABLE 3

LINEAR REGRESSION ANALYSIS OF ^{13}C CHEMICAL SHIFT PARAMETERS IN THE LINEAR PERMETHYLPOLYSILANES

No. of observations: 11
Variables: 4
Standard deviation in predicted ^{13}C chemical shift: ±0.12 ppm
Correlation constant R: 0.9990
Constant term B: 1.9

Carbon on silicon in position 1	A_l in ppm [a]
α	−4.4
β	1.2
γ	0.3
δ	0.1

[a] A negative sign means an upfield shift.

TABLE 4

COMPARISON OF EXPERIMENTAL ^{29}Si CHEMICAL SHIFTS (ppm) WITH THE VALUES CALCULATED USING THE ^{13}C CHEMICAL SHIFTS

Compound	Position	$\delta(^{29}\mathrm{Si})_{\mathrm{exptl.}}$	$\delta(^{29}\mathrm{Si})_{\mathrm{calcd.}}$	$\delta_{\mathrm{expt}} - \delta_{\mathrm{calc}}$ difference
Si_2Me_6	Si(1)	—19.6	—19.4	—0.2
Si_3Me_8	Si(1)	—15.9	—16.4	+0.5
	Si(2)	—48.4	—47.9	—0.5
Si_4Me_{10}	Si(1)	—16.1	—15.5	+0.4
	Si(2)	—44.7	—44.3	—0.4
Si_5Me_{12}	Si(1)	—15.0	—15.5	+0.5
	Si(2)	—43.4	—43.1	—0.3
	Si(3)	—40.7	—40.4	—0.3
Si_6Me_{14}	Si(1)	—14.9	—15.5	+0.6
	Si(2)	—43.1	—43.4	+0.3
	Si(3)	—39.2	—39.5	+0.3
Si_5Me_{10}		—42.1	—45.9	+3.8
Si_6Me_{12}		—41.9	—41.9	+3.1
Si_7Me_{14}		—41.7	—42.5	+0.8
Si_8Me_{16}		—39.9	—40.4	+0.5

the ratio of their chemical shift ranges (3.08). This term is then modified by the number of attached carbons, n_C, and silicons, n_{Si}. A comparison of these calculated values with the experimental shifts (Table 4) shows very good agreement (standard deviation 0.43). This relationship implies that the ^{29}Si and ^{13}C chemical shifts of the permethyl compounds are determined by the same factors.

The large values of the α additive constants in the additivity relationships described above show that the ^{29}Si and ^{13}C chemical shifts of polysilanes are dominated by the immediate structural environment. However the β, γ and δ additive constants are not negligible, indicating that more distant atoms also make significant contributions to the chemical shift. Similar results were observed in the correlation of the ^{13}C chemical shifts of the alkanes [14].

In order to account for the behavior of the additive constants we will follow the approach used in recent theoretical studies [15,16] of ^{29}Si shielding, which explain silicon chemical shifts only in terms of the local paramagnetic term, ignoring local diamagnetic and long-range effects [17,18]. Because the local paramagnetic term is highly dependent on electronegativity, the large upfield shift (α effect) observed for the polysilanes when a methyl group is replaced by a trimethylsilyl group can be attributed mainly to the electronegativity difference between these groups. However, another factor which may contribute to this upfield shift is γ proton-proton interaction between methyl protons on adjacent silicon atoms. Similar γ interactions between protons are believed to be responsible for the anomalous upfield shifts found in the ^{13}C NMR, for carbons attached to methyl groups in the γ position.

If α-silicon substitution causes an upfield shift in the ^{29}Si NMR, why does

TABLE 5

A COMPARISON OF THE CALCULATED AND EXPERIMENTAL ^{29}Si AND ^{13}C CHEMICAL SHIFTS FOR THE CYCLIC PERMETHYLPOLYSILANES, $(SiMe_2)_n$ (n = 5 to 8)

Compound	$\delta(^{29}Si)$			$\delta(^{13}C)$		
	calcd.	exptl.	Δ	calcd.	exptl.	Δ
Si_5Me_{10}	−40.7	−42.1	−1.4	−4.5	−6.3	−1.8
Si_6Me_{12}	−39.5	−41.9	−2.4	−4.2	−6.0	−1.8
Si_7Me_{14}	−38.3	−41.7	−3.4	−3.9	−5.2	−1.3
Si_8Me_{16}	−38.1	−39.9	−1.8	−3.8	−4.5	−0.7

β-silicon substitution cause a downfield shift? Replacement of a methyl group in the β position with less electronegative trimethylsilyl would be expected to further increase the shielding at the central silicon atom. A possible rationalization is that the inductive shielding effect of the β-trimethylsilyl group is not sufficient to compensate for the through-space (γ proton-proton) shielding which is lost when the methyl group is replaced.

For branched and cyclic alkanes it was necessary to include additional correction factors to account for the ^{13}C chemical shifts [14]. These factors were interpreted as arising from steric and geometric considerations which might also apply to the branched and cyclic polysilanes. Very little chemical shift data is yet available for branched and cyclic polysilanes, but the additivity parameters derived from the linear polysilanes are not sufficient to describe the behavior of the cyclic compounds. From Table 5 it is evident that the calculated (from eq. 1) and experimental ^{29}Si and ^{13}C chemical shifts for the cyclic polysilanes do not agree well. In all cases the observed shifts are to higher field than the calculated values. The ^{13}C shielding difference, $\Delta(^{13}C)$, (0.7 to 1.8 ppm) of the methyl carbons is most likely a result of increased through-space methyl interaction resulting from conformational restrictions imposed by the rings. As the ring size increases the increased bond flexibility leads to more nearly free rotation and shifts of the larger rings gradually approach the linear values, as the data for Si_7Me_{14} and Si_8Me_{16} suggest.

The usual relationship between $\delta(^{29}Si)$ and $\delta(^{13}C)$ (eq. 2) also does not hold for the cyclosilanes. The agreement is good for $(Me_2Si)_8$ but becomes poorer for smaller ring size. The ^{29}Si nuclei in $(Me_2Si)_5$ and $(Me_2Si)_6$ especially seem to experience an additional deshielding effect, beyond that predicted from the ^{13}C NMR chemical shifts.

A possible source of such deshielding is the presence of a ring current in the smaller polysilane rings. Although ring currents are normally considered only for π-electrons, theory does not preclude their presence in saturated systems. Pople has suggested that a ring current may be partially responsible for the deshielding of equatorial protons in cyclohexanes [19], and ring currents have also been claimed in cyclopropane compounds [20]. Because of the low ionization potentials of the framework σ electrons in polysilanes, ring currents might be larger for cyclosilanes than for cycloalkanes [21].

Unlike the ^{13}C and ^{29}Si chemical shifts the ^{1}H shifts show no consistent trends (Table 6). The data also show a considerable sensitivity of the proton

TABLE 6

^{1}H CHEMICAL SHIFT DATA FOR THE PERMETHYLPOLYSILANES

Compound	$\delta(^1H)$					
	CCl_4 solvent [a]			C_6D_6 solvent		
	Si(1)	Si(2)	Si(3)	Si(1)	Si(2)	Si(3)
Si_2Me_6	0.04			0.01		
Si_3Me_8	0.08	0.07		0.00	0.04	
Si_4Me_{10}	0.11	0.09		0.15	0.20	
Si_5Me_{12}	0.09	0.12	0.15	0.12	0.17	0.20
Si_6Me_{14}	0.10	0.14	0.19	0.14	0.20	0.25
Si_5Me_{10}			0.14			0.21
Si_6Me_{12}			0.13			0.20
Si_7Me_{14}			0.13			0.21
Si_8Me_{16}			0.14			

[a] Data taken from ref. 5.

shifts to solvent variation. The variation found in the proton chemical shifts suggests that it may be dangerous to use these shift values to evaluate electronic effects occurring at the molecular backbone.

Proton-coupled ^{29}Si NMR spectra for cyclosilanes

Most of the published data on ^{29}Si NMR of organosilicon compounds have been obtained using proton decoupling to enhance signal strength and simplify the spectrum. Proton-coupled ^{29}Si NMR spectra of organosilanes are available only for Me_nSiX_{4-n} compounds [22] and for a few methylsiloxanes [23]. We report here the proton-coupled spectra for $Me_3SiSiMe_3$ and for the cyclic silanes $(Me_2Si)_n$, n = 5—7 together with computer simulations * (Fig. 3).

A ^{29}Si atom in $(Me_2Si)_n$ is coupled to protons both on attached methyl groups and on methyl groups bonded to adjacent silicons. The ^{29}Si spectrum is therefore the X portion of an $A_6B_{12}X$ (or $A_6A'_{12}X$) system, and so might be quite complex. The observed spectra are unexpectedly simple, because (1) only first-order coupling is important ($J_{AB} = 0$), and (2) the ratio between the two proton—silicon spin coupling constants is fortuitously close to 2/1. The spectral lines therefore all appear at multiples of the smaller coupling ^3J(SiH).

The narrowest lines and best resolution are obtained for $(Me_2Si)_5$ for which the ratio $^2J(SiH)/^3J(SiH)$ is exactly 2.0 within experimental error. For the six- and seven-membered rings the ratios deviate from 2.0 and the lines are correspondingly broader. The simplicity of the NMR spectra of the cyclic permethylpolysilanes confirms the fluxional nature of these molecules in solution, mentioned in our earlier publications [24].

Coupling constants

A variety of one, two and three bond coupling constants were determined

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* Simulations of the proton-coupled spectra were carried out using the program NUMARIT kindly provided by Professor J.S. Martin. Modifications necessary to simplify the nineteen-spin system included factorings resulting from magnetic equivalence and twofold frame symmetry [25].

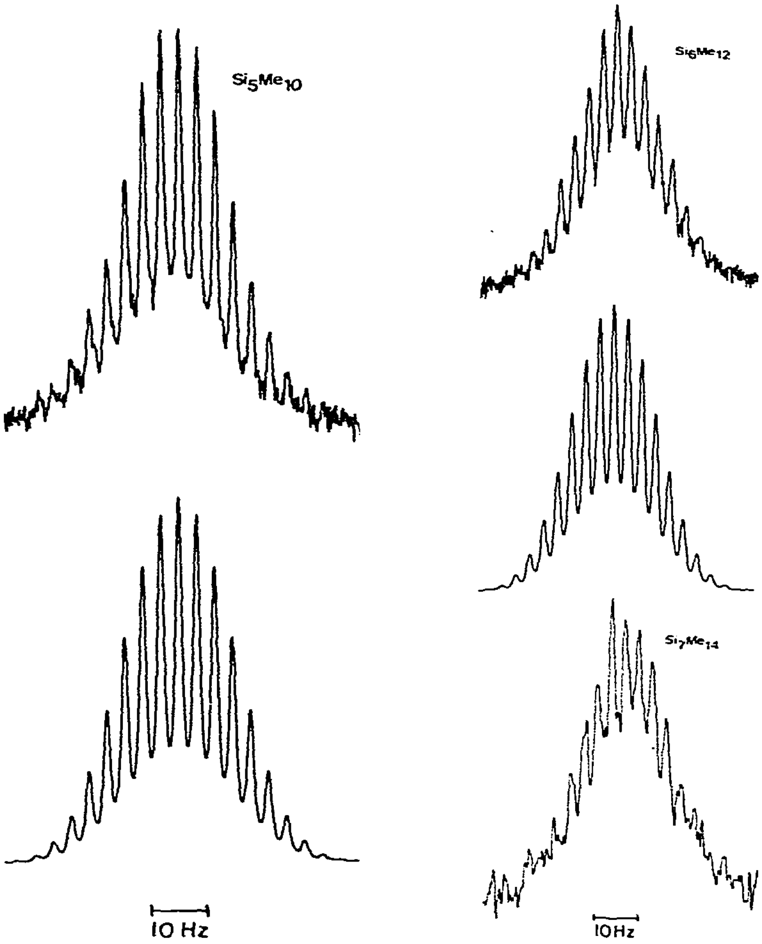

Fig. 3. Proton coupled ^{29}Si NMR spectra of cyclopolysilanes. Left, observed spectrum for $(Me_2Si)_5$ (top) and computer simulation (bottom). Right, observed spectra for $(Me_2Si)_6$ (top) and $(Me_2Si)_7$ (bottom), and computer simulation for $(Me_2Si)_6$ (center).

for the permethylpolysilanes (Table 7). Although there are no extraordinary differences between the linear and cyclic compounds it is worth noting several things. First the ^1J(Si—C) values for the cyclic silanes are similar to those found for the $SiMe_2$ group in the linear silanes, as is expected because the chemical shifts of the linear and cyclics both fall in the same area.

The ^3J(CH) values from Table 7 are clearly very similar to the ^3J(SiH) values. The smaller natural abundance of ^{13}C makes their observation as satellites in the ^{1}H NMR spectra difficult because the ^{29}Si satellites cover them. They must therefore be determined from the proton-coupled ^{13}C NMR spectra. The near equivalence of these three bond couplings suggest a similar amount of *s* character is carried through the Si—Si—C—H and C—Si—C—H bonds.

The narrow range of Si—H couplings makes it difficult to assign any significance to these values other than to note that the cyclic polysilanes exhibit some systematic difference from the linear compounds. This is most obvious in

TABLE 7

COUPLING CONSTANTS (Hz) BETWEEN ^{29}Si AND VARIOUS OTHER NUCLEI IN THE PERMETHYLPOLYSILANES

Compound	^1J(C—H)	^1J(Si—C)	^2J(Si—H)	^2J(C—H)	^3J(Si—H)	^3J(C—H)
Si_2Me_6	119.8	43.6	6.5	5.7	2.7	2.7
Si_3Me_8						
α-group	119.0	43.8	6.4	—	2.6	—
β-group	119.0	37.0	6.4	—	—	—
Si_4Me_{10}						
α-group	120.0	44.8	6.3	—	2.7	—
β-group	121.0	—	6.2	—	2.0	—
Si_5Me_{12}						
α-group	—	40.0	6.4	5.5	2.7	—
β-group	—	—	6.0	3.5	3.0	—
γ-group	—	—	—	3.4	—	—
Si_6Me_{14}						
α-group	120.0	43.5	6.6	5.5	3.1	—
β-group	121.0	—	6.3	3.2	3.0	—
γ-group	122.0	—	—	3.2	3.1	—
Si_5Me_{10}	121.3	37.7	6.4	—	3.2	2.9
Si_6Me_{12}	121.6	37.7	6.1	—	3.2	2.9
Si_7Me_{14}	119.6	—	6.1	—	3.2	2.7

the ^3J(SiH) couplings which are consistently larger in the cyclic compounds than in the linear ones. Also the ^2J(SiH) coupling found for Si_5Me_{10} is larger than the usual value observed for the $SiMe_2$ groups in the linear polysilanes.

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