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PROTON NMR SPECTRA OF METHYLPOLYSILANES*

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The methylpolysilanes have been the subject of much recent research[1,2]. Little systematic work has been done on the nuclear magnetic resonance of these substances, but NMR spectra of a few such compounds have been published incidental to preparative studies[3–8,15]. This paper reports the results of a systematic investigation of the proton NMR of some methylated polysilanes. Principal objectives in this work were (1) to determine the chemical shifts and coupling constants in linear and cyclic permethylpolysilanes, and compare the results with those found by Brown and Morgan[9] for permethylpolystannanes; and (2) to study the effects of substituents on the NMR properties of polymethyldisilanes and -trisilanes.

EXPERIMENTAL

Nearly all of the substances studied were known compounds, obtained by published methods; references to the syntheses are given in Tables 1 and 3. The syntheses of $(SiMe_2)_5$ and $(SiMe_2)_7$ will be described separately[14]. Physical properties of the products were checked with those reported in the literature. All compounds

TABLE 1

PROTON NMR CHEMICAL SHIFTS FOR PERMETHYL POLYSILANES
In CCl_4 solution in ppm (δ) from tetramethylsilane

	Terminal	2	3	4	5	*Ref. to prepn.*
Me_4Si	0.00					
$Me(SiMe_2)_2Me$	−0.040					10
$Me(SiMe_2)_3Me$	−0.079	−0.067				11
$Me(SiMe_2)_4Me$	−0.109	−0.089				11
$Me(SiMe)_5Me$	−0.090	−0.122	−0.153			12
$Me(SiMe_2)_6Me$	−0.101	−0.142	−0.192			12
$Me(SiMe_2)_7Me$	−0.105	−0.152	−0.205			12
$Me(SiMe_2)_8Me$	−0.097	−0.135	−0.189	−0.205		12
$Me(SiMe_2)_9Me$	−0.095	−0.132	−0.183	−0.201	−0.205	13
$Me(SiMe_2)_{10}Me$	−0.098	−0.135	−0.186	−0.204	−0.209	13
$(SiMe_2)_5$		−0.135				14
$(SiMe_2)_6$		−0.132				15
$(SiMe_2)_7$		−0.125				14

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TABLE 2

CONCENTRATION DEPENDENCE OF PROTON CHEMICAL SHIFTS FOR $Me_{10}Si_4$

Units are ppm downfield from tetramethylsilane; concentrations are v/v in carbontetrachloride.

100%	50%	20%	10%	6%	2%	
0.107	0.097	0.090	0.089	0.085	0.085	$\Delta = 0.022$
0.133	0.120	0.112	0.109	0.103	0.103	$\Delta = 0.030$

TABLE 3

PROTON NMR CHEMICAL SHIFTS FOR SUBSTITUTED DI- AND TRISILANES

Conc.	*Ref. to prepn.*	*Compound*	*Chemical shifts, δ, (ppm)*				
			$Si(CH_3)_3$	$Si(CH_3)_2$	$Si(CH_3)_2X$	Si–H	C_6H_5
neat		Me_4Si	0.000				
neat	10	$Me_3SiSiMe_3$	−0.055				
neat	8	$Me_3SiSiMe_2H$	−0.096	−0.108[a]		−3.75[b]	
neat	16	$Me_3SiSiMe_2Cl$	−0.148	−0.435			
neat	17	$Me_3SiSiMe_2Ph$	−0.060	−0.339			−7.25
neat	18	$(Me_3SiSiMe_2)_2O$	−0.057	−0.163			
neat	11	$Me_3SiSiMe_2SiMe_3$	−0.097	−0.087			
neat	7	$Me_3SiSiMe_2SiMe_2H$	−0.103	−0.125	−0.145[a]	−3.86[b]	
20%	7	$Me_3SiSiMe_2SiMe_2Cl$	−0.141	−0.176	−0.497		
50%	7	$Me_3SiSiMe_2SiMe_2Ph$	+0.007	−0.080	−0.382		−7.30
neat	18, 19	$(Me_3SiSiMe_2SiMe_2)_2O$	−0.067	−0.082	−0.178		

[a] Center of a doublet. [b] Center of a septet.

except those with Si–Cl bonds were purified by gas chromatography, using a $30' \times \frac{1}{4}''$ column packed with 30% SE-30 silicone on Chromosorb W. The gas chromatographic trace also served as an indication of purity; minimum purity of all of the compounds studied is estimated at 99%.

Most of the proton NMR spectra were determined on a Varian A60, 60-megacycle spectrometer. Because of the possible confusion of tetramethylsilane resonance with that of the sample, each spectrum was determined both with and without 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 coupling were determined at 100 cps sweep width. The chemical shifts to silanic (Si-H) protons were determined at 250 or 500 cps sweep width, as required by circumstances, and couplings to these protons were determined at 50 cps sweep width. Sweep time was 250 sec in all cases. For the linear nonasilane and decasilane, a Varian HA-100, 100 megacycle spectrometer, was used at a sweep width of 50 cps and sweep time of 500 sec with a lock on benzene at 3231 cps.

Experimental results are given in Figs. 1 and 2 and Tables 1–4. Chemical shifts in Tables 1–3 are in parts per million (δ); the values were measured from tetramethylsilane taken as zero. Error (to 90% confidence) in values given to 0.001 ppm is ±0.002 ppm. Coupling constants, in Table 4, are in cycles per second. Error in ^{29}Si–proton coupling constants is ±0.1 cps and in ^{13}C–proton coupling constants is ±0.5 cps. The few cases where errors are larger than these are noted in the Tables.

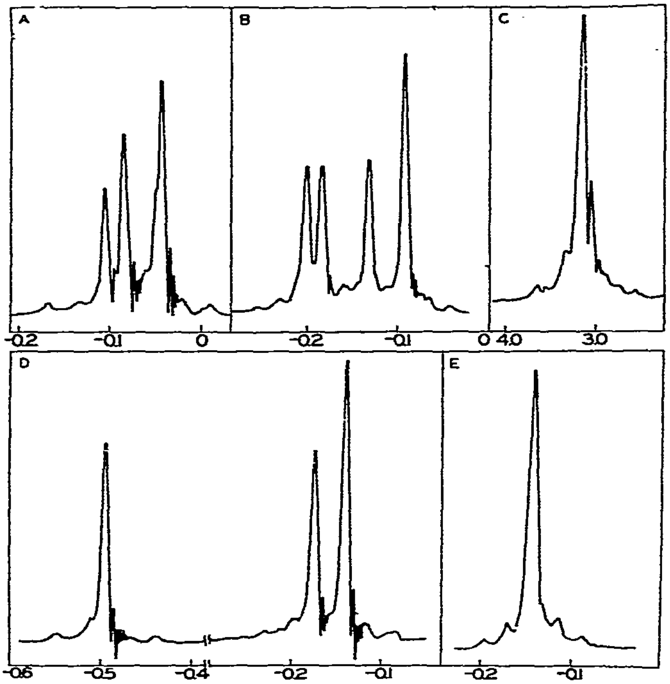

Fig. 1. Proton NMR spectra of methylpolysilanes; units are ppm downfield from tetramethylsilane. A, $CH_3[Si(CH_3)_2]_5CH_3$; B, $CH_3[Si(CH_3)_2]_8CH_3$; C, $CH_3[Si(CH_3)_2]_3CH_3$; D, $CH_3[Si(CH_3)_2]_3Cl$; E, $[Si(CH_3)_2]_6$.

RESULTS

Chemical shifts

The following generalization can be drawn for permethylpolysilanes: *the chemical shift of the methyl protons appears at lower field as the distance of the methyl group from the end of the chain increases.* For instance in the spectrum of dodecamethylpentasilane, shown in Fig. 1A, the three resonances at -0.090, -0.122 and -0.153 ppm (δ) are due to the protons of methyl groups on silicons in the 1, 2 and 3 positions respectively. Because for this compound each of the peaks has different intensity, the assignment is unambiguous. In other cases, for instance octadecamethyloctasilane (Fig. 1B), several peaks have the same intensity and a completely unambiguous assignment cannot be made from this spectrum alone. However, the chemical shifts for protons at a particular position vary little from compound to compound, so assignment of the resonances can be made by analogy from compounds of different chain length. The cyclic compounds all show a single resonance at nearly the same chemical shift, about -0.13 ppm downfield from TMS (Table 1).

As the distance from the end of the chain increases, the difference in chemical shift between methyl groups on adjacent silicon atoms becomes small. For long permethylpolysilane chains, the environment of methyl groups far from the end of the chain becomes essentially equivalent, and coalescence of proton resonances is expected. At 60 megacycles, this limit was reached with eicosamethylnonasilane. In order to split the methyl proton resonances for the fourth and fifth carbon atoms

TABLE 4

NMR COUPLING CONSTANTS, IN CYCLES PER SECOND

Compound	*$Si(CH_3)_3$*	*$Si(CH_3)_2$*	*$Si(CH_3)_2X$*	*$Si\text{-}Si(CH_3)_3$*
Me_4Si	6.75			
$Me_3SiSiMe_3$	6.5			2.7
$Me(SiMe_2)_3Me$	6.4	6.4		2.6
$Me(SiMe_2)_4Me$	6.3	6.2		2.7
$Me(SiMe_2)_5Me$	6.4	6.0[b]		2.7
$Me(SiMe_2)_5Me$	6.6	6.3[b]		3.1
$(SiMe_2)_5$		6.3		
$(SiMe_2)_6$		6.4		
$(SiMe_2)_7$		6.3		
$Me_3SiSiMe_2H$[c]	6.6		6.9	2.8
$Me_3SiSiMe_2Cl$	6.9		6.6	3.8
$Me_3SiSiMe_2Ph$	6.6		6.7	3.0
$(Me_3SiSiMe_2)_2O$	6.7		6.4	3.1
$Me(SiMe_2)_3H$[d]	6.8	[a]	6.6	[a]
$Me(SiMe_2)_3Cl$	6.8	6.6	6.6	2.7
$Me(SiMe_2)Ph$	6.7	6.5	6.9	2.6
$[Me(SiMe_2)_3]_2O$	6.6	6.5	6.5	2.8

[a] Not measurable. [b] Data for internal 3-silicon atom; $J(Si\text{-}CH_3)$ not measurable for second silicon atom. [c] $J[(CH_3)_2Si\text{-}H]$ 4.75 cps. [d] $J[(CH_3)_2Si\text{-}H]$ 4.5 cps.

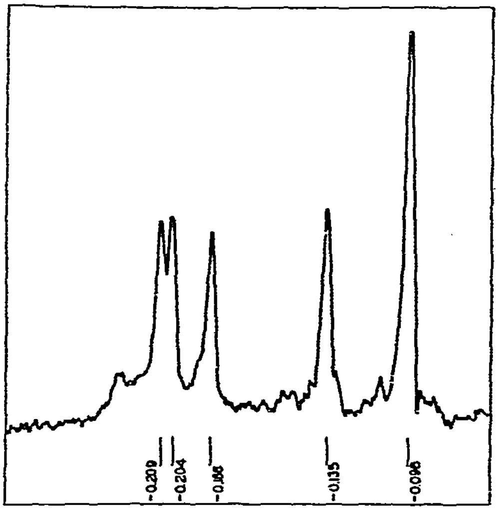

Fig. 2. Proton NMR of $CH_3[Si(CH_3)_2]_{10}CH_3$ at 100 Mc, in ppm downfield from tetramethylsilane.

in the Si_9 and Si_{10} compounds it proved necessary to operate at 100 megacycles, using the Varian HA-100 spectrometer. The resulting spectrum for the Si_{10} compound is shown in Fig. 2. The chemical shifts of methyl protons in permethylpolytin compounds appear to behave similarly, although data are more limited for the tin compounds[9].

Octamethyltrisilane represents an exception to the rule stated above, in that the chemical shift for methyl protons on the central silicon atom is at slightly *higher*

$Si\text{–}Si(CH_3)_2$	$Si\text{–}Si(CH_3)_2X$	$Si(CH_3)_3$	$Si(CH_3)_2$	$Si(CH_3)_2X$
		118.0		
		119.0		
[a]		119.0	119.0	
2.0		120.0	121.0	
3.0				
3.0, 3.1		120.0	121.0, 122.0	
3.2			121.0	
3.4			120.0	
3.2			[a]	
	2.8	120.0		121.0
	1.8	121.0		122.0
	2.8	119.0		118.0
	2.3	118.5		118.0
[a]	2.3	119.5	120.0	
3.0±0.2	1.9	122.0	122.3	124.0
2.7±0.2	2.5	120.5	120.0	120.0
[a]	2.5±0.2	119.0	119.0	119.0

field than for the terminal methyl groups (Fig. 1C). This molecule is unique among the permethylpolysilanes in several ways. First, only in this compound is there a silicon atom attached to two trimethylsilyl groups, and so the chemical environment of the central methyl groups is not quite like that in any of the other compounds. More important, however, in permethylpolysilanes with more than three Si atoms in the chain, there are always conformations in which the internal methyl groups are closely approached by methyl groups two silicon atoms distance on the chain. Only in octamethyltrisilane are the internal methyl groups free of this kind of steric interaction. This can be clearly shown by examination of models. The unique steric environment of the internal methyl protons in the trisilane compound is, we believe, the most likely reason for their abnormal chemical shift.

The chemical shifts for the polysilanes proved to be somewhat concentration dependent. This is illustrated in Table 2 for decamethyltetrasilane. The largest change is shown by the low-field peak, which shifts 0.030 ppm upon dilution of the neat liquid to 2% (v/v) in carbon tetrachloride. The data reported in Table 1 is at 10% (v/v) concentration in CCl_4 for all liquids, and at 10% (w/v) for solids except the linear nonasilane and decasilane and the cyclic heptamer which were studied at 2% (w/v).

NMR spectra were also obtained for permethyldi- and -trisilanes substituted at the end of the chain with H, Cl, phenyl, or –O– (disiloxane). Data for chemical shifts are shown in Table 3. All of these substituents are electronegative with respect to silicon, and all deshield the protons of the methyl groups on the silicon atoms to which they are attached. The spectrum of 1-chloroheptamethyltrisilane is illustrative (Fig. 1D). This effect is greatest (about 20 cps) for chlorine, and decreases in the order Cl > phenyl > –O– > H in both series.

For the compounds with Si–Cl bonds, the protons on remote methyl groups also seem to be deshielded, but the deshielding is rapidly attenuated along the chain.

For the other compounds, deshielding is found only for the protons on the silicon directly attached to the substituent, and in some cases the other methyl protons come into resonance at slightly higher field than in the analogous unsubstituted compounds (Table 3).

^{13}C and ^{29}Si coupling constants

In studying compounds of the permethylpolytin series, Brown and Morgan[9] found that J(Sn–CH$_3$) decreases and J(Sn–Sn–CH$_3$) increases with increasing catenation. A linear relationship between J(Sn–CH$_3$) and percent s character in the tin orbital bonding to carbon has been proposed by Holmes and Kaesz[20], and Brown and Morgan point out that if this relationsip is accepted, the observed trends indicate decreasing s character in the Sn–C bonding orbitals and hence increasing s character in the Sn–Sn bonds. There is at present no evidence that Si–C–H coupling constants depend solely on s-character in the silicon bonding orbital[21]. However, it seemed worthwhile to measure these constants carefully in the polysilane series, to see if trends similar to those for the tin compounds could be found.

Silicon contains 4.5% of ^{29}Si which with nuclear spin 1/2 gives rise to doublet side bands in Si–C–H compounds. In some of the polysilanes it proved possible to measure both J(Si–CH$_3$) and J(Si–Si–CH$_3$), the coupling constant to the β-silicon atom (Table 4). However, the values of these coupling constants are small, and for the long chain compounds with many kinds of methyl groups it was not usually possible to make an unambiguous assignment for the overlapping sidebands.

In the permethylpolysilanes, the value of J(Si–CH$_3$) varies only over the small range 6.75–6.3 cps. This coupling constant is generally slightly smaller for internal than for terminal silicon atoms within a given compound this difference is usually 0.2 or 0.3 cps, just barely outside the estimated error limits of ±0.1 cps. These coupling constants appear to decrease with catenation in the same way as the analogous constants for the polytin compounds. However the differences are very small in the silicon series, at least partly because the coupling constants themselves are small and so cannot be measured with great percentage accuracy.

J(Si–SiCH$_3$) is quite variable in magnitude, from a low of 1.8 for some substituted compounds to a high of 3.4 the cyclic hexamer, $[Si(CH_3)_2]_6$. Substituent effects on J(Si–Si–CH$_3$) are apparently large enough to obscure trends due to catenation. Among all of the compounds studied, J(^{13}C–H) varies only over the small range from 118 to 124 cps. In the permethylpolysilanes, this coupling constant shows a slight increase with increasing catenation.

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SUMMARY

Proton nuclear magnetic resonance spectra have been determined for the linear permethylpolysilanes through Si$_{10}$, the cyclic permethylpolysilanes (SiMe$_2$)$_n$ where n = 5 through 7, and eight monosubstituted polymethyldisilanes and trisilanes.

In linear permethylpolysilanes, the chemical shift of the methyl protons generally appears at lower field as the distance of the methyl group from the end of the chain increases. Electronegative substituents decrease the shielding of methyl protons on silicon atom to which they are attached, the effect decreasing in the order Cl > phenyl > O > H. The coupling constant $J(\text{Si–CH}_3)$ decreases slightly with increasing catenation, in the same way as found previously for analogous polymethyltin compounds[9], but differences are quite small for the polysilanes.

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