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^{29}Si AND ^{13}C NMR SPECTRA OF CHLORO- AND FLUORO-SUBSTITUTED LINEAR PERMETHYLPOLYSILANES

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Summary

^{29}Si and ^{13}C NMR spectra are reported for the three halopolysilane series Me(SiMe$_2$)$_n$Cl, Cl(SiMe$_2$)$_n$Cl and F(SiMe$_2$)$_n$F, where $n = 2$ to 6. Except for the dihalodisilanes (XSiMe$_2$)$_2$, data for all of the compounds fit linear relationships based on substituent constants for chlorine or fluorine atoms in the α, β and γ positions. The effects of halogen substitution on ^{29}Si and ^{13}C chemical shifts are rapidly attenuated along the polysilane chain, becoming negligible four atoms away from the halogen. The NMR data provide no evidence for long-range electronic transmission from chlorine or fluorine in halopermethylpolysilanes of the type suggested by other workers [1].

In 1974 Allred and Boberski showed that α,ω-dichloropermethylpolysilanes react regioselectively with methyl Grignard reagent to produce the corresponding monochlorosilanes (eq. 1) [2]. Selectivity became more pronounced as the

$$\mathrm{Cl(SiMe_2)_nCl + CH_3MgI \rightarrow CH_3(SiMe_2)_nCl} \quad (1)$$

chain length increased from $n = 2$ to $n = 6$. The lower reactivity of the monchloro compared to the α,ω-dichloropolysilanes was attributed to back-donation of electrons from chlorine into vacant polysilane orbitals, which increased with increasing length of the silane chain. The same authors have published proton NMR spectra of dihalo- and monohalo-permethylpolysilanes which were interpreted as supporting the model involving long-range transmission of electrons from Cl → Si dative bonding [3].

In the accompanying paper we have commented on the lack of correlation between ^{1}H and ^{29}Si chemical shifts in the permethylpolysilanes, and suggested that the distance of protons from the molecular framework makes them poor candidates for probing electronic effects at the backbone of these molecules [4]. Theoretical approaches to ^{29}Si shielding [5,6] generally assume that contributions arise only from the paramagnetic term in the manner originally

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established by Saika and Slichter for fluorine shifts [7]. The paramagnetic term is given by eq. 2, where ΔE_{av} is the average excitation energy, r_p and r_d are the

$$\sigma_p = -\frac{2e^2h^2}{3m^2c^2}\frac{1}{\Delta E_{av}}\{\langle r_p^{-3}\rangle \cdot p + \langle r_d^{-3}\rangle \cdot D\} \tag{2}$$

average distances of the valence p and d electrons from the examined nucleus, and P and D are expressions for the "unbalance" of the valence p and d electrons [8]. The P and D terms, and probably also r_p and r_d, should be affected by changes in the electronic environment consequent upon dative π-bonding. The ^{29}Si shifts should therefore be a good probe for examining these effects. In order to better assess the importance of chain length on electron distribution in the halosilanes we have determined the ^{29}Si and ^{13}C chemical shifts for many of the linear monochloro- and α,ω-dichloro-permethylpolysilanes and some α,ω-difluoropolysilanes.

Experimental

NMR spectra. All ^{29}Si NMR spectra were obtained on a Varian XL-100-15 NMR spectrometer using concentrated benzene-d_6 solutions in a 12 mm NMR sample tube. Broad band proton decoupling was employed to enhance signal strength by eliminating the multiplets arising from spin—spin coupling. The nuclear Overhauser enhancement which normally accompanies the decoupling was suppressed by employing a gyrocode gating technique so that signal intensities could be used for spectral analysis [9].

^{13}C NMR spectra were run on the JEOL FX-60 NMR spectrometer in 5 mm sample tubes, using the same sample as employed for ^{29}Si spectra whenever possible.

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

α,ω-Dichloropermethylpolysilanes. These were prepared by direct chlorination of the appropriate cyclic permethylpolysilane using the method reported earlier [10]. The various dichlorosilanes were separated by vacuum distillation. The infrared and proton NMR spectra of these compounds were identical with the published spectra [3,10].

Monochloropermethylpolysilanes. These were obtained from the appropriate dichlorosilane by methylation with methylmagnesium iodide in the manner reported by Allred and Boberski [2]. After separation of the various components by vacuum distillation the monochloro species were characterized by comparing their IR and ^{1}H NMR spectra with the values in the literature [3,10].

α,ω-Difluoropermethylsilanes. These compounds were synthesized in our laboratories by Mr. R. Knibbs. The general procedure is to add a portion of the corresponding dichlorosilane in benzene to a stirred mixture of H_2SO_4 and $NH_4F \cdot HF$. The reaction is allowed to stir overnight under nitrogen. The benzene layer is drawn off and the H_2SO_4 portion is washed several times with additional benzene. The combined benzene portions are washed several times with aqueous $NH_4F \cdot HF$ and dried over $NH_4F \cdot HF$ and sodium bisulfite. The

benzene layer is decanted and solvent is then removed. The difluorosilane is then purified by distillation under reduced pressure. The compounds were identified by NMR, IR, UV, mass spectrometry and elemental analysis.

Results and discussion

Substituent parameters

^{29}Si and ^{13}C NMR chemical shifts for the monochlorosilanes are given in Table 1 along with the shifts of the parent permethylsilanes for comparison. The ^{29}Si and ^{13}C chemical shifts of the permethyl compounds were reported in the preceding paper and shown to fit a linear equation using a series of additivity terms [4]. Qualitative examination of data in Table 1 shows that the shifts of the first three silicons in the monochlorosilanes vary systematically from the shifts of the permethyl compounds. An extension of the additivity scheme established for the permethyl series was therefore derived in which the chlorine atoms are treated as substituents. Chlorine substituent parameters, S_l, summarized in Table 2, describe how the chlorine atoms change the shifts of the parent compounds. The terms α, β and γ are used to describe the position of the chlorine relative to the silicon atom of interest. The ^{29}Si substituent parameters derived for the monochloro series fit the observed data with a standard deviation of 0.39 ppm, quite small considering the overall 75.5 ppm chemical shift range observed for this series of compounds. The ^{13}C parameters show a comparably good fit (SD = 0.15 ppm).

An additional check on the predictive values of these additivity terms is their ability to account for the chemical shifts in the α,ω-dichloro series. By using eq. 3 we can determine the chemical shift of any silicon in a position k in a

$$\delta(^{29}\text{Si})(k) = \delta(^{29}\text{Si})(k)\ \text{parent} + \sum_l n_l S_l(k) \qquad (3)$$

chain. The chemical shift of this silicon is equal to the chemical shift of a silicon in the same position in the unsubstituted chain plus the sum of appropriate substituent terms, $S_l(k)$. The notation $S_l(k)$ refers to the substituent term corresponding to the halogen in a position l relative to the silicon k under consideration and n_l indicates the number of such groups. An analogous equation was used to predict ^{13}C chemical shifts for the dichloro compounds. As can be seen from the comparison of experimental and calculated shifts (Table 3), except for the dichlorodisilane the fit is quite good (standard deviations of 0.47 ppm for ^{29}Si and 0.17 ppm for ^{13}C).

The additive substituent constants for chlorines in Table 2 change sign from positive to negative as their distance from the silicon or carbon atom becomes greater. This change in sign is interpreted as resulting from a balance between two opposing effects, one of which is deshielding attributable to the highly electronegative chlorine substituent. This large deshielding effect accounts for the pronounced downfield shift of the ^{29}Si directly attached to Cl (Table 2) as well as the moderate downfield shift of the carbons attached to this silicon. The weak shielding of the ^{29}Si nucleus upon substitution of chlorine in the more remote γ position can be explained as resulting from a through-space interaction between chlorine lone-pairs and the protons of the methyl groups

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TABLE 1

^{29}Si AND ^{13}C CHEMICAL SHIFTS OF SOME MONOCHLOROPOLYSILANES COMPARED TO THE PARENT PERMETHYLPOLYSILANES

Compound	δ(^{29}Si)						δ(^{13}C)					
	Si(1)	Si(2)	Si(3)	Si(4)	Si(5)	Si(6)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Si_2Me_6	−19.6	−19.6					−2.4	−2.4				
$ClSi_2Me_5$	22.8	−18.1					2.0	−3.1				
Si_3Me_8	−16.0	−48.5	−16.0				−1.4	−6.9	−1.4			
$ClSi_3Me_7$	26.8	−45.6	−16.2				3.0	−7.3	−1.6			
Si_4Me_{10}	−15.1	−44.7	−44.7	−15.1								
$ClSi_4Me_9$	27.0	−42.1	−45.0	−15.0								
Si_6Me_{14}	−15.0	−43.1	−39.2	−39.2	−43.1	−15.0	−1.1	−5.4	−4.1	−4.1	−5.4	−1.1
$ClSi_6Me_{13}$	26.7	−40.3	−39.7	−39.2	−43.0	−14.9	3.3	−5.9	−4.5	−4.4	−5.6	−1.2

TABLE 2

CHLORINE SUBSTITUENT PARAMETERS (S_l) FOR THE CHLOROPOLYSILANES, IN ppm [a]

Chlorine position [b]	$S_l(^{29}Si)$	$S_l(^{13}C)$
α	+42.2	+4.4
β	+2.5	−0.5
γ	−0.3	−0.4

[a] Positive values refer to downfield shifts. [b] The position of the chlorine relative to the silicon to which the methyl is attached.

TABLE 3

EXPERIMENTAL vs. CALCULATED ^{29}Si AND ^{13}C CHEMICAL SHIFTS FOR THE α, ω-DICHLOROPOLYSILANES [a]

Compound	$\delta(^{29}Si)$			$\delta(^{13}C)$		
	Si(1)	Si(2)	Si(3)	C(1)	C(2)	C(3)
$Cl(SiMe_2)_2Cl$	17.6 (25.1)			1.1 (1.5)		
$Cl(SiMe_2)_3Cl$	24.9 (25.9)	−43.8 (−43.5)		3.0 (2.7)	−7.7 (−7.9)	
$Cl(SiMe_2)_4Cl$	26.6 (26.8)	−42.6 (−42.5)		3.2 (3.3)	−6.3 (−6.5)	
$Cl(SiMe_2)_5Cl$	26.8 (27.2)	−41.0 (−40.9)	−41.5 (−41.3)	3.3 (3.3)	−5.9 (−6.0)	−4.8 (−5.0)
$Cl(SiMe_2)_6Cl$	26.6 (27.2)	−40.9 (−40.6)	−39.8 (−39.5)	3.3 (3.3)	−6.0 (−5.9)	−4.6 (−4.5)

[a] Calculated values are given in parentheses.

TABLE 4

NMR SPECTRAL DATA FOR SOME α, ω-DIFLUOROPERMETHYLSILANES

Compound	Position [a]	Chemical shifts in ppm				Coupling constants in Hz				
		^{19}F [b]	^{1}H [c]	^{13}C [c]	^{29}Si [c]	$^{1}J(SiF)$	$^{2}J(SiF)$	$^{2}J(CF)$	$^{3}J(CF)$	$^{3}J(HF)$
$F(SiMe_2)_2F$		−6.9		0.5	27.9	306	39.8	7.0	6.5	
$F(SiMe_2)_3F$	1	−9.4	0.28	1.1	37.0	308	25.8	12.2	1.8	8.8
	2		0.12	−8.0	−48.8					
$F(SiMe_2)_4F$ [d]	1	−8.3	0.29	1.4	37.9	309	27.8	12.2	1.3	8.8
	2		0.18	−6.7	−47.6					
$F(SiMe_2)_5F$	1	−8.2	0.30	1.5	38.0	310	25.8	12.0	2.4	8.7
	2		0.20	−6.2	−45.9					
	3		0.27	−5.2	−42.0					
$F(SiMe_2)_6F$	1	−8.2	0.31	1.5	38.0	310	23.8	12.2	2.2	8.4
	2		0.21	−6.0	−45.6					
	3		0.30	−4.6	−39.9					

[a] These positions refer to the distance of the silicon and attached groups from the end. [b] Internal C_6F_6 is used as reference. [c] Internal TMS is used as reference. [d] $^{5}J(CF)$ 0.4 Hz.

TABLE 5

FLUORINE SUBSTITUENT PARAMETERS (S_l) FOR THE DIFLUOROPOLYSILANES, IN ppm [a]

Fluorine position [b]	$S_l(^{29}Si)$	$S_l(^{13}C)$
α	+53.0	+2.6
β	−2.6	−0.7
γ	−0.7	−0.5

[a] Positive values refer to downfield shifts. [b] The position of the fluorine relative to the silicon to which the methyl is attached.

on this silicon. This type of interaction has been recognized as a contributing factor to the ^{13}C shifts of haloalkanes *. Because the inductive deshielding is attenuated with increasing distance from the chlorine atom this through-space shielding can become important enough to dominate over the deshielding effect at the more remote positions.

The NMR spectral data for the difluoropolysilanes are compiled in Table 4. The previously described chlorosilane data suggests that even in the absence of NMR shifts for the monofluorosilanes a series of substituent parameters (Table 5) can be developed using only the ^{29}Si and ^{13}C shifts for the longer chains to derive them. This amounts to assuming that no effect of the fluorine atom is transmitted beyond the third silicon in a chain. These parameters when used in eq. 3 produce chemical shifts which correspond to the observed ^{29}Si shifts with a standard deviation of 0.17 ppm and the ^{13}C shifts with a 0.15 ppm deviation. As in the case of the dichlorosilanes the disilane is excluded from the fit and the trisilane also shows substantial deviations in the ^{29}Si shifts.

Other NMR data for the fluorosilanes also indicate that no change in the electronic character of the silicon chain occurs for the longer polysilanes. First, the ^{19}F shifts of the four- to six-membered chains are remarkably similar. The dramatic changes for the disilane and trisilane parallel those observed in the ^{29}Si spectra. The $^{1}J(SiF)$ coupling constants also remain substantially the same throughout the entire series again indicating the independence of one fluorine from the other in the longer chains. As was the case for the ^{19}F chemical shifts, the one-bond SiF couplings exhibit larger variations for the shorter chains.

Deviations from additivity similar to those shown by the dihalodisilanes were found in the ^{13}C NMR spectra of 1,2-dihaloethanes [11]. For the dihaloethanes these deviations were attributed to perturbations of the electron distribution at the carbon nuclei because of interactions between vicinal halogens in the gauche rotamer. Analogous direct Cl—Cl interactions may lead to the additional shielding observed for the 1,2-dihalodisilanes.

Conclusions

The NMR chemical shift data for the halosilanes provide no evidence for increased back-donation with increasing chain length. Such a dependence

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* This γ-chlorine substituent effect can produce a net shielding only if the through-space shielding effect of a chlorine is greater than that of a methyl group. Analysis of the published data show that this is true for the haloalkanes [9].

would not be expected to produce the systematic trends and additive relationships found for the ^{29}Si and ^{13}C shifts of the chlorine and fluorine substituted silanes. Deviations from additivity are observed only for 1,2-dihalodisilanes, where they are probably due to a steric or through-space effect rather than to π-bonding. Moreover, the influence of chlorine and fluorine substituents is rapidly attenuated with increasing chain length as shown by the need for only three substituent parameters for each halogen to interpret the shifts *.

The differences in chemical reactivity of α-chlorosilanes and α,ω-dichloropolysilanes reported by Boberski and Allred can reasonably be ascribed to differences, either electronic or steric, in the transition states for the Grignard coupling reactions for these species, rather than to differences in electronic transmission in the ground state. Other evidence put forward in support of the long-range transmission theory consists of (a) reduction potentials for α-chloro- and α,ω-dichloro-polysilanes [12], and (b) proton chemical shift data for the same classes of compounds [2,3]. The reduction potentials are subject to the same kind of objection as the reactivity data; they may reflect differences in the stabilities of the anions after electron transfer or of the molecules adsorbed at the electrode surface, rather than ground state differences **.

Of all of the evidence offered for long-range electronic transmission, only the proton NMR chemical shifts necessarily reflect ground-state effects. Boberski and Allred observed that (1) in $X(SiMe_2)_nX$ compounds the proton resonance for the $SiMe_2X$ groups tend to shift upfield with increasing chain length, and (2) the chemical shifts for the same $SiMe_2X$ groups in monohalopermethylsilanes occur upfield from those of the corresponding α,ω-dihalopermethylsilanes, and (for the chlorides) this difference increases with increasing chain length.

The differences in $\delta(^1H)$ noted by Boberski and Allred are quite small, generally 0.03 to 0.05 ppm. This is not larger than the differences in proton chemical shifts observable on changing solvent, which can be as large as 0.03 ppm (CCl_4 vs. Et_2O) or 0.09 ppm (CCl_4 vs. C_6D_6). The small effects which are observed are found only for the $SiMe_2X$ protons. If long-range transmission of back-bonding from halogen to Si were taking place one would logically expect a similar upfield shift for the $SiMe_3$ protons of $X(SiMe_2)_6CH_3$ vs. $CH_3(SiMe_2)_6CH_3$, but this is not observed. Moreover, the chemical shift differences reported by Boberski and Allred appear to be independent of the nature of the halogen (F, Cl or I). This fact alone suggests that dative bonding is not responsible for the effects which are observed.

The reasons for the small differences in the $SiMe_2X$ proton chemical shifts reported by Boberski and Allred are not clear, but we believe they must be due to other things than long-range electronic transmission; possibilities include specific solvation effects or weak intermolecular interactions. Further experiments to elucidate the causes of these small chemical shift effects, and of the reactivity differences described by Boberski and Allred, now seem warranted.

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* Our results do not eliminate the possibility of dative π-bonding from halogen to silicon in these compounds. Rahther they suggest that any such dative bonding is essentially independent of chain length in the ground state of the chloro- and fluoro-polysilanes.

** The reduction potentials reported for halosilanes may in any case require reinterpretation, because recent work by Corriu et al. apparently shows that the species reduced in these experiments was HCl formed by hydrolysis rather than the chlorosilane [13].

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