

SILICON — 29 AND CARBON — 13 NMR SPECTRA
OF THE COMPOUNDS OF THE TYPE $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{OR}^*$

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²⁹Si- and ¹³C-NMR chemical shifts are presented for a number of compounds of the general type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{OR}$ with the substituents $\text{R} = \text{H}, \text{CH}_3, \text{Si}(\text{CH}_3)_3, (\text{CH}_2)_m\text{Si}(\text{CH}_3)_3,$ and $\text{C}(\text{O})\text{CH}_3$. In both spectra the acetoxy substituted derivatives appear different from all the others. The ²⁹Si chemical shifts are more sensitive to the alkyl chain length than to the nature of the substituent R, for m larger than two, the effects of OR groups are small, but practically in all cases these effects are diamagnetic. Such diamagnetic effects are in agreement with the polarization of the trimethylsilyl group as calculated by the Del Re method but such an interpretation leads to discrepancies in predicted shifts in other compounds. The ¹³C chemical shifts follow the dependence on the total net charge on the carbon atom but considerable deviations from additivity of substituent effects are observed in compounds with $m = 1$ and 2.

In continuation of our studies¹⁻⁷ of NMR spectra of organosilicon compounds of the type



aimed at better understanding of the factors contributing to the observed chemical shifts of the nuclei present in these molecules we have investigated ²⁹Si and ¹³C NMR spectra of the compounds of this type having $n = 0$ (i.e. trimethylsilyl derivatives) and $\text{Y} = \text{OR}$, where the substituent R is $\text{H}, \text{CH}_3, (\text{CH}_2)_m\text{Si}(\text{CH}_3)_3, \text{Si}(\text{CH}_3)_3,$ or $\text{C}(\text{O})\text{CH}_3$ group. The results are presented in this communication.

RESULTS AND DISCUSSION

The observed ²⁹Si and ¹³C chemical shifts are given in Table I. The chemical shifts were measured by the same technique (CW mode, external referencing) and on the same spectrometer as described earlier¹.

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²⁹Si Chemical Shifts. The data in Table I confirm the usual expectation that the silicon chemical shifts in the studied compounds approach the shifts in alkyltrimethylsilanes as the length of the alkyl chain *m* becomes sufficiently large. The only exceptions to this trend are the hydroxysubstituted derivative with *m* = 3 and all the acetoxysubstituted compounds which will be discussed later. However, the OR substituents shift the ²⁹Si resonance surprisingly to a higher field (negative SCS values Δ(²⁹Si)) relative to the parent alkyltrimethylsilanes. Previously, upfield SCS were observed in such compounds of the type I in which electronegative substituents Y could polarize the Si—X groups (in X—Si—(CH₂)_m—Y fragments with X = Cl,

TABLE I
²⁹Si- and ¹³C-NMR Chemical Shifts in the Compounds of the Type (CH₃)₃Si(CH₂)_mOR^a

<i>m</i>	R	δ(²⁹ Si)	Δ(²⁹ Si) ^b	CH ₃ Si	δ(¹³ C) ^c				R ^d (O—C)	R ^e (CH ₃)
					C-α	C-β	C-γ	C-δ		
1	H	-2.5	-2.5	-4.4	54.2				—	—
	CH ₃	-2.1	-2.1	-3.5	66.9				62.7	62.7
	C ₂ H ₅	-2.6	-2.6	-3.9	63.6				69.8	14.4
	R ^g	-3.6	-3.6	-4.7	68.7				68.7	-4.7
	Si(CH ₃) ₃ ^h	-2.0	-2.0	-4.6	53.8				69.9	-2.1
	C(O)CH ₃	0.3	0.3	-2.5	58.1				169.9	20.8
2	H	-2.0	-3.6	-2.6	20.4	57.3				
	CH ₃	-0.1	-1.7	-1.4	18.1	69.4			57.3	57.3
	R ^g	-0.4	-2.0	-1.3	18.2	66.6			66.6	-1.3
	Si(CH ₃) ₃ ⁱ	-1.3	-2.9	-1.9 ^f	20.3	57.7			—	-2.4 ^f
	C(O)CH ₃	-1.0	-2.6	-2.6	16.6	60.8			168.4	19.6
	3	H	1.7	1.0	-1.3	12.8	27.4	64.9		
CH ₃		0.4	-0.3	-2.6	12.2	23.5	74.8		57.2	57.2
R ^g		0.0	-0.7	-2.4	12.1	23.5	72.5		72.5	-2.4
C(O)CH ₃		0.9	0.2	-2.3	12.1	23.0	66.1		168.6	20.0
4		H	0.4	-0.2	-1.9	16.2	19.8	36.1	61.0	
	R ^g	0.4	-0.2							
	Si(CH ₃) ₃ ^j	0.1	-0.5	-1.3 ^f	15.6	19.4	35.7	60.8		-2.5 ^f
	C(O)CH ₃	1.3	0.7	-1.6	16.6	20.6	32.7	63.7	169.3	20.6

^a All the chemical shifts in δ-scale, (ppm units, relative to external TMS, paramagnetic shifts positive) error ±0.3 ppm. ^b Δ = δ((CH₃)₃Si(CH₂)_mOR) - δ((CH₃)₃Si(CH₂)_mH), the ²⁹Si chemical shifts in (CH₃)₃Si(CH₂)_mH compounds taken from ref.⁷. ^c The position of carbon atoms relative to the silicon atom. ^d Structurally different carbon atoms. ^e Methylcarbons of different types. ^f The assignment of the two lines can be interchanged. ^g R = (CH₃)₃Si(CH₂)_m. ^h δ(²⁹SiO) = 16.1. ⁱ δ(²⁹SiO) = 13.1. ^j δ(²⁹SiO) = 13.9.

TABLE II
Total Net σ -Electron Changes in $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_m\text{OR}$ Compounds, Calculated by the Del Re Method^a

<i>m</i>	R	Q_{Si}	$Q_{\text{CH}_3}^b$	$Q_{\text{C}-\alpha}$	$Q_{\text{C}-\beta}$	$Q_{\text{C}-\gamma}$	$Q_{\text{C}-\delta}$	Q_{O}	$Q_{\text{R}(\text{OC})}^b$	$Q_{\text{R}(\text{CH}_3)}^b$
1	H	-0.012	-0.140	-0.008	—	—	—	-0.447	—	—
	CH ₃	-0.008	-0.141	-0.004	—	—	—	-0.261	-0.024	-0.024
	C ₂ H ₅	-0.008	-0.141	-0.004	—	—	—	-0.266	0.024	-0.106
	R ^c	-0.008	-0.141	-0.003	—	—	—	-0.254	-0.003	—
	Si(CH ₃) ₃	-0.008 ^d	-0.141	-0.005	—	—	—	-0.331	—	-0.146
2	H	0.017	-0.145	-0.086	0.041	—	—	-0.457	—	—
	CH ₃	0.017	-0.145	-0.087	0.029	—	—	-0.272	-0.025	-0.025
	R ^c	0.017	-0.145	-0.087	0.028	—	—	-0.276	0.028	—
	Si(CH ₃) ₃	0.017 ^e	-0.145	-0.087	0.028	—	—	-0.342	—	-0.146
3	H	0.021	-0.145	-0.097	-0.055	0.035	—	-0.458	—	—
	CH ₃	0.021	-0.145	-0.098	-0.056	0.023	—	-0.274	-0.025	-0.025
	R ^c	0.021	-0.145	-0.098	-0.056	0.022	—	-0.278	0.022	—
	Si(CH ₃) ₃	0.021 ^e	-0.145	-0.098	-0.056	0.022	—	-0.343	—	-0.146
4	H	0.021	-0.145	-0.099	-0.067	-0.060	0.034	-0.458	—	—
	R ^c	0.021	-0.145	-0.099	-0.067	-0.062	0.022	-0.278	0.022	—
	Si(CH ₃) ₃	0.021 ^e	-0.145	-0.099	-0.067	-0.062	0.021	-0.342	—	-0.146

^a Details of the calculations and parameters used are given in ref.³. ^b Q_{C} of the group indicated by the subscript. ^c R = $(\text{CH}_2)_m\text{Si}(\text{CH}_3)_3$.
^d Q_{Si} in C-Si-C, in O-Si-C Q_{Si} = 0.230. ^e Q_{Si} in C-Si-C, in O-Si-C Q_{Si} = 0.229.

OC_2H_5 , F, and others but not if $\text{X} = \text{CH}_3$) so that the electron density at the silicon nucleus has been increased. In agreement with the theories of silicon shielding^{8,9}, only downfield SCS (positive values) of electronegative substituents Y were observed in trimethylsilyl derivatives, which finding was taken as an additional evidence for the absence of $\text{Si}\dots\text{Y}$ "through space" interaction^{3,10}, with electron transfer in the direction $\text{Si}\leftarrow\text{Y}$. The only exceptions so far reported⁴ were the chemical shift in fluoromethyltrimethylsilane (but not in 3-fluoropropyl- or 5-fluoropentyltrimethylsilane) and in 2-aminoethyltrimethylsilane³ (but not in aminomethyl- or 3-aminopropyltrimethylsilane). It might therefore occur that the presently reported negative SCS values for trimethylsilyl derivatives indicate the mentioned "through space" interaction. This seems, however, unlikely since the observed SCS values depend only very little on the nature of the group R (except for $\text{R} = \text{C}(\text{O})\text{CH}_3$). An explanation of the negative SCS values in the trimethylsilyl derivatives which is consistent with the other cases of observed negative SCS values is offered by the electron distributions calculated by the simple Del Re method.

According to these charge distributions in alkyltrimethylsilanes⁷, fluoroalkyltrimethylsilanes⁴, and in the presently studied compounds (Table II), the inductive effects of fluorine and of the OR groups are so strong and propagate so (as given by the empirical Del Re parameters³) that the OR groups polarize the $\text{Si}-\text{C}$ bonds of the trimethylsilyl groups in the derivatives with $m = 1$ and even 2 so that the total (positive) charge on the silicon atom decreases (actually it becomes negative) below that in the parent alkyltrimethylsilane; similarly does fluorine in the compound with $m = 1$. Since the theories^{8,9,14-16} in accord with other experimental findings predict for tetraalkylsilanes increasing shielding with decreasing total (positive) charge on the silicon atom, the described changes in the total charges due to the substitution of one hydrogen atom of the alkylgroup by F or OR groups should lead to negative SCS values as observed.

Such interpretation would be in accord with the interpretation of other observed negative SCS but it must be mentioned, that the Del Re calculations also predict negative SCS for aminomethyltrimethylsilane³ and chloromethyltrimethylsilane¹⁷ while positive shifts were observed^{3,18}. As it is apparent from Table III the much more elaborate CNDO/2 calculations for some model compounds (which might not be adequate) lead to the same predictions of SCS except for chloromethyl derivative. On the basis of these results we can only conclude that it is not certain whether the above discussed agreement with the signs of SCS is not only fortuitous. Obviously, the effects are too small and the calculations and the theories are only very approximate as well as the correlations with the total charges.

As already mentioned, the acetoxy derivatives exhibit somewhat different chemical shifts than the rest of the studied compounds, the difference is most striking (a small positive SCS) in the case of the compound with $m = 1$, in which the acetylation of the corresponding alcohol causes about 2.5 ppm downfield shift of ^{29}Si resonance (and

not null shift as would follow from the data of ref.²² which are in error since they give in several cases $\delta(^{13}\text{C})$ of CH_3Si for $\delta(^{29}\text{Si})$). In some conformations of this compound the carboxyl oxygen atom can get very close to the silicon atom (the shortest distance between the two atoms is 1.7 Å if standard bond lengths and angles²³ are assumed while the sum of the van der Waals radii is 3.6 Å (ref.²⁴). Under such circumstances the effects of electric field and magnetic anisotropy cannot be estimated.

In the carbon analogues of the studied compounds the quaternary carbon chemical shift exhibits quite different SCS. According to the available data (Table IV) this car-

TABLE III

Net Charges on Silicon Atom Calculated by CNDO/2 Method

Compound	Q_{Si}	Compound	Q_{Si}
$\text{H}_3\text{SiCH}_3^a$	0.569	$\text{H}_3\text{Si}(\text{CH}_2)_2\text{OH}^d$	0.584
$\text{H}_3\text{SiCH}_2\text{OH}^b$	0.551	$\text{H}_3\text{Si}(\text{CH}_2)_3\text{OH}^d$	0.560
$\text{H}_3\text{SiCH}_2\text{F}^b$	0.537	$(\text{CH}_3)_3\text{SiCH}_2\text{OH}^d$	0.563
$\text{H}_3\text{SiCH}_2\text{NH}_2^b$	0.454		
$\text{H}_3\text{SiCH}_2\text{Cl}^c$	0.586		

^a Staggered conformation. For the details of CNDO/2 calculations: ^b ref.¹⁹; ^c ref.²⁰; ^d ref.²¹.

TABLE IV

¹³C-NMR Chemical Shifts in Some Tert-Butyl Derivatives of the Type $(\text{CH}_3)_3\text{C}(\text{CH}_2)_m\text{R}$

<i>m</i>	R	$\text{CH}_3(\text{C})$	C	$\text{CH}_2\text{-}\alpha^a$	$\text{CH}_2\text{-}\beta^a$	$\text{CH}_2\text{-}\gamma^a$	
1	H^b	31.6	28.0	31.6	—	—	—
	OH^c	26.6	32.9	72.9	—	—	—
	$\text{OSi}(\text{CH}_3)_3$	25.5	31.8	71.9	—	—	—
	$\text{OC}(\text{O})\text{CH}_3$	26.6	31.5	73.4	—	—	—
2	H^b	28.7	30.3	36.5	8.5	—	—
	OH^c	30.1	30.0	46.7	59.2	—	—
	OH^d	29.71	29.44	46.20	58.98	—	—
	$\text{OSi}(\text{CH}_3)_3$						
3	H^b	29.5	30.6	47.3	18.1	15.1	—
	$\text{OSi}(\text{CH}_3)_3$	29.1	29.7	40.0	27.9	62.7	—
	H^b	29.2	30.1	44.1	27.0	23.7	13.9

^a Position relative to quaternary carbon atom. ^b Data taken from ref.¹¹. ^c Data converted from ref.¹² using $\delta(\text{CS}_2) = 192.8$. ^d Data taken from ref.¹³.

bon chemical shift varies with the nature of the substituent R only if $m = 1$, in higher alkyl derivatives the quaternary carbon occurs always at $\delta = 30.2 \pm 0.5$. In agreement with the general trends in the shielding of carbons in aliphatic alcohols, α and β carbons are deshielded and γ carbon is shielded in neopentyl alcohol (relatively to neopentane) and therefore the SCS values of the quaternary carbons are positive. The shifts calculated according to equations of Roberts and coworkers¹² from the shifts in 2,2-dimethylbutane agree satisfactorily with those observed, the difference between the two values exceeds the standard deviation¹² only in the case of the shift of quaternary carbon. Acetylation of the alcohol brings about 0.5 ppm downfield shift of the α carbon and 1.4 ppm upfield β effect on the quaternary carbon. Acetylation shifts of these directions have been observed in other compounds²⁵ though somewhat larger effects were considered typical²⁶. Obviously, in the comparison with the

TABLE V

¹³C Chemical Shifts of Methylene Carbons Calculated According to the Additivity of SCS in $(\text{CH}_3)_3\text{Si}^*(\text{CH}_2)_m\text{OR}$ Compounds^a

<i>m</i>	R	δ/SCS^b			δ/SCS^b			δ/SCS^b			δ/SCS^b		
		C- α	δ_{calc}^a	Δ^c	C- β	δ_{calc}^a	Δ^c	C- γ	δ_{calc}^a	Δ^c	C- δ	δ_{calc}^a	Δ^c
4	$(\text{CH}_3)_3\text{Si}^*$	3.1			1.0			1.0			0.2		
	H ^d	13.9	17.0	-0.8	19.4	20.4	-0.6	35.3	36.3	-0.2	61.7	61.9	-0.9
	Si(CH ₃) ₃ ^e	12.9	16.0	-0.4	18.3	19.3	0.1	34.4	35.4	0.3	61.3	61.5	-0.7
3	$(\text{CH}_3)_3\text{Si}^*$	4.0			1.5			2.6					
	H ^d	10.3	14.3	-1.5	26.1	27.6	-0.2	63.9	66.5	-1.6			
2	$(\text{CH}_3)_3\text{Si}^*$	1.9			0.3								
	H ^d	17.9	19.8	0.6	57.3	57.6	-0.6						
	CH ₃ ^f	14.4	16.3	1.8	67.4	67.7	1.7						
	Si(CH ₃) ₃ ^e	17.3	19.2	1.1	56.5	56.8	0.9						
	C(O)CH ₃ ^f	13.5	15.4	1.2	59.5	59.8	7.0						
1	$(\text{CH}_3)_3\text{Si}^*$	2.1											
	H ^d	49.3	51.4	2.8									
	CH ₃ ^f	60.0	62.1	4.8									
	C ₂ H ₅ ^f	57.3	59.4	2.1									
	R ^g	66.9	69.0	-0.3									
	C(O)CH ₃ ^f	50.4	52.5	-5.5									

^a The shifts calculated as $\delta_{\text{calc}} = \delta(\text{H}(\text{CH}_2)_m\text{OR}) + \text{SCS}((\text{CH}_3)_3\text{Si}^*)$. The carbon position relative to the silicon atom. ^b Unless R = $(\text{CH}_3)_3\text{Si}^*$, the chemical shift of the corresponding carbon in $\text{H}(\text{CH}_2)_m\text{OR}$ compound. If R = $(\text{CH}_3)_3\text{Si}^*$ the SCS values of $(\text{CH}_3)_3\text{Si}$ taken from ref.⁷ are given. ^c $\Delta = \delta_{\text{obs}} - \delta_{\text{calc}}$. ^d Data of ref.¹² converted using $\delta(\text{SC}_2) = 192.8$. ^e Data taken from ref.²⁸. ^f Data of ref.²⁵ converted using $\delta(\text{CS}_2) = 192.8$. ^g R = $(\text{CH}_2)_m\text{Si}(\text{CH}_3)_3$.

carbon analogues, the acetoxymethyltrimethylsilane with its acetylation shifts appears also anomalous.

The magnitudes of acetylation shifts in other compounds were interpreted in the terms of steric effects²⁵. In some instances, the steric effects on silicon shielding in organosilicon compounds were shown to be different from those in their carbon analogues, namely, steric upfield shifts were observed in *cis*-1,2-bis(trimethylsilyl)ethene while the quaternary carbons in its carbon analogue were shifted downfield (relative to *trans*-1,2-di(tert-butyl)ethene)²⁷. Therefore, it seems possible that the steric effects are at play here too but such a conclusion would be premature at present especially as it is not supported by ¹³C chemical shifts of the acetoxy group; more data on acetoxyalkylsubstituted silanes are needed to justify such an interpretation.

¹³C Chemical Shifts. As in other carbonfunctional organosilicon compounds of the type I the ¹³C chemical shifts in the studied compounds fit reasonably well in the established correlations^{3,29} of the chemical shift with the total net charge Q_C on the given carbon atom as calculated by the simple Del Re method using the empirical parameters given elsewhere³. For the obvious reasons the largest spread of the data points around the correlation line is observed for the carbon atoms bonded to the oxygen atom.

In the cases when the ¹³C chemical shift data are available for $\text{H}(\text{CH}_2)_m\text{OR}$ compounds the additivity of substituent effects of OR and $(\text{CH}_3)_3\text{Si}$ groups on the shielding of methylene carbons could be tested. The results are summarized in Table V.* Though the data are rather limited they seem to indicate that the additivity is well satisfied if the two substituents are separated by four or three methylene carbon atoms. For shorter separations sizable deviations are observed especially in compounds substituted by the acetoxy group. It is not clear, however, whether these deviations are caused by changes in conformer populations or molecular geometry (relative to the monosubstituted alkanes) or by a direct interaction of the two substituents.

Finally, it should be mentioned that the substituent effects of $\text{OSi}(\text{CH}_3)_3$ group (both on ¹³C and ²⁹Si chemical shifts) are almost identical with the corresponding effects of OH group. This similarity of the effects of the two groups has been noted before for rigid skeletons (of steroids³⁰ and adamantane derivatives³¹).

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* The calculated shift, δ_{calc} , is the sum of SCS's of the two substituents and of the shift $\delta(\text{HCH})$ of the corresponding carbon in the appropriate hydrocarbon, *i.e.* $\delta_{\text{calc}} = \text{SCS}(\text{OR}) + \text{SCS}(\text{Me}_3\text{Si}) + \delta(\text{HCH})$ or, which is the same, $\delta_{\text{calc}} = \text{SCS}(\text{Me}_3\text{Si}) + \delta(\text{HCOR})$, where $\delta(\text{HCOR})$ is the shift of the corresponding carbon atom in $\text{H}(\text{CH}_2)_m\text{OR}$ compound.

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