

SILICON-29, CARBON-13 AND PROTON NMR SPECTRA OF PHENYL AND BENZYL SUBSTITUTED SILANES*

NGUYEN-DUC-CHUY^a, V.CHVALOVSKÝ^a, J.SCHRAML^a, M.MÄGI^b and E.LIPPMAA^b

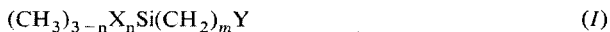
^a Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát

^b Institute of Cybernetics, Estonian Academy of Sciences, Tallinn, USSR

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²⁹Si, ¹³C and ¹H NMR data are presented for a series of related phenyl- and benzyl-substituted silanes and the present state of shielding theory of heavier nuclei is outlined. Several empirical correlations are found to hold between pairs of data (the most notable being linear relationships between the Si and the C-4 chemical shifts in the two classes of compounds). The results confirm that the CH₂SiR₃ group acts as an electron donor to the benzene ring in benzylsilanes, while SiR₃ is an electron acceptor in phenylsilanes.

In order to account for the properties of the compounds of general formula *I*, in which we are currently



interested¹⁻⁵, interactions depicted schematically in Fig. 1 have been proposed in the literature for electronegative atoms Y with unshared electrons (for other, less relevant, types of interaction see ref.⁵). In an attempt to decide among these interactions we have undertaken an extensive NMR study which would eventually involve all the magnetically active nuclei (²⁹Si, ¹³C, ¹⁴N, ¹⁷O, ¹⁹F, and ¹H) encountered in these molecules. At the onset of this work it was hoped that through these nuclei we could probe, though indirectly, the environment of various atoms in different places in the molecules and thus get a picture of the changes in the electron distribution throughout the series of compounds. Though some preliminary accounts of our work have been published⁶⁻⁹, the present paper begins a series of papers in which we, for the first time, shall try to interpret the NMR spectra of carbonfunctional silanes (*I*) in structural terms. We start this series with the class of compounds (*I*) which have a phenyl group for the substituent Y since relations between NMR parameters and structure are best documented for benzene derivatives and since formation of pseudocyclic structures (interaction D, E and F of Fig. 1) is unlikely to take place in this case (in contrast to the case of Y = NR₂ for which such interactions have been suggested in the literature¹⁰).

In this paper we shall deal with ²⁹Si, ¹³C and ¹H NMR only. The present readily availability of ¹H and ¹³C NMR spectrometers, data and structural correlations are contrasted by our limited knowledge of ²⁹Si NMR. Only a few years back, the im-

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improvements of experimental techniques since the first cumbersome measurements of ^{29}Si NMR (ref.¹¹⁻¹³) (spin stabilization, time-sharing, frequency sweep, spectrum accumulation, proton-decoupling)¹⁴⁻¹⁶ permitted measurements of large series of compounds¹⁷ and the present research could be initiated. In the meantime the development of the Fourier transform (FT) technique made measurements of diluted samples and internally referenced silicon chemical shifts possible. (Since the bulk of the present work had been done before FT technique was available to us, we give here only the results obtained by continuous wave (CW) method.)

The first papers¹¹⁻¹³ on ^{29}Si NMR interpreted the changes in ^{29}Si chemical shifts in terms of the inductive effect and $(p \rightarrow d)_\pi$ interactions of the silicon atom with directly bonded electron donors. The recent explosion of the ^{29}Si NMR field has brought not only new data but also new, conflicting and contradictory theoretical approaches. Till this chaos in shielding theory is solved, any interpretation of silicon

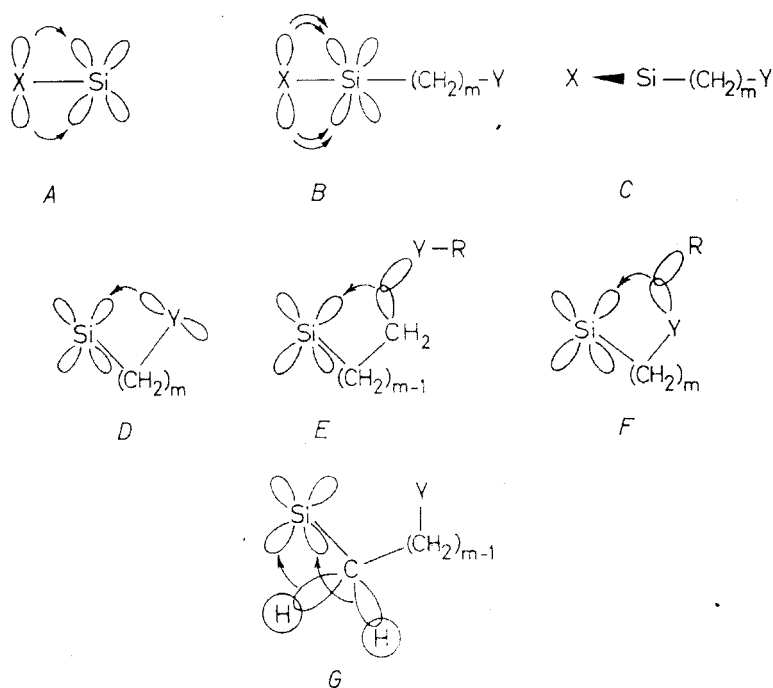


FIG. 1

Interactions Proposed for $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{Y}$ Compounds

A $(p-d)_\pi$ Interaction X—Si; *B* enhanced $(p-d)_\pi$ interaction X—Si; *C* polarized X—Si σ bond; *D* $(p-d)_\sigma$ interaction Y—Si; *E* $\sigma-d$ (3 center) interaction; *F* $\sigma-d$ (3 center) interaction; *G* hyperconjugation. (Arrows indicate the direction of electron transfer, depending on the nature of Y, substituent R might be present).

shielding must be considered as hypothetical. For this reason we shall be more concerned in finding empirical correlations and rules affecting silicon shifts and will try to reach structural conclusions on the basis of the resonances of nuclei with a somewhat clearer interpretation or with sufficient background material to make meaningful comparisons.

EXPERIMENTAL

Compounds studied in this paper were prepared in the course of some of our previous studies¹⁸⁻²⁴. The only exception was trifluorobenzylsilane which was prepared anew according to the known procedure^{21,25}. Some of the samples had to be purified either by distillation or by preparative g.l. chromatography. The purity and identity of the samples were checked by g.l. chromatography and by NMR spectroscopy.

Scales. All the ¹H, ¹³C, and ²⁹Si chemical shifts reported in the present paper are given in the δ -scale, *i.e.* in p.p.m. relative to the line of the same nuclei in tetramethylsilane (TMS) with the shifts to lower field (paramagnetic shifts, lower shielding) being positive.

From the chemical point of view, TMS is, due to its chemical inertness (for a review of negative examples see²⁶), superior to the siloxanes or alkoxy silanes sometimes used as references in ²⁹Si NMR work. Though the latter compounds have signals at higher fields than TMS, they are known to associate with proton donors^{26,27} and have a reactive Si—O bond. Also, TMS appears to be a more universal reference compound, serving all the three very important nuclei ¹H, ¹³C, and ²⁹Si. The δ -scale used here is that accepted in ¹H and ¹³C NMR spectroscopy. Its early and universal acceptance in ²⁹Si NMR studies would be beneficial to everybody active in the field.

²⁹Si and ¹³C NMR spectra were measured using the time-sharing spectrometer and experimental technique previously described¹⁴. In short, the two spectra were measured at 11.91 and 15.09 MHz, resp., using a 512 channel CAT (Nokia LP 4050) to accumulate CW absorption — mode frequency-swept spectra. The spectra were observed both with and without proton decoupling. The shifts were digitally measured in neat samples (except for (C₆H₅)₄Si and (C₆H₅)₃.SiCH₂OH which were measured in chloroform solutions) with 0.2 to 0.3 p.p.m. maximum error and referenced to external TMS.

¹H NMR spectra were measured on a modified Tesla BS 477 spectrometer operating at 60 MHz. The spectra were measured in 1 : 1 and 1 : 9 (volume) solutions in tetrachloromethane (dried over P₂O₅ and distilled) containing less than 10 mg/l of water. For convenience 8% (v/v) of cyclohexane was added to the tetrachloromethane to serve as a secondary reference compound and to provide a lock signal. Ethoxy and fluoro derivatives were measured with a drop of hexamethyldisilane (prepared by the described method²⁸) or dioxane, resp., added to have a convenient lock signal. The chemical shifts were converted to δ -scale using the shift of cyclohexane $\delta = 1.436$ p.p.m.²⁹. Since the determination of ¹H—²⁹Si coupling constants was not always possible in diluted solutions, neat liquids were also measured. Concentration dependence of the chemical shifts was very small, no extrapolation to infinite dilution was made.

Spectral assignment of ²⁹Si resonance is no problem in the compounds under study which each contain only one silicon atom. Assignment of proton lines to CH₂ and CH₃ protons is also trivial. The spectra of these parts of the molecules were analysed as the first-order spectra only; no attempt has been made to analyse the phenyl proton part of the spectra. In carbon-13 NMR spectra the assignment of CH₂ and CH₃ lines with the use of undecoupled spectra and off-resonance

decoupling was not difficult. The aromatic parts of these spectra could be assigned only after some considerations. In general, lines of carbons C-1 and C-4 could be differentiated from those of C-2 and C-3 on intensity ground (the number indicates the position of the ring carbon atom relative to silyl substituent). Lines of C-1 and C-4 differ in the nuclear Overhauser enhancement (NOE) observed with protons being noise decoupled; the NOE is larger for C-4 lines. Lines of C-2 and C-3 carbons were assigned on the basis of the empirical finding that shifts of *meta* carbons are the least affected by substitution³⁰. The assignment offered in the present work was confirmed in a limited study in which *para* substituted phenylsilanes and benzylsilanes were measured, and the shifts of the ring carbon atoms agreed well with those predicted on the basis of the additivity relationship and the shifts in phenyl- and benzylsilanes³¹. In two benzylsilanes, however, the shifts of C-2 and C-3 carbon atoms (differing by 0.6 p.p.m.) could not be assigned.

TABLE I
²⁹Si and ¹³C NMR Chemical Shifts in Phenylsilanes C₆H₅R^a

R	No ^b	δ (²⁹ Si)	$\Delta_0\delta$ (²⁹ Si) ^c	C-1 ^d	C-2 ^d	δ (¹³ C)	C-3 ^d	C-4 ^d	CH ₃ -Si
Si(CH ₃) ₃	1	-5.1	-5.1	139.4	132.8	127.3	128.3	-1.0	
Si(CH ₃) ₂ Cl	2	19.9	-10.0	136.2	133.2	128.3	130.3	2.4	
Si(CH ₃)Cl ₂	3	17.9	-13.9	132.2	132.4	127.7	131.0	5.1	
SiCl ₃	4	-0.8	-13.0	131.4	133.1	128.6	132.8	-	
Si(CH ₃) ₂ (OC ₂ H ₅)	5	5.1	-8.4	137.8	133.0	127.4	129.0	-1.8 ^e	
Si(CH ₃)(OC ₂ H ₅) ₂	6	-20.2	-14.1	133.8	132.9	126.7	128.8	-4.9 ^f	
Si(OC ₂ H ₅) ₃	7	-59.4	-14.9	131.3	134.2	127.2	129.5	- ^g	
Si(CH ₃) ₂ F	8	19.8 ^h	-15.6	136.0 ⁱ	132.9	127.9	130.1	-1.5 ^j	
Si(CH ₃)F ₂	9	-12.4 ^k	-21.2	129.7	133.0	128.0	131.5	-5.8 ^l	
SiF ₃	10	-73.2 ^m	-21.4	120.1 ⁿ	133.9	128.1	132.7	-	
SiH ₃	11	-59.9	^o	127.5	135.5	127.7	129.4	-	
Si(C ₆ H ₅) ₃		^p		134.5 ^q	136.6 ^q	128.1 ^q	129.9 ^q	-	
Si(C ₆ H ₅)H ₂		-33.6	^o	131.6	136.0	128.4	130.2	-	
Si(CH ₃)(C ₆ H ₅) ₂		-11.9	^o	136.4	135.6	128.0	129.6	-2.9	
Si(C ₆ H ₅) ₂ CH ₂ OH		-15.5 ^q	^o	133.1 ^q	135.7 ^q	128.6 ^q	129.8 ^q	^r	

^a All chemical shifts are in δ -scale (*i.e.* p.p.m. units, positive values indicate shifts to lower field from TMS line), maximum error ± 0.3 p.p.m., measured in neat liquids. ^b Serial number of the compound for reference in figures. ^c Substituent effect of phenyl groups directly attached to silicon, defined as $\Delta_0\delta = \delta(\text{C}_6\text{H}_5\text{R}) - \delta(\text{CH}_3\text{R})$. ^d Aryl carbon, position relative to the substituent. ^e δ (¹³C) in C₂H₅O 18.5 and 58.1 p.p.m. for CH₃ and CH₂ carbons, resp. ^f δ (¹³C) in C₂H₅O 17.5 and 57.4 p.p.m. for CH₃ and CH₂ carbons, resp. ^g δ (¹³C) in C₂H₅O 17.9 and 58.2 p.p.m. for CH₃ and CH₂ carbons, resp. ^h $J_{\text{F-Si}} = 278 \pm 2$ Hz. ⁱ $J_{\text{F-C}} = 16.5 \pm 1$ Hz. ^j $J_{\text{F-C}} = 16.5 \pm 1$ Hz. ^k $J_{\text{F-Si}} = 287 \pm 2$ Hz. ^l $J_{\text{F-C}} = 16.5 \pm 1$ Hz. ^m $J_{\text{F-Si}} = 268 \pm 2$ Hz. ⁿ $J_{\text{F-C}} = 25 \pm 2$ Hz. ^o Data not available. ^p Could not be measured because of low solubility. ^q Measured in CHCl₃ solution. ^r δ (¹³C) in CH₂O 53.5 p.p.m.

RESULTS AND DISCUSSION

NMR data for phenyl- and benzylsilanes are collected in Tables I–III.

The chemical shift δ^A (of the ^{29}Si or ^{13}C nucleus) was determined from frequency-swept spectra as

$$\delta^A = (\nu^A - \nu^R)/\nu_0, \quad (1)$$

where $\nu^A - \nu^R$ is the difference between the resonance frequencies of a sample (ν^A) and reference (ν^R , R = TMS here) and ν_0 is the oscillator frequency employed for recording the spectra (ν_0 was fixed to 11.91 and 15.09 MHz for ^{29}Si and ^{13}C NMR, resp.). Since ν_0 could differ from ν^R or ν^A by as much as 6 kHz¹⁴, the chemical shift is with a precision of $2 \cdot 10^{-11}$ equal³² to the difference of the shielding constants σ_{obs}^R and σ_{obs}^A (which are of the order of magnitude $10^{-5} - 10^{16}$)

$$\delta^A = \sigma_{\text{obs}}^R - \sigma_{\text{obs}}^A \quad (2)$$

of the nuclei in the reference and sample positions.

Following Buckingham, Schaefer and Schneider³³ both σ_{obs}^R and σ_{obs}^A (the difference of which was measured in neat liquids using external referencing) can be written as the sums of the shielding constants of the isolated molecules (σ) and contributions originating outside the molecule: the overall bulk susceptibility effect (σ_b), contributions from anisotropy in the molecular susceptibility (σ_a), from van der Waals forces between the molecules (σ_w), from the electric field of neighbouring molecules (σ_e), and specific interactions (σ_s). Thus

$$\delta^A = -\sigma^A + \sigma^R + \Delta(\sigma_b + \sigma_a + \sigma_w + \sigma_e + \sigma_s), \quad (3)$$

where the symbol Δ denotes the difference between the corresponding terms of reference (R) and sample (A).

For the following discussion we have no other choice but, while keeping the reference compound constant, to identify the changes in δ with the changes in $-\sigma^A$, ignoring thus variation in all the Δ 's.

In principle, $\Delta\sigma_b$ could be eliminated from Eq. (3) either by employing an internal reference or by application of a bulk susceptibility correction. As the preferable internal referencing was not feasible for technical reasons, we decided against applying the correction for the same reasons as discussed by Hunter and Reeves¹³. Other Δ terms of Eq. (3) can be evaluated or eliminated through gas phase or solvent effect studies but these have so far dealt very little with ^{29}Si NMR and we have no reliable estimate of the total magnitude of the Δ terms for this nucleus. According to the available data on SiF_4 (ref.³⁴) and $\text{Si}(\text{CH}_3)_4$ (ref.^{35,36}) we estimated that in a series of related compounds the variation in the sum of the Δ terms should not-exceed

TABLE II
 ^{29}Si and ^{13}C NMR Chemical Shifts in Benzylsilanes $\text{C}_6\text{H}_5\text{CH}_2\text{R}^a$

R	No ^b	$\delta(^{29}\text{Si})$		
		δ	$\Delta\delta^c$	$\bar{\Delta}\delta^d$
$\text{Si}(\text{CH}_3)_3$	1	0.4	0.4	-1.2
$\text{Si}(\text{CH}_3)_2\text{Cl}$	2	26.6	-3.3	<i>f</i>
$\text{Si}(\text{CH}_3)\text{Cl}_2$	3	26.9	-4.9	-7.1
SiCl_3	4	7.2	-5.0	-7.4
$\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$	5	11.7	-1.8	-4.1
$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$	6	-11.9	-5.8	-5.2
$\text{Si}(\text{OC}_2\text{H}_5)_3$	7	-52.7	-8.2	-6.8
$\text{Si}(\text{CH}_3)_2\text{F}$	8	27.4 ^j	-8.0	<i>f</i>
$\text{Si}(\text{CH}_3)\text{F}_2$	9	-2.9 ^m	-11.7	<i>f</i>
SiF_3	10	-64.2 ^p	-12.4	<i>f</i>
SiH_3	11	-56.0	<i>f</i>	<i>f</i>
$\text{CH}_2\text{Si}(\text{CH}_3)_3$		1.1	<i>f</i>	<i>f</i>
$\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$		31.6	<i>f</i>	<i>f</i>
$\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$		1.1	<i>f</i>	<i>f</i>
$\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$		1.0	<i>f</i>	<i>f</i>

^a All chemical shifts are in δ -scale (*i.e.* p.p.m. units, positive values indicate shifts to lower field from TMS line), maximum error ± 0.3 p.p.m., measured in neat liquids. ^b Serial number of the compounds for reference in figures. ^c Substituent effect defined by Eq. (13). ^d Substituent effect defined by Eq. (14). ^e Aryl carbon, position relative to the substituent. ^f Data not available. ^g $\delta(^{13}\text{C})$ in $\text{C}_2\text{H}_5\text{O}$ 18.3 and 57.6 p.p.m. for CH_3 and CH_2 carbons, resp. ^h $\delta(^{13}\text{C})$ in $\text{C}_2\text{H}_5\text{O}$ 18.0 and 57.5 p.p.m. for CH_3 and CH_2 carbons, resp. ⁱ $\delta(^{13}\text{C})$ in $\text{C}_2\text{H}_5\text{O}$ 17.5 and 57.8 p.p.m.

1–2 p.p.m. With such precision the shielding constant, which is treated in the theory of nuclear shielding, is given as

$$\sigma^A = \text{const.} - \delta^A. \quad (4)$$

Attempts to interpret variations in shielding constants have largely been based on models in which σ is split into various contributions. Thus the shielding constant σ^A may be written^{37,38} as

$$\sigma^A = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B \neq A} \sigma^{AR} + \sigma^{A,\text{ring}}. \quad (5)$$

The interpretation of the terms in Eq. (5) is as follows:

TABLE II
(Continued)

$\delta(^{13}\text{C})$					
C-1 ^e	C-2 ^e	C-3 ^e	C-4 ^e	CH ₃ -Si	CH ₂ -Si
139.1	127.2	127.2	123.1	-2.2	26.7
135.9	127.6	127.6	124.1	0.6	28.2
133.6	128.2	128.2	125.3	4.0	30.6
131.1	128.5	128.5	126.0	—	32.6
138.4	127.5	127.5	123.4	-2.8	26.5 ^g
137.6	127.7	127.7	123.6	-5.8	23.8 ^h
136.9	128.0	127.2	123.6	—	20.1 ⁱ
136.9	127.9	127.9	124.1	-2.4 ^k	26.2 ^l
133.6	127.8	127.8	124.6	6.7 ⁿ	22.1 ^o
131.0	128.4	128.4	125.8	—	15.3 ^q
139.4	128.5 ^r	127.9 ^r	124.9	—	16.0
145.0	128.1	128.1	125.7	1.5	18.9 ^s
141.4	127.8 ^r	127.2 ^r	125.6	5.0	23.2 ^t
142.4	128.6	128.6	125.9	-1.4	16.7 ^u
142.9	128.8	128.8	126.2	-0.9	17.2 ^v

for CH₃ and CH₂ carbons, resp. ^j $J_{\text{F-Si}} = 285.6 \pm 2$ Hz. ^k $J_{\text{F-C}} = 14.9 \pm 1$ Hz. ^l $J_{\text{F-C}} = 12.5 \pm 1$ Hz. ^m $J_{\text{F-Si}} = 297.2 \pm 2$ Hz. ⁿ $J_{\text{F-C}} = 16.6 \pm 1$ Hz. ^o $J_{\text{F-C}} = 13.0 \pm 1$ Hz. ^p $J_{\text{F-Si}} = 281.0 \pm 2$ Hz. ^q $J_{\text{F-C}} = 17.5 \pm 1$ Hz. ^r Tentative assignment. ^s $\delta(^{13}\text{C})$ for CH₂-Ph carbon 30.4 p.p.m. ^t $\delta(^{13}\text{C})$ for CH₂-Ph carbon 28.4 p.p.m. ^u $\delta(^{13}\text{C})$ for CH₂-Ph and CH₂-CH₂-Ph carbons 40.3 and 26.4 resp. ^v $\delta(^{13}\text{C})$ for CH₂-Ph, CH₂CH₂Ph and CH₂CH₂CH₂Ph carbons 36.4, 36.4 24.4 p.p.m., resp.

a) σ_d^{AA} is the diamagnetic contribution arising from electronic circulations centered on atom A. This contribution is identified with the diamagnetic part of Ramsey expression for shielding³⁹

$$\sigma_d^{\text{AA}} = (e^2/3mc^2) \sum_k \langle r_k^{-1} \rangle, \quad (6)$$

in which the mean inverse distances of electrons k from the nucleus A in the molecular ground state are summed over the electrons k on atom A.

b) σ_p^{AA} is a paramagnetic contribution due to restricted currents on atom A (ref.³⁹). In the approximation of average excitation energy, ΔE_{av} , this term can be expressed as⁴⁰

$$\sigma_p^{\text{AA}} = -(2e^2\hbar^2/3m^2c^2 \Delta E_{\text{av}}) \{ \langle r_p^{-3} \rangle \cdot P^{\text{A}} + \langle r_d^{-3} \rangle \cdot D^{\text{A}} \}, \quad (7)$$

TABLE III
¹H-NMR Data for Benzylsilanes C₆H₅CH₂R

R	Chemical shift δ^a				
	C ₆ H ₅ ^c	CH ₂ —Si	CH ₃ —Si	CH ₂ O ^d	CH ₃ —C ^d
Si(CH ₃) ₃	6.99	2.028	-0.016	—	—
Si(CH ₃) ₂ Cl	7.07	2.353	0.357	—	—
Si(CH ₃)Cl ₂	7.13	2.616	0.660	—	—
SiCl ₃	7.18	2.841	—	—	—
Si(CH ₃) ₂ (OC ₂ H ₅)	7.02	2.100	0.040	3.580	1.125
Si(CH ₃)(OC ₂ H ₅) ₂	7.06	2.100	-0.018	3.679	1.139
Si(OC ₂ H ₅) ₃	7.07	2.090	—	3.690	1.128
Si(CH ₃) ₂ F	7.10	2.203	0.166	—	—
Si(CH ₃)F ₂	7.10	2.273	0.222	—	—
SiF ₃	7.18	2.456	—	—	—
SiH ₃	7.07	2.226 ⁱ	—	—	—

^a Chemical shifts as measured in 10% solutions and converted to δ -scale (p.p.m. units, positive values for the shifts to lower field from TMS line) using chemical shift of cyclohexane $\delta = 1.436$ p.p.m., maximum standard error ± 0.003 p.p.m. ^b Coupling constants in Hz, homonuclear coupling constants determined in 10% solutions, others in 50% solutions unless otherwise indicated.

where the average inverse cubes of distances of the valence p and d electrons from nucleus A are multiplied by P^A and D^A , resp., which are complex expressions⁴⁰ that represent the "unbalance" of the valence p and d electrons.

c) σ^{AB} represents the effects from currents on other atoms in the molecule ("neighbour anisotropy" effects)³⁸.

d) $\sigma^{A,ring}$ is the ring current contribution arising from nonlocalised circulations within the molecule³⁸.

The last two contributions are generally believed to be of smaller magnitude than the former two terms, at least for atoms other than hydrogen^{38,40}.

Since Saika and Slichter³⁷ demonstrated that the σ_p^{AA} term alone accounts for the main aspect of fluorine chemical shifts, it has been generally accepted that the changes in the shifts of "heavier nuclei" are due to the changes in this paramagnetic term. In keeping with this view, the theory of ³¹P shieldings of Letcher and van Wazer⁴¹ neglects the σ_d^{AA} term (being 10^{-2} as large as σ_p^{AA} for the ³¹P nucleus⁴¹) and considers $\langle r_p^{-3} \rangle / \Delta E_{av}$ and $\langle r_d^{-3} \rangle / \Delta E_{av}$ to be constant for a given coordination number⁴¹.

This was the situation until recently when it has been shown⁴² that in some cases variations in the average excitation energy provides the most promising interpreta-

TABLE III
(Continued)

Coupling constants ^b						
$J_{29\text{Si}-1\text{H}}$		$J_{13\text{C}-1\text{H}}$		$J_{19\text{F}-1\text{H}}$		$J_{\text{H}-1\text{H}}$
$\text{CH}_2\text{-Si}$	$\text{CH}_3\text{-Si}$	$\text{CH}_2\text{-Si}$	$\text{CH}_3\text{-Si}$	$\text{CH}_2\text{-Si}$	$\text{CH}_3\text{-Si}$	$\text{CH}_2\text{-CH}_3$
8.2	6.5	120.0	119.0	—	—	—
8.8	7.0	120.7	121.2	—	—	—
10.0	7.4	123.2	123.7	—	—	—
11.3	—	125.3	—	—	—	—
8.7	6.6	119.4 ^e	119.7 ^e	—	—	—
9.4	6.7	119.2 ^e	119.6 ^e	—	—	6.9
11.0	—	119.9 ^e	—	—	—	7.0
<i>f</i>	6.7	123.0	119.2 ^g	5.6	7.2	—
<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	4.4	6.2	—
<i>f</i>	<i>f</i>	121.8 ^h	<i>f</i>	2.8	—	—
<i>f</i>	—	<i>f</i>	—	—	—	—

ed, maximum standard error ± 0.2 Hz. ^c Broad line or multiplet, error ± 0.02 p.p.m. ^d Position of the center of multiplet. ^e Estimated error ± 0.8 Hz, only one satellite line could be measured. ^f Could not be measured. ^g Strongly concentration dependent. ^h Estimated error ± 1.0 Hz. ⁱ $J_{\text{H-SiC-H}} = 3.9$ Hz.

tion and when it has been calculated⁴³ that non-local contributions to σ_d can contribute as much as 35% of the total σ_d . It has also been claimed⁴⁴ that the diamagnetic contribution σ_d^{AA} is much more important than previously recognized.

Another possibility to that given by Eq. (5) is, following Feeny, Sutcliffe, and Walker⁴⁵, to split up the σ^{A} constant into contributions arising from electric fields created by polar groups (σ_{electric}) and contributions from electric charge densities ($\sigma_{\text{electronic}}$)

$$\sigma^{\text{A}} = \sigma_{\text{electric}}^{\text{A}} + \sigma_{\text{electronic}}^{\text{A}}, \quad (8)$$

where σ_{electric} (or its change) may be calculated from the expression

$$\sigma_{\text{electric}}^{\text{A}} = AE_z + B(E^2 + \langle E^2 \rangle) \quad (9)$$

(E is the electric field produced at nucleus A by point dipoles placed at the centers of any polar bonds in the molecule, E_z is the component of this field acting along the bond direction, and $\langle E^2 \rangle$ is the time-averaged square of the electric fields that can be estimated from polarisability and ionisation potential, A and B are constants).

$^{29}\text{Si-NMR}$

Of the above approaches having some theoretical rigour only that based on Eq. (7) has been recently applied to silicon-29 shieldings⁴⁶ (with the exception of correlations with electronic charges^{47,48}). This theory⁴⁶ neglects all other terms in Eq. (5) but σ_p^{AA} , and in Eq. (7) it neglects d -electron contribution against that of p -electrons and makes use of the average excitation energy approximation. Despite that (1) it has been shown that neglecting σ_d^{AA} is not always justifiable⁴⁴ and that (2) substitution of central silicon atom causes variations in ΔE_{av} (through the removal of degeneracy of electronic levels⁴⁹) and (3) that van den Berghe and van der Kelen⁵⁰ claim σ^{AR} and $\sigma_{\text{electric}}^{\text{A}}$ (and σ_d^{A}) to be the major factors influencing silicon shielding, the theory⁴⁶ has been remarkably successful in predicting shifts in compounds of the $(\text{CH}_3)_{4-n}\text{X}_n\text{Si}$ type.

In compounds of this type linear dependence of the shift on electronegativity of atom X was observed by earlier workers¹¹⁻¹³. Additional high field shifts that were noted when X = O, N and F were originally¹¹⁻¹³ associated with the formation of $(p \rightarrow d)_\pi$ bonds X—Si. The result of the opposing influences of the inductive effect and $(p \rightarrow d)_\pi$ interaction on the shielding of the silicon is the “sagging” pattern of the observed dependence of the silicon shift ($\delta(\text{Si})$) on n (the number of electronegative $(p \rightarrow d)_\pi$ donors X in the molecule). This pattern is illustrated for some series of these compounds on Fig. 2. (Numerical values used in this plot were obtained by us⁵¹ except for those for the series with X = F which were taken from ref.³⁴. Our values reproduce well the trends given in the earlier work¹¹⁻¹³ but are considered more precise.)

Johannesen, Brinckman and Coyle³⁴ warned against such interpretation of ^{29}Si shifts in these “chemically reasonable” changes in bonding parameters without a quantitative treatment. The fact that the mentioned quantitative theory⁴⁶ can account for the “sagging” pattern without considering d -orbitals makes their role in determining silicon-29 chemical shielding at least problematic.

As it is apparent from the comparison of Figs 2A and 2B with 2C the trends already discussed (2C) are very well reproduced when one methyl group is replaced by a phenyl or benzyl group, however the shifts become more diamagnetic (except for the compound with $n = 0$) and the “sagging” pattern becomes slightly less pronounced on going from methyl to benzyl and to phenyl compounds.

This close similarity is well illustrated by linear regression of $\delta(\text{Si})$ in compounds of type I with Y = C_6H_5 ($m = 0$ or 1) with $\delta(\text{Si})$ in the series with Y = CH_3 ($m = 0$):

$$\delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{C}_6\text{H}_5 = -6.25 + 1.06\delta(\text{Si}) \quad (10)$$

$$\text{(for } (\text{CH}_3)_{4-n}\text{X}_n\text{Si)}$$

(correl. coef. $r = 0.994$, ten data points of Figs 2B and 2C),

$$\delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{C}_6\text{H}_5) = -13.9 + 1.06\delta(\text{Si}) \quad (11)$$

$$\text{(for } (\text{CH}_3)_{4-n}\text{X}_n\text{Si)}$$

(correl. coef. $r = 0.988$, ten data points of Figs 2A and 2C), which clearly demonstrate that the substituents X are the major factors determining the silicon-29 shielding and that hybridisation changes or substitution on the carbon atom bonded to the silicon are of minor importance only.

This is also confirmed by exceedingly good linear regression that holds between the shifts in benzyl and phenyl derivatives:

$$\delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{C}_6\text{H}_5) = 7.48 + 1.01\delta(\text{Si}) \quad (12)$$

$$\text{(for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiC}_6\text{H}_5)$$

(correl. coef. $r = 0.999$, eleven data points of Table I and II). With respect to the slope which is almost one, the intercept of 7.48 p.p.m. represents the average shift of the resonance in benzylsilanes to lower field of the resonance in corresponding phenylsilanes. A part of the difference between the shieldings in phenyl- and benzylsilanes could come from $\sigma^{\text{A,ring}}$ contribution of the benzene ring. Calculations using

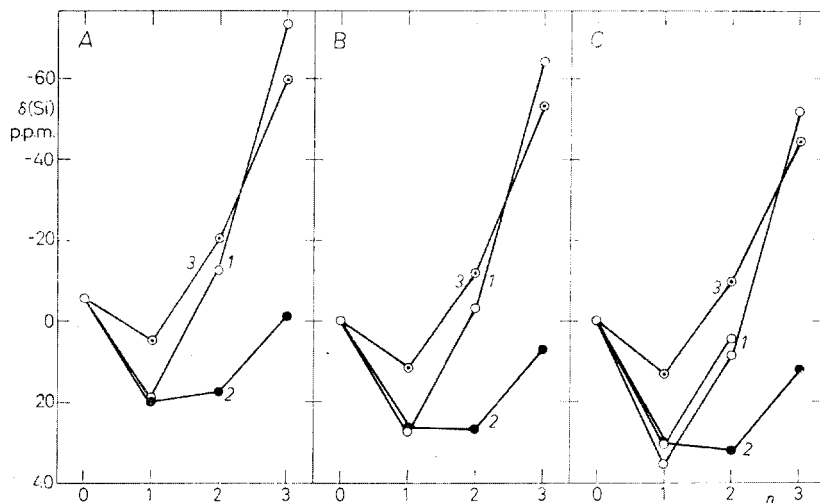


FIG. 2

Dependence of Silicon-29 Chemical Shift $\delta(\text{Si})$ on n in $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{Y}$ Compounds

$A m = 0, Y = \text{C}_6\text{H}_5$; $B m = 1, Y = \text{C}_6\text{H}_5$; $C m = 1, Y = \text{H}, \text{F}, \text{Cl}; 3 \text{OC}_2\text{H}_5$ (in 2C data of ref.¹³ and ref.³⁴ are given for F derivatives).

the standard tables of ring current effects⁵² gave for $\sigma^{\text{A,ring}}$ these estimates: -0.80 p.p.m. ($z = 0, p = 2.3$) in phenylsilanes and between -0.64 p.p.m. ($z = 0, p = 2.5$) and -0.17 p.p.m. ($z = 1.3, p = 2.5$) in benzylsilanes (negative sign indicates deshielding), *i.e.* the ring current effect operates in the direction opposite to that of structural effects; it actually decreases the value of the difference by some $0.2-0.6$ p.p.m. (c. 10%). (According to the new tables⁵³ this decrease would be slightly smaller, $0.2-0.4$ p.p.m.) This contribution can be neglected.

In accord with preliminary communications⁶⁻⁹ and other studies^{31,51,54} the minor influence of the remote substituent Y in a compound of type (I) can be evaluated as the substituent effects which are defined as:

$$\bar{\Delta}\delta(\text{Si}) = \delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{C}_6\text{H}_5) - \delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_3) \quad (13)$$

and

$$\begin{aligned} \bar{\Delta}\delta(\text{Si}) = & \delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{C}_6\text{H}_5) - \\ & - \delta(\text{Si}) \text{ (for } (\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_2\text{CH}_3). \end{aligned} \quad (14)$$

Their values are also given in Table II (data of refs^{6,9,31,51,54} were used in combination with the present results in deriving these values) and the plot of the dependence of the substituent chemical shift (SCS) $\Delta\delta(\text{Si})$ on the number n for three substituents X is shown on Fig. 3. Comparison of this graph with analogous graphs drawn for other combinations of substituent X and Y^{6-9,31,51,54} (compound of I type) reveals considerable similarity and regularity. Thus: 1) the substituent effect is not a constant (in contrast to other authors' claim¹⁶), 2) the variation in $\Delta\delta$ is monotonous; $\Delta\delta$ becomes more negative as n is increased, 3) the dependence is roughly linear in the series with X = OC₂H₅ (the same is observed in ethoxysilanes with Y = NH₂, Cl, CH₃COO), while, 4) in the series with X = Cl or F some leveling off of the effect is observed (the same is true in the series with the same X's and Y = Cl; data on other series are not available), 5) the slope of the approximately linear dependence in the ethoxy series is slightly larger than the corresponding slope in aminomethylsilanes but is smaller than that in chloro- or acetoxymethylsilanes^{31,51}. The ratio of these slopes is roughly proportional to the ratio of the values of σ_I^{aliph} constants of these groups⁵⁵ (C₆H₅, NH₂, Cl, and CH₃COO).

These trends and the similarities observed for different substituents Y exclude the possibility of the formation of pseudocyclic structures either by mechanisms D or E or F of Fig. 1.

The present status of shielding theory as outlined above does not permit a more detailed discussion of the observed trends in structural terms. We shall offer one of the possible hypothetical interpretations in subsequent papers where compounds with more electronegative substituents Y will be investigated and also the trends in $\bar{\Delta}\delta$ discussed.

^{13}C -NMR

In accord with the general trends in monosubstituted benzenes^{56,57} the data of Tables I and II show that of the aryl carbon atoms the substitution affects most the shift of the C-1 carbon atom. The shifts of C-4, C-2 and C-3 carbons follow in that order of sensitivity if phenyl and benzyl derivatives are considered separately; the overall ranges of C-4 and C-3 shifts are similar. With the exception of the least sensitive C-3 carbon the ranges of the observed shifts in substituted phenylsilanes are larger than those in benzylsilanes; the ranges of C-1 and C-3 shifts overlap in the two classes of compounds while those of C-2 and C-4 do not. It is interesting to note how the C-1 shift in $\text{C}_6\text{H}_5(\text{CH}_2)_m\text{SiX}_3$ compounds depends on m , the number of methylene groups. In $-\text{SiH}_3$ derivatives, the change of m from 0 to 1 changes this shift similarly as it does in the carbon analogues (Table IV), 11.9 and 6.4 p.p.m., resp. In $-\text{Si}(\text{CH}_3)_3$ derivatives the same change of m has only a negligible effect (-0.3 p.p.m.) which is contrasted by the considerable effect in the carbon analogues (10.5 p.p.m.). The compounds with $m = 0$ have the C-1 carbon shielded by some 10 p.p.m. more in organosilicon compounds than in their carbon counterparts. With increasing m the shift in silanes becomes closer to that in alkylbenzenes.

Also in accord with the general trends in ^{13}C -NMR and specifically with the trends in alkylbenzenes^{58,59} substitution of three hydrogen atoms on the silicon atom in $-\text{SiH}_3$ derivatives by three methyl groups decreases the shielding of β (relative to the methyl substituent) carbon atoms (*i.e.* C-1 in phenylsilanes and

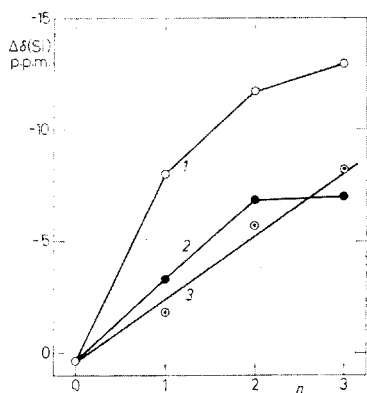


FIG. 3
Dependence of Silicon Substituent Chemical Shift $\Delta\delta(\text{Si})$ of C_6H_5 in Benzylsilanes
1 F; 2 Cl; 3 OC_2H_5 .

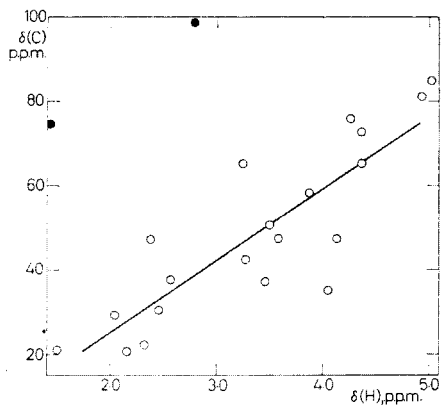


FIG. 4
Correlation between Carbon and Proton Chemical Shifts of Benzylic Methylene Group (Data of ref.⁶³, the size of points is not related to the experimental error.)

CH_2Si in benzylsilanes, which vary over a similar range of 19.3 and 17.3 p.p.m., resp.) and increases that of γ carbon atoms (*i.e.* C-2 in phenylsilanes and C-1 in benzylsilanes). The increase of the shielding in the γ position is in silanes smaller than in their carbon analogues which fact is consistent with the interpretation of the so called⁶⁰ “ γ -effect” in terms of nonbonded interaction which are, due to the longer C—Si than C—C bond length, smaller in silanes than in alkylbenzenes.

The trends in the shifts of C-1, C-2, CH_2 —Si and CH_3 —Si carbons in the series of $-\text{SiX}_3$, $-\text{SiX}_2\text{CH}_3$, $-\text{SiX}(\text{CH}_3)_2$ and $-\text{Si}(\text{CH}_3)_3$ derivatives depend on the nature of the substituent X and do not break into categories according to the relative position of the carbon to the substituent. Thus, in contrast to $-\text{SiH}_3$ derivatives, methyl substitution decreases almost linearly the shielding of C-1 carbon (γ carbon) in benzylsilanes with X = Cl, F, OC_2H_5 , in phenylsilanes the first methyl group replacing the substituent X increases the shielding of C-2 carbon (also γ carbon) for the same X, the effects of successive substitution are small and in different directions; there is no apparent relationship between the shifts of γ -carbon atoms in the two types of compounds. In phenylsilanes with X = phenyl the C-2 carbon is found at even lower field than that in phenylsilanes. (This might be related to the hindered rotation about the phenyl-Si bond, which, according to Harris and Kimber⁶¹, probably becomes more hindered as the number of phenyl groups attached to the silicon atom increases.)

Of the β carbon atoms the shielding of C-1 in phenylsilanes (independently of X) decreases with methyl substitution. The shielding of methyl (CH_3 —Si) and methylene (CH_2 —Si) carbon atoms increases with the increasing number of fluorine atoms or ethoxygroups bonded to the silicon atom (and is also high in benzylsilane); an increasing number of chlorine atoms, however, decreases the shielding of methylene carbon atoms.

Though the chemical shift of methylene carbons obviously depends on a multitude of structural factors⁶² only the dependence on substituent electronegativity (E_X) has so far been described for benzyl compounds⁶³. According to this (linear) dependence, an increase in shielding corresponds to a decrease of substituent electronegativity in $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ compounds. In this and in a similar dependence reported (with less scatter) for benzylic proton chemical shifts⁶³ considerable deviations occurred in two cases (tetrabenzyl titanium and tetrabenzyl zirconium) in which information from other sources indicated the presence of special interactions between the substituent X and C-1 carbon atoms⁶³.

In order to have a means that would indicate such anomalous interactions without necessary recourse to other information sources and would be applicable also in cases when the electronegativity of the substituents is not known we have plotted (Fig. 4) carbon chemical shifts against those of protons in benzylic CH_2 groups (data of ref.⁶³). Obviously there is a good linear correlation between the two chemical shifts ($r =$

= 0.852, twenty points). The two points with deviations considerably exceeding the scatter (not included in least-squares calculations) correspond to the two mentioned cases with special interactions. Apparently, deviations in plots analogous to that in Fig. 4 can serve as indications of anomalous behaviour or structure and, in the case of deviation in such a plot, the trend in carbon (or proton) shielding can be interpreted in terms of substituent electronegativity only with caution. In the case of substituted benzylsilanes, the analogous plot (Fig. 5) shows, with due regard to the smaller scatter that is a consequence of smaller variation in the structure of the compounds as compared to those demonstrated on Fig. 4, that the trend in the series of methylchlorobenzylsilanes (points 1–4) agrees with the general trend of Fig. 4, but the trend in methylfluorobenzylsilanes (points 1, 8–10) is opposite. Accordingly, the trend in shieldings of methylchlorobenzylsilanes can be interpreted as indicating increasing electronegativity of the $-\text{SiCl}_n(\text{CH}_3)_{3-n}$ group with an increasing number n of chlorine atoms bonded to the silicon atom. Interpretation of the trends in fluoro and ethoxy derivatives is not clear. Considerable deviations observed for $-\text{SiF}_3$ and $-\text{SiH}_3$ (Fig. 5) derivatives are in the direction opposite to that observed in the cases of tetrabenzyl zirconium or titanium. Anomalous behaviour of tetrabenzyl titanium has been explained^{63,64} on the basis of an X-ray study by electron donation from C-1 carbon to the metal leading to electron draining from the benzylic methylene group to the C-1 carbon.

As already mentioned, ^{13}C -NMR spectra of monosubstituted benzenes are one of the best documented types of spectra^{56,57}. Various correlations between the chemical shifts of these carbons and Hammett substituent constants or electron densities were observed for carbon atoms in the *para* position (C-4); shifts of other carbons show much less regularity being affected also by other factors^{56,57}. This is apparently also the reason why there is a good linear correlation between carbon chemical shifts in substituted phenyl- and benzylsilanes only in the case of the C-4 carbon ($r = 0.894$ for eleven data points, $r = 0.960$ if the point of $-\text{SiH}_3$ derivatives is omitted) — Fig. 6, in the cases of C-1, C-2, and C-3 carbons correlation coefficients are 0.584 (or 0.800 if $-\text{SiH}_3$ derivatives are omitted), 0.333, and 0.584, resp.

The difference between the C-4 carbon shifts in phenyl- and benzylsilanes is

$$\begin{aligned}\Delta\delta(\text{C-4}) &= \delta(\text{C-4 in } \text{RC}_6\text{H}_5) - \delta(\text{C-4 in } \text{RCH}_2\text{C}_6\text{H}_5) = \\ &= -40.2 + 0.37\delta(\text{C-4 in } \text{RCH}_2\text{C}_6\text{H}_5)\end{aligned}$$

(the numerical values were obtained from the least-squares fit of the data in Fig. 6) which gives in the observed range of chemical shifts an average value 6.0 ± 0.5 p.p.m. This is the amount by which the carbon at the *para* position is shielded less in substituted phenylsilanes than in corresponding benzylsilanes. This difference corresponds⁷ to the total charge density being by 0.02 units more negative at the

para carbon atom in benzylsilanes than in the corresponding phenylsilanes and, similarly, to σ^+ constant of CH_2R groups to be by 0.5 units more negative than that of R groups. In making these estimates⁷ the most recent correlations^{6,5} were employed despite that they involve carbon-13 chemical shifts obtained under different conditions than those used here (internally referenced FT spectra measured in 10% solutions in tetrachloromethane). But since the difference 6.0 p.p.m. represents an average value of the differences in the chemical shifts in pairs of closely related compounds that were measured under identical conditions the value of the difference should not differ from the true value by more than 20%.

Estimates of σ^+ constants for various silyl- or silylmethyl groups that could be derived from the quoted correlations and individual chemical shifts would be considerably less reliable similarly as would be estimates of σ_p constants based on other published correlations^{5,6} which, though employing the shifts obtained under similar conditions as here show considerably larger scatter around the least-squares line. Therefore, instead of attempting to obtain new estimates of these constants a confirmation of estimates made previously^{6,6} (or, more precisely, confirmation of the estimated trends in these constants) was sought. The present results indeed confirm that these σ_p (Table V) values are essentially correct for it was found that the C—4 carbon chemical shift can be correlated with σ_p constants in substituted phenylsilanes;

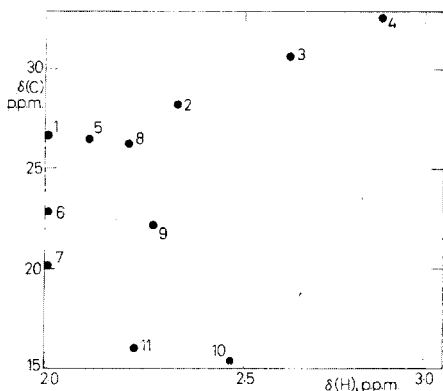


Fig. 5

Correlation between Carbon and Proton Chemical Shift of Benzylic Methylene Group in Substituted Benzylsilanes (The size of points corresponds to the experimental error, numbering of the points is that of Table II.)

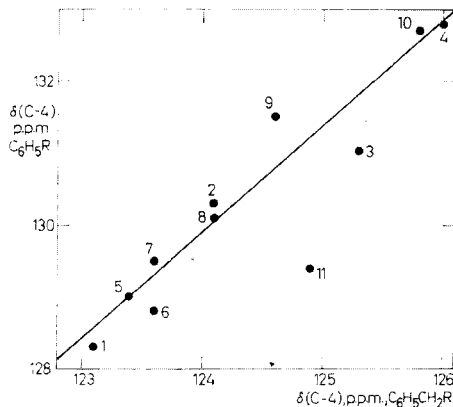


FIG. 6

Correlation between C—4 Carbon Chemical Shift in Substituted Phenyl- and Benzylsilanes (Numbering of the points is that of Tables I and II, the solid line is the least-square fit with the point for $-\text{SiH}_3$ derivatives omitted, the size of points is not proportional to the experimental error.)

the correlation with σ_p (DM) constants⁶⁶ (determined from dipole moments) is slightly better than ($r = 0.931$, eleven data points) that with σ_p (NMR) constants⁶⁶ (determined from $^1\text{H-NMR}$) which has for eleven data points correlation coefficient $r = 0.899$. Analogous correlations (employing substituent constants for substituents R) for substituted benzylsilanes $\text{C}_6\text{H}_5\text{CH}_2\text{R}$ are considerably worse ($r = 0.784$ or 0.854 for the two types of constants).

Another possibility to estimate substituent constants from present data is offered by recently reported empirical multiple correlations^{67,68} of shifts of aryl carbon with \mathcal{F} and \mathcal{R} constants of Swain and Lupton⁶⁹ and Q parameter introduced by Schaefer and coworkers⁷⁰. According to these correlations the shift of each of four different carbon atoms in monosubstituted benzenes can be expressed as a linear combination of \mathcal{F} , \mathcal{R} and Q (ref.^{67,68}). That is, in order to determine the constants for a substituent it would be sufficient to measure four aryl carbon chemical shifts in a single spectrum of benzene substituted by the substituent in question and then least-square calculations would yield the desired constants. Despite their low precision it would be valuable to have even very rough estimate of Q parameters of silyl groups. We shall explore this possibility in our study of vinylsilanes when it will be possible to test whether the derived values of Q parameter are meaningful. Preliminary results indicate that it is not the case; apparently these correlations apply only to axially symmetric substituents.

$^1\text{H-NMR}$

Since proton spectra of phenylsilanes can only rarely be analysed at 60 MHz (ref.⁷¹) and since the proton spectra of other groups bonded to the silicon atom in phenylsilanes have been described⁷¹, the spectra of substituted phenylsilanes were not measured in the present study. Effects of structure on $^1\text{H-NMR}$ spectra of benzyl derivatives in general^{63,72} and substituted benzylsilanes in particular^{63,71} have been studied only little.

Chemical shifts. In benzyl compounds the aromatic protons do not show strong dependence on substituent electronegativity⁶³; in compounds studied here, where only positions of the centers of phenyl proton multiplets could be determined, the trend suggested by the data of Table III for the ring protons (increasing shielding with increasing number of electronegative substituent on the silicon atom) cannot be seriously discussed on its own. The trend in methylene (CH_2Si) proton shifts is, however, significant. According to the dependence of Zetta and Gatti⁶³ the observed values can be interpreted as indicating increasing electronegativity of $-\text{Si}(\text{CH}_3)_{3-n}\text{X}_n$ group with the number n of chlorine or fluorine atom attached to the silicon atom. Stronger dependence on n in the series of chloro than in fluoro derivatives, especially when compared with higher electronegativity of fluorine than chlorine and with relative insensitivity of the proton shift to the number of ethoxy groups, could be

discussed in the terms of comparative $(p-d)_\pi$ donating ability of these groups. Then, it would be found that chloride is the weakest of the three donor groups. This would be in accord with other observations⁷³.

Coupling constants. The two silicon-29 coupling constants ($^2J_{29\text{Si}-^1\text{H}}$ in CH_2Si and CH_3Si groups) show, in cases when both constants could be determined, similar dependence on substitution; both constants increase with increasing number of electronegative substituents on the silicon atom. The coupling constant for CH_2 protons

TABLE IV

Carbon-13 NMR Chemical Shifts δ of C-1 Aryl Carbon Atom in Some Monosubstituted Benzenes $\text{C}_6\text{H}_5\text{R}^a$

R	δ	R	δ	R	δ	R	δ
SiH_3	127.5	$\text{Si}(\text{CH}_3)_3$	139.4	CH_3	137.69 ^b	$\text{C}(\text{CH}_3)_3$	150.55 ^b
CH_2SiH_3	139.4	$\text{CH}_2\text{Si}(\text{CH}_3)_3$	139.1	CH_2CH_3	144.09 ^b	$\text{CH}_2\text{C}(\text{CH}_3)_3$	139.5 ^c
		$(\text{CH}_2)_2\text{Si}(\text{CH}_3)_3$	145.0				
		$(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	142.4				

^a Chemical shifts in δ -scale relative TMS, results of the present work unless indicated otherwise.

^b Taken from ref.⁵⁸. ^c C-4 in this compound is at 125.7 p.p.m. converted from ref.⁵⁹ using δ for CS_2 192.8.

TABLE V

Substituent Constant σ_p of Silyl Groups R^a

Substituent R	$\text{Si}(\text{CH}_3)_3$	$\text{Si}(\text{CH}_3)_2\text{Cl}$	$\text{Si}(\text{CH}_3)\text{Cl}_2$	SiCl_3	$\text{Si}(\text{CH}_3)_2(\text{C}_2\text{H}_5\text{O})$	
$\sigma_p(\text{DM})^b$	-0.05	0.30	0.41	0.43	(0.12) ^d	
$\sigma_p(\text{NMR})^c$	0.06	0.15	0.42	0.37	(0.10) ^d	
	$\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})_2$	$\text{Si}(\text{C}_2\text{H}_5\text{O})_3$	$\text{Si}(\text{CH}_3)_2\text{F}$	$\text{Si}(\text{CH}_3)\text{F}_2$	SiF_3	SiH_3
$\sigma_p(\text{DM})^b$	(0.18) ^d	(0.19) ^d	0.23	0.40	0.51	0.07
$\sigma_p(\text{NMR})^c$	(0.15) ^d	(0.10) ^d	0.15	0.28	0.51	0.10

^a Values taken from ref.⁶⁶. ^b Estimated from dipole moments of $p\text{-R-C}_6\text{H}_4\text{CH}_3$ compounds.

^c Estimated from NMR coupling constants $J_{13\text{C}-^1\text{H}}$ in the methyl group of $p\text{-R-C}_6\text{H}_4\text{CH}_3$ compounds. ^d Value for analogous methoxy derivative.

is always larger than that for CH_3 protons. At present, these trends cannot be interpreted in structural terms for there is not sufficient theoretical background for such interpretation though numerous data are scattered through literature. The same is true for the observed decrease of ${}^2J_{19\text{F}-1\text{H}}$ coupling constants with increasing number of fluorine atoms bonded to silicon. The trends in carbon-13 coupling constants are difficult to understand. Coupling constant ${}^1J_{13\text{C}-1\text{H}}$ in CH_2Si group varies monotonously only in chloro derivatives, in which an increase in the coupling constants is accompanied by a decrease of shielding of both proton and carbon of the CH_2Si groups. This is in keeping with general trends known for this type of coupling⁷⁴. In ethoxy derivatives the constant varies only very little (similar to the proton chemical shift in these compounds). In contrast to chloro derivatives this coupling in fluoro-derivatives appears anomalous: the coupling constant is smaller in trifluoro than in the monofluoro derivatives. This resembles the anomalous trend in the carbon chemical shift of this group in these compounds.

Structural Conclusions

According to the difference in C-4 carbon chemical shifts, the total charge density is by 0.02 units more negative at this carbon in benzylsilanes than in phenylsilanes bearing the same substituent on silicon. This difference can be accounted for in two ways: 1) by a decrease in the density in phenylsilanes due to the electron accepting properties of silicon and/or 2) by electron donation to the benzene ring from $-\text{CH}_2-\text{Si}(\text{CH}_3)_{3-n}\text{X}_n$ groups in benzylsilanes. Since the shifts in benzylsilanes are smaller and in phenylsilanes larger than the shifts of benzene it is most likely that both mentioned factors contribute to the observed difference; the proportion of the factors varies with substitution as the C-4 chemical shift varies in the two classes of compounds (with their difference being almost constant). In some cases shielding of C-4 carbon in benzylsilanes is as low as it is in neopentylbenzene (Table IV, note ϵ).

Electron release by $-\text{CH}_2\text{SiR}_3$ groups is currently explained by a hyperconjugative mechanism (*e.g.*^{75,76}). The present results cannot add anything to this picture or distinguish between the two mechanisms of silicon withdrawal of electrons from the ring as they are discussed in literature. The two mechanisms are: a) $(\pi - d)_\pi$ back-bonding from the phenyl ring π -orbital to vacant $3d$ orbitals of silicon⁷⁷ and b) hyperconjugative interaction⁷⁸ of phenyl π -electrons with \sum_π and \sum_π^* orbitals of silicon-substituent bonds. Qualitative agreement of the difference in total electron density with the results of the calculation of Nagy and Réffy^{79,80} (0.03 units) who included in their calculations both $(\pi - d)_\pi$ bonding in phenylsilanes and hyperconjugation and "long-bonds" in benzylsilanes cannot be taken as conclusive.

²⁹Si-NMR shows that the silicon atom is in benzylsilanes always less shielded (by 7.5 p.p.m.) than it is in phenylsilanes. If silicon shielding can be related to the electron density around this nucleus, then this finding is in perfect harmony with the

just discussed difference in C-4 shieldings. According to the trends in silicon-29 shieldings formation of cyclic structures (Fig. 1D, E and F) seems unlikely.

Several anomalies (most notably for $-\text{SiH}_3$ and $-\text{SiF}_3$ derivatives) mentioned in the discussion of the spectra suggest that it would be dangerous to attempt a generalized interpretation of bonding situation in benzyl- and phenylsilanes. Apparently depending on other substituents, the character of the phenyl-silicon bond or phenyl- $-\text{CH}_2$ -silicon bonds varies with the nature of the substituents and symmetry of the silyl groups.

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