Journal of Organometallic Chemistry, 137 (1977) 145—155
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

^{13}C NMR STUDIES OF ORGANOSILANES

III *. SILICON—PHENYL BONDING IN PHENYLSILANES

P.E. RAKITA *

Department of Chemistry, University of Minnesota, Duluth, MN 55812 (U.S.A.)

and L.S. WORSHAM

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27514 (U.S.A.)

(Received April 8th, 1977)

Summary

Carbon-13 NMR data for 25 phenylsilanes have been obtained and analyzed. Several substituents (viz. n-butyl, vinyl, allyl, t-butoxy) not previously considered were included in this study. The results, combined with earlier work, indicate no anomalous behavior of the silicon—phenyl bond as a function of the other substituents on the silicon atom. The importance of steric effects on the chemical shift due to groups three (*gauche*) and four (*syn-axial*) bonds removed from the phenyl group is demonstrated. Hammett σ^+ values for several silyl groups are estimated and correlations between ^{19}F and ^{13}C data for phenylsilanes are noted.

Introduction

Among the magnetic resonance techniques used to study organosilicon compounds, ^{13}C NMR has received the least attention. This is surprising since with the advent of commercial Fourier Transform instruments, ^{13}C NMR is now a widely available technique, involves considerably fewer experimental and instrumental difficulties than ^{29}Si NMR, and has the potential to provide more useful information about electronic structure and bonding in complex molecules than ^{1}H NMR.

Other ^{13}C NMR studies of organosilanes have been mostly theoretical in nature. The method has been widely employed in studying the interaction between silicon, or another metalloid, and a substituent capable of p_π—d_π bonding [1]. Silicon interactions with the π-system of phenyl rings [2—6], as

---

* For part II, see ref. 16.

well as the oxygen of siloxyethers [7—11] and siloxanes [10] have been examined *. Carbon-13 spectra of other phenyl compounds have been thoroughly explored. [14].

In a previous paper [15] we reported the ^{13}C NMR spectra of 38 phenylsilanes and correlated the observed chemical shifts in terms of some empirical substituent-chemical-shift (SCS) parameters. Owing to the limited data at that time, we were unable to interpret those results in chemically meaningful terms. We have subsequently studied 25 more phenylsilanes with four additional substituents on the silicon atom, as well as some related benzylsilanes. This expanded data set allows some conclusions to be drawn about the nature of the silicon—phenyl bond and the substituent effect of various silyl groups. In addition, the assumptions made earlier about the additivity of empirical SCS parameters have been tested and shown to be valid.

Experimental

Compounds. Those phenylsilanes containing vinyl or allyl substituents were commercial samples obtained from Petrarch Systems, Levittown, PA, and used as received. The alkoxyphenylsilanes were prepared by standard procedures as described elsewhere [15—17]. The preparation of the n-butylphenylsilanes will be reported separately [18]. Boiling points and analytical data for two new alkoxyphenylsilanes are reported below:

Methylphenyl-t-butoxysilane. 71—77°C/5.3 mmHg. Anal. Found: C, 67.05; H, 9.64. $C_{11}H_{18}OSi$ calcd.: C, 67.98; H, 9.34%.

Methyldiphenyl-t-butoxysilane. 111—112°C/0.25 mmHg. Anal. Found: C, 75.61; H, 8.40. $C_{17}H_{22}OSi$ calcd.: C, 75.50; H, 8.20%.

Spectra. Carbon-13 NMR spectra were obtained using a Varian XL-100 Spectrometer (operating at 25.2 MHz) equipped with FT mode and a Varian 620/L computer with disk accessory. An internal deuterium lock ($CDCl_3$ was employed with broad-band proton noise decoupling. In most cases, accumulation of 400—1000 transient responses was sufficient to obtain an adequate spectrum. Samples were studied as 25—40% w/w solutions in $CDCl_3$ with 2—5% $CHCl_3$ or TMS as internal reference. Chemical shifts are reported on the TMS scale, positive shifts being downfield from TMS. Samples with internal $CHCl_3$ were converted using the relationship $\delta(CHCl_3) = +77.20$ ppm. Spectral reproducibility was typically 0.04 ppm.

Chemical shifts assignments were made by noting systematic variations in the spectra with changes in substituents. Relative signal intensities and previously noted [15] ranges of resonances were also used. The assignments show a high degree of internal consistency and agree with the results from other studies.

Calculations. Regression analyses and correlations including plots were performed on IBM 360/65 and Cyber 74 computers using both SAS and SPSS statistical routines.

---

* Recently, it has been suggested by Pitt that mechanisms other than p—d bonding may at least partially explain some of the properties of organosilanes [12,13].

Results

^{13}C NMR spectra of phenylsilanes. The ^{13}C NMR spectra of twenty-five phenyl silanes of the type $C_6H_5SiX_3$ (X = CH_3, n-C_4H_9, C_2H_3, C_3H_5, C_6H_5, H, Cl, OR; R = CH_3, C_2H_5, t-C_4H_9) have been recorded and assigned (Table 1). These data, together with those reported earlier [15], constitute a set of 63 compounds for which ^{13}C spectra were obtained under identical conditions. The data reported here include compounds with n-butyl, vinyl, allyl, and t-butoxy substituents which have not been previously studied.

Correlation diagrams of the four phenyl resonances exhibited considerable scatter ($r_{i,o} = -0.483$, $r_{i,m} = -0.522$, $r_{i,p} = -0.638$, $r_{o,m} = 0.079$, $r_{o,p} = -0.142$, and $r_{m,p} = 0.746$). As noted earlier [15], the non-alkoxy phenylsilanes (26 compounds) showed a high *meta—para* correlation ($r_{m,p} = 0.958$). The remaining correlations increased slightly but were not deemed significant ($r_{i,o} = -0.404$, $r_{i,m} = -0.731$, $r_{i,p} = -0.632$, $r_{o,m} = -0.192$, and $r_{o,p} = -0.294$).

^{13}C NMR spectra of trimethylsilylalkylbenzenes. The ^{13}C NMR spectra of three trimethylsilylalkylbenzenes; $C_6H_5(CH_2)_nSi(CH_3)_3$ where $n = 1$, 2, and 3; have also been recorded and assigned (Table 2). Similarly the spectra of 1-trimethylsilylindane and 1-trimethylsilylindene were determined (Table 3).

Assignments of shifts in the compounds, $C_6H_5(CH_2)_nSi(CH_3)_3$, were made in the same manner as those for the phenylsilanes and agreed with data available in the literature [6]. Like the phenylsilanes, the *ortho* resonance in these compounds was downfield of the *meta* resonance. Unlike the phenylsilanes, however, the resonance of the *para* carbon was upfield from that of the *meta* carbon.

Assignments of the ^{13}C resonances for trimethylsilylindene have been previously attempted [19,20]. Because of a disagreement in the assignment of the aromatic carbons, we have determined the spectra of trimethylsilylindane and -indene. The results are given in Table 3 and Fig. 1. The key to making the correct assignments is that the substituent effect of a trimethylsilyl group is additive provided the carbon framework and other factors are kept constant. For the benzyl compounds, unambiguous assignments of the aromatic carbons have previously been made [6,13,21,22]. The effect of replacing H with trimethylsilyl group is a downfield shift at the *ipso* carbon ($\Delta\delta_i = +2.5$), and upfield shifts at the other ring positions ($\Delta\delta_o = -1.2$, $\Delta\delta_m = -0.5$, $\Delta\delta_p = -1.7$). A comparable pattern is noted for the tin derivative, but the magnitude of the effect is greater. For the indanyl series, Adcock and coworkers have unambiguously assigned the resonances in indanyltrimethyltin [21,22] and comparing these with the shifts in the parent hydrocarbon indane, the additivity of the substituent effect for the trimethylstannyl group is clearly apparent. Thus, using the shift factors for benzyltrimethylsilane compared with toluene, and applying these to the indane framework, the following shifts for indanyltrimethylsilane can be calculated: C-4, 123.9; C-5, 124.5; C-6, 125.7; C-7, 123.2; C-8, 146.4; C-9, 142.7. These agree remarkably well with the observed values (Table 3). To make the assignments in the silylindene, it is assumed that the presence of the double bond will have the least effect on C-5 and C-7 and these signals are assigned by comparison with indanyltrimethylsilane. Carbon-4 and C-6 are likewise related to the indane, and the resulting assignments are in complete agreement with those previously proposed by Luzikov, Sergeyev and Ustynyuk [20].

TABLE 1

OBSERVED AND CALCULATED ^{13}C NMR CHEMICAL SHIFTS FOR PHENYLSILANES, $C_6H_5SiX_3$

X_3	*ipso*	*ortho*	*meta*	*para*
$Me(OMe)_2$ [a]	133.41 [b]	133.72	127.63	129.85
	(133.84) [c]	(133.69)	(127.64)	(129.75)
$(OEt)_3$	130.75	134.49	127.58	130.06
	(130.45)	(134.67)	(127.50)	(130.04)
Me_2O-t-Bu	140.53	133.30	127.60	129.02
	(140.22)	(133.19)	(127.58)	(129.00)
Me_2Al [d]		133.60	127.73	128.98
	(138.42)	(133.59)	(127;70)	(128.98)
Me_2Bu	139.68	133.55	127.71	128.72
	(139.31)	(133.54)	(127.70)	(128.78)
$MeBu_2$	138.90	133.82	127.66	128.66
	(138.76)	(133.88)	(127.70)	(128.72)
MePhO-t-Bu	138.64	134.17	127.58	129.54
	(138.38)	(134.22)	(127.63)	(129.26)
$PhAl_2$	134.82	134.92	127.72	129.37
	(134.77)	(135.00)	(127.74)	(129.38)
MeBuPh	137.41	134.36	127.68	128.94
	(137.46)	(134.57)	(127.76)	(129.03)
MeHO-t-Bu	137.97	133.61	127.76	129.54
	(137.65)	(133.74)	(127.72)	(129.53)
MeViH	135.22	134.52	127.92	129.39
	(135.38)	(134.51)	(127.95)	(129.44)
MeAlH	135.54	134.29	127.82	129.35
	(135.66)	(134.14)	(127.84)	(129.34)
MeViOEt	136.15	133.81	127.67	129.54
	(136.09)	(133.95)	(127.74)	(129.60)
$Vi(OEt)_2$	133.04	134.56	127.77	130.11
	(132.95)	(134.44)	(127.67)	(130.00)
MeAl(OEt) [d]		133.58	127.67	129.52
	(136.38)	(133.58)	(127.63)	(129.50)
MeBuCl	135.60	133.31	128.03	130.20
	(135.72)	(133.45)	(128.00)	(130.13)
Bu_2OEt	136.96	133.87	127.69	129.28
	(136.90)	(133.86)	(127.62)	(129.23)
BuPhOEt	135.51	134.62	127.74	129.63
	(135.60)	(134.55)	(127.69)	(129.54)
Bu_2H	136.07	134.62	127.79	129.06
	(136.19)	(134.43)	(127.83)	(129.07)
BuPhH	134.64	135.10	127.92	129.43
	(134.89)	(135.12)	(127.90)	(129.38)
$Ph(OMe)_2$ [d]	132.12	134.56	127.63	130.06
	(132.00)	(134.70)	(127.69)	(130.00)
$Ph(OEt)_2$ [d]	133.12	134.67	127.60	129.95
	(133.02)	(134.70)	(127.63)	(130.00)
$ViMe_2$ [d]	138.28	133.80	127.78	128.98
	(137.95)	(133.96)	(127.82)	(129.09)
MePhVi [d]	136.14	134.78	127.10	129.27
	(136.10)	(134.98)	(127.87)	(129.34)
PhViOEt [d]	134.7	134.88	127.73	129.82
	(134.24)	(134.97)	(127.80)	(129.85)
MeBuH [d]		134.29	127.83	129.13
	(136.74)	(134.09)	(127.85)	(129.13)
Rms deviation (ppm)	0.26	0.11	0.04_4	0.068

---

[a] Me, methyl; Et, ethyl; Bu, butyl; Vi, vinyl; Al, allyl; Ph, phenyl; [b] In ppm downfield from TMS. [c] Calculated values in parentheses. [d] Not included in regression analysis.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS ^{a} OF TRIMETHYLSILYLALKYLBENZENES, C_6H_5—$(CH_2)_n$—$Si(CH_3)_3$

n	Methyl	*ipso*	*ortho*	*meta*	*para*	C_α ^{b}	C_β	C_γ
0	−1.11	140.33	133.29	127.77	128.79			
1	−1.94	140.28	128.10	127.98	123.90	27.10		
2	−1.75	145.26	128.27	127.78	125.46	30.06	18.68	
3	−1.64	142.73	128.50	128.23	125.64	39.99	26.15	16.62

[a] In ppm downfield from TMS. [b] C_α is bonded to the *ipso* carbon.

Regression analysis. Data for the combined set of sixty-three phenylsilanes were analyzed using the equation:

$$\delta_x{}^a = k^a + \sum_{i=1}^{P} n_i \delta_i{}^a + \sum_{i=j}^{P} \sum_{j \geqslant i}^{P} n_{ij} \delta_{ij}{}^a \qquad (1)$$

where $\delta_x{}^a$ is the chemical shift of the *a*-th carbon (*i*, *o*, *m*, and *p*) in the *x*-th

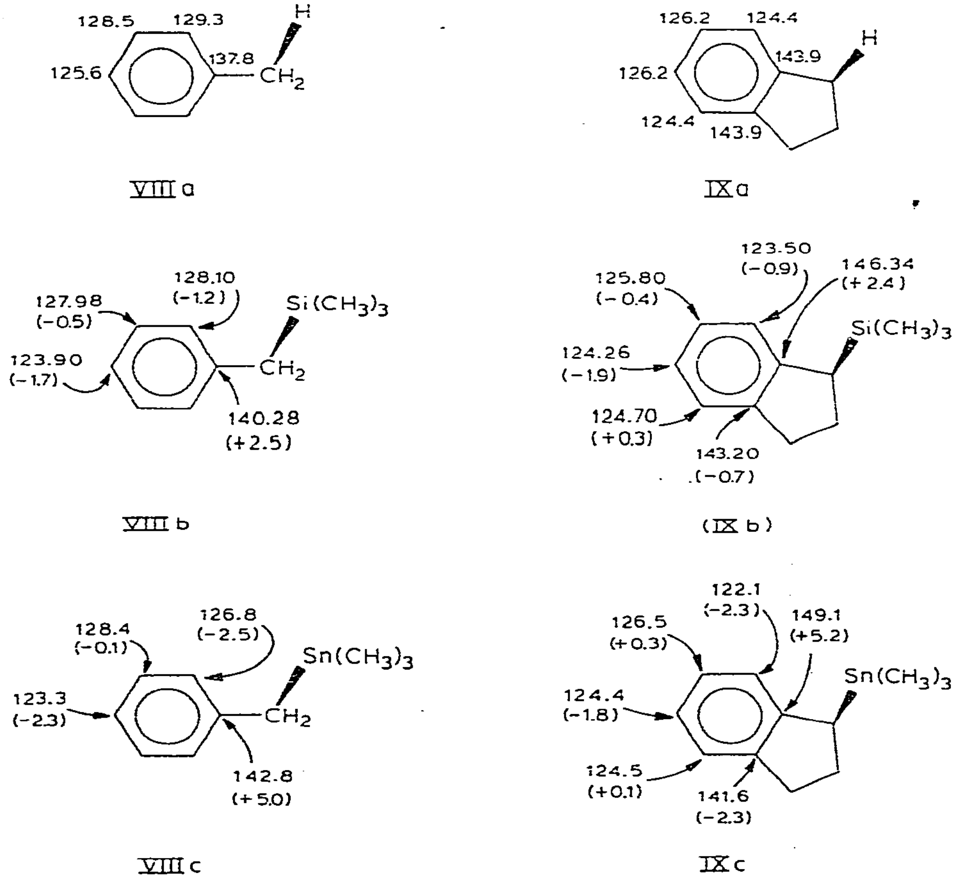
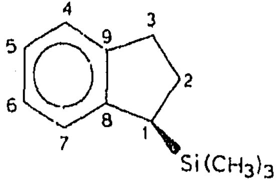
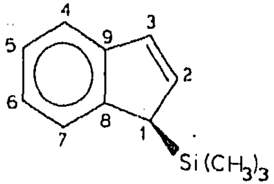


Fig. 1. ^{13}C NMR chemical shifts and substituent shift factors for benzyl and indanyl derivatives.

TABLE 3

^{13}C NMR CHEMICAL SHIFTS [a] OF 1-TRIMETHYLSILYL-INDANE AND -INDENE

	Methyl	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Ref.
	−2.68	27.51	32.84	34.72	124.71	124.26	125.79	123.50	146.34	143.20	This work
	−2.59 −1.3 −2.2	46.37 47.7 46.8	135.53 136.9 135.5	120.92 130.4 129.4	122.56 125.1 121.4	124.71 122.4 124.1	128.83 124.0 125.2	123.56 126.2 122.9	145.23 145.5 145.6	144.02 146.7 144.5	This work 19 20

---

[a] In ppm downfield from TMS.

TABLE 4

REGRESSION PARAMETERS FOR PHENYLSILANES, $C_6H_5SiX_3$ [a]

	ipso	*ortho*	*meta*	*para*
k	139.86 ± 0.14	133.20 ± 0.05	127.72 ± 0.02	128.84 ± 0.03
δ_{Ph}	−1.85 ± 0.07	1.02 ± 0.03	0.05 ± 0.01	0.25 ± 0.02
δ_{Cl}	−3.59 ± 0.14	−0.09 ± 0.03	0.30 ± 0.01	1.35 ± 0.02
δ_{OR}	−2.37 ± 0.15	−0.01 ± 0.04	−0.04 ± 0.02	0.51 ± 0.03
δ_{H}	−2.57 ± 0.10	0.55 ± 0.04	0.14 ± 0.01	0.35 ± 0.02
δ_{Vi}	−1.91 ± 0.18	0.76 ± 0.07	0.10 ± 0.03	0.25 ± 0.05
δ_{Al}	−1.62 ± 0.14	0.38 ± 0.05	−0.01 ± 0.02	0.15 ± 0.03
δ_{Bu}	−0.55 ± 0.09	0.34 ± 0.03	−0.01 ± 0.01	−0.06 ± 0.02
δ_{Cl-Cl}	0.81 ± 0.17			
δ_{OR-OR}	−1.27 ± 0.13	0.50 ± 0.05		−0.11 ± 0.04
δ_{H-H}	−1.40 ± 0.13	0.34 ± 0.05		
δ_{β}	0.51 ± 0.11		−0.03 ± 0.01	
$\delta_{\beta-\beta}$	0.40 ± 0.11			−0.11 ± 0.01
δ_{H-OR}				0.17 ± 0.04
multiple regression coefficient	0.994	0.990	0.980	0.995

[a] In ppm. Positive sign indicates downfield from TMS.

compound, n_i the number of substituents of type i from the set of p substituents, δ_i^a the SCS parameters for a substituent of i-type, n_{ij} the number of pairwise combinations of i and j, δ_{ij}^a the second order SCS parameter, and k^a a constant. Trimethylphenylsilane was chosen as the reference compound and $\delta_{CH_3}{}^a$ and $\delta_{CH_3-j}{}^a$ were defined as zero.

In a preliminary analysis with the parameters δ_{Ph}, δ_{Vi}, δ_{Al}, δ_{Bu}, δ_{H}, δ_{Cl}, δ_{OR}, and δ_{β}*, fair correlations between observed and calculated chemical shifts were achieved for all four carbons. With the addition of all possible pairwise combinations, the correlation improved greatly ($r_i = 0.997$, $r_o = 0.998$, $r_m = 0.992$, and $r_p = 0.999$). However, it was found that most of the pairwise terms were not significant and could be dropped without appreciably changing the correlation. It was also noted in the initial regression analysis of thirty-eight phenylsilanes that carbons, which were a part of an alkoxy substituent and greater than two bonds removed from the oxygen, had very little effect upon the chemical shifts of the aromatic carbons [15].

The final results are listed in Table 4 and the calculated chemical shifts for the new compounds are included in Table 1.

The chemical shift of the *ipso* carbon could be described with twelve parameters: δ_{Ph}, δ_{Cl}, δ_{OR}, δ_{H}, δ_{Vi}, δ_{Al}, δ_{Bu}, δ_{β}, δ_{Cl-Cl}, δ_{OR-OR}, δ_{H-H}, and $\delta_{\beta-\beta}$; resulting in a correlation between the observed and calculated shifts of 0.994. Nine parameters: δ_{Ph}, δ_{Cl}, δ_{OR}, δ_{H}, δ_{Vi}, δ_{Al}, δ_{Bu}, δ_{OR-OR}, and δ_{H-H}; were required to describe the effect which the silicon moiety had upon the *ortho* resonance ($r_o = 0.990$). In contrast, no particular pairwise term seemed necessary to predict the chemical shift of the *meta* carbon ($r_m = 0.980$). The effect of the silicon

---

* This term indicates the number of β-substituents on the alkoxy carbon: $Si-O-C_{\alpha}-C_{\beta}-C_{\gamma}$.

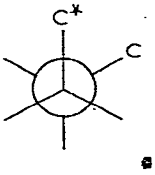
substituent upon the resonance of the *para* carbon could likewise be described in term of δ_{Ph}, δ_{Cl}, δ_{OR}, δ_{H}, δ_{Vi}, δ_{Al}, δ_{Bu}, δ_{OR-OR}, $\delta_{\beta-\beta}$, and δ_{H-OR} ($r_p = 0.995$).

Discussion

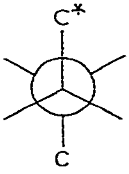
Validity and utility of empirical SCS parameters. The addition of four new substituents (viz. vinyl, allyl, n-butyl, and t-butoxy) to the original set of phenylsilanes permitted a test of our previous assumption of the reliability of SCS parameters derived from partial sub-sets of data. Table 4 lists the final regression parameters obtained for fifty-five phenylsilanes. The ratio of compounds correlated to parameters required varied from 4.2 for the *ipso* carbon to 6.1 for the *meta* carbon. Moreover, the fifty-five compounds used in this study represent 19.3% of the set of 286 possible phenylsilanes containing the substituents; CH_3; C_6H_5, C_2H_3, C_3H_5, n-C_4H_9, H, Cl, and alkoxy with zero to three β-carbons. This corresponds to compounds per parameter ratios of 22.0 for the *ipso* carbon to 31.8 for the *meta* carbon.

Significantly, the parameters δ_{Ph}, δ_{H}, δ_{Cl}, and δ_{OR} obtained in this study did not appreciably differ from the values for those substituents obtained earlier. Thus, the inclusion of vinyl, allyl and n-butyl substituents did not alter the effect of the other groups as determined by the values of the SCS parameters *.

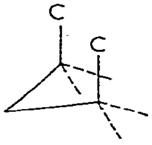
Substituent effects. The observed shifts of the ^{13}C phenyl resonances are in accord with results that have been discussed in several previous publications [2,3,5,8,15]. No anomalous behavior was observed with the inclusion of the four additional groups (n-butyl, vinyl, allyl, t-butoxy). While the NMR data alone are insufficient to permit detailed conclusions concerning the relative importance of inductive, resonance, and steric effects, it seems clear that the same factors which determine the phenyl chemical shifts in α-substituted toluenes [14,23] are operative for the phenylsilanes. In particular, the upfield shift of a carbon three bonds removed from a substituent in a *gauche* conformation [24] and downfield shift due to a four-bond *syn-axial* arrangement [25] in organic systems are mirrored in these results for the organosilanes.



gauche



anti



syn-axial

$$\delta_{C^*(gauche)} < \delta_{C^*(anti)}$$

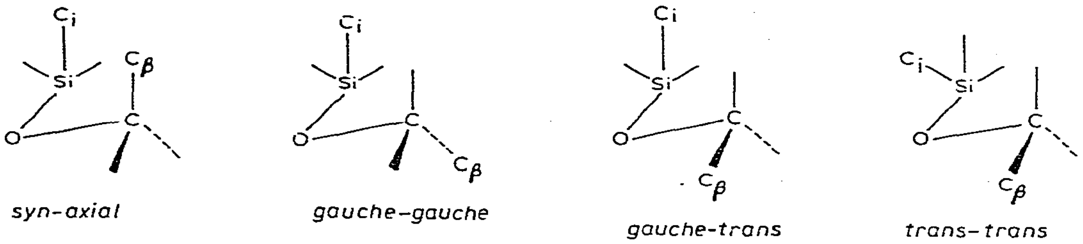
This is particularly apparent in the three series of alkoxysilanes: $(CH_3)_2$-C_6H_5SiOR, $CH_3(C_6H_5)_2SiOR$, $CH_3(C_6H_5)HSiOR$; OR = OCH_3, OC_2H_5, O-i-C_3H_7, O-t-C_4H_9. The downfield *ipso* shift is an example of the δ-effect. The β-carbon of the alkoxy substituent is four bonds removed from the *ipso* carbon. As an

---

* Twenty-nine of the possible thirty-six pairs of substituents were represented in the complete data set.

ethoxy group replaces a methoxy group, the β-carbon can adopt any of four conformations relative to the *ipso* carbon; *syn—axial*, *gauche—trans*, *gauche—gauche*, or *trans—trans*.

Since the *syn-axial* orientation of a substituent leads to a deshielding of the carbon being observed, any contribution of this conformation will produce a downfield shift of the *ipso* resonance. Successive β-substitution (viz. i-propoxy and t-butoxy) lead to further downfield shifts (Fig. 2). However, with the substitution of a t-butoxy group for an i-propoxy group, one β-carbon must always be *syn-axial* or approximately *syn-axial* to the *ipso* carbon, leading to an abrupt downfield shift.



Although the changes in shifts of the *para* carbon are not as intense as those of the *ipso* carbon, similar trends are visible. By contrast, the shift is upfield as

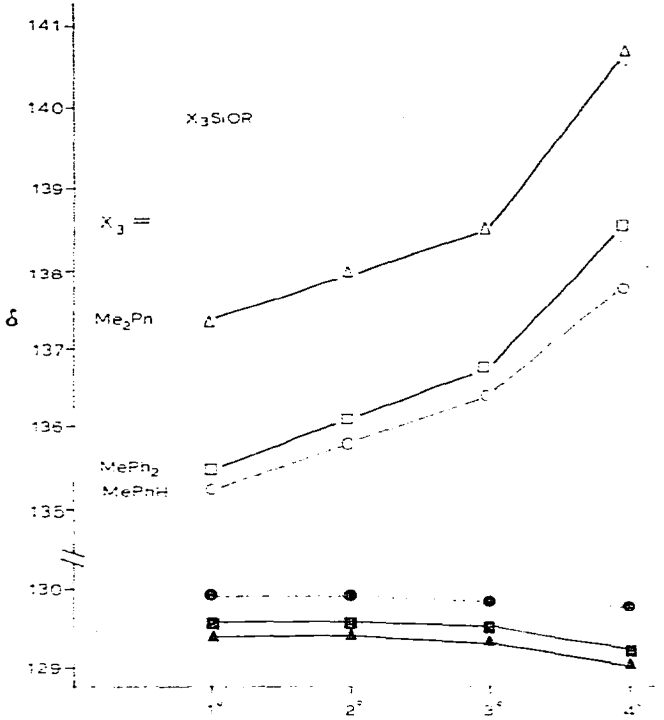


Fig. 2. Variation of the *ipso* (open points) and *para* (solid points) resonances of several phenylalkoxysilanes as a function of the alkoxide group: 1° methoxy, 2° ethoxy, 3° i-propoxy, 4° t-butoxy. Triangles = $Me_2PhSiOR$, squares = $MePh_2SiOR$, circles = $MePhHSiOR$.

TABLE 5

CALCULATED σ^+ VALUES FOR SEVERAL SILYL GROUPS BASED ON ^{13}C NMR CHEMICAL SHIFTS OF THE *para*-CARBON IN $C_6H_5SiX_3$

SiX_3	δ_p	σ^+
$CH_2Si(CH_3)_3$	123.90	—0.50
$Si(OCH_2CH_2)_3N$	127.74	—0.08
$Si(CH_3)_3$	129.97	+0.03
$Si(C_6H_5)_3$	129.61	+0.12
SiH_3	129.78	+0.14
$Si(OC_2H_5)_3$	130.06	+0.17
$SiCl_3$	132.73	+0.46

opposed to the downfield shift of the *ipso* resonance upon successive β-substitution (Fig. 2).

Hammett parameters for silyl groups. The relationship between the *para* carbon chemical shift of monosubstituted benzenes and the Hammett σ^+ constant of the substituent is well established [26]. Others [21] have used this result to estimate σ^+ values for various metallo—methyl substituents including the trimethylsilylmethyl group. Using the data of Levy and co-workers [26], we determined the following relationship * between σ^+ and δ_p:

$$\sigma^+ = 0.1081\ (\Delta\delta), \text{ where } \Delta\delta = 128.50 - \delta_p$$

Calculated values for several commonly encountered silyl groups are given in Table 5.

Correlation of ^{13}C and ^{19}F results. In previous studies of organosilanes, use

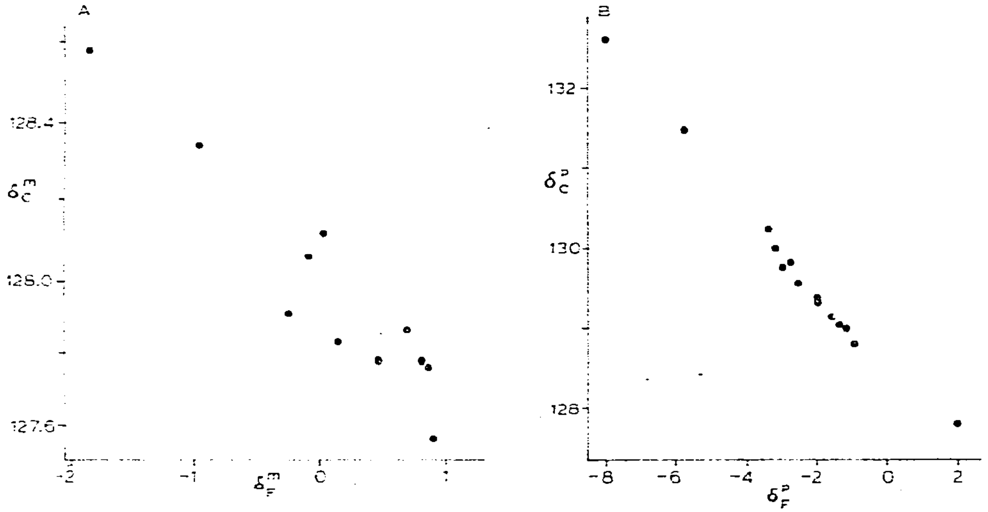


Fig. 3. Correlation of ^{19}F chemical shifts of $FC_6H_4SiX_3$ with ^{13}C chemical shifts of $C_6H_5SiX_3$. (A) *meta*-F vs. *meta*-C, (b) *para*-F vs. *para*-C.

---

* $r = 0.979$ for thirteen compounds. The regression line was forced through the origin ($\delta_{C_6H_6} = 128.50$, $\sigma_H^+ = 0.0$).

has been made of the ^{19}F NMR chemical shifts of *para-* and *meta*-fluorophenyl derivatives as a probe for studying substituent effects on silicon [27,28]. Although there are some doubts about the interpretation of the results [29], ^{19}F NMR data can serve as a useful guide for measuring the interaction of substituents with the phenyl group. Fluorine-19 data were available for fluorophenyl analogs of several silanes reported here, and correlations between the ^{13}C and ^{19}F data were made. A high correlation ($r = 0.994$) between $\delta^{p}{}_{^{19}\mathrm{F}}$ and $\delta^{p}{}_{^{13}\mathrm{C}}$ was obtained and a smaller ($r = 0.945$), though still highly significant, correlation exists for the *meta*-carbon vs. *meta*-fluorine resonances (Fig. 3).

References

1 For a review of the importance of *d*-orbitals in organosilicon chemistry, see E.A.V. Ebsworth in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. I, Part I, Marcel Dekker, Inc., New York, N.Y., 1968, pp. 1—104.
2 C.D. Schaeffer, J.J. Zuckerman and C.H. Yoder, J. Organometal. Chem., 80 (1974) 29.
3 S.Q.A. Rizvi, B.D. Gupta, W. Adcock, D. Doddrell and W. Kitching, J. Organometal. Chem., 63 (1973) 67.
4 M. Bullpitt, W. Kitching, W. Adcock and D. Doddrell, J. Organometal. Chem., 116 (1976) 161.
5 J. Schraml, Nguyen-Duc-Chuy, V. Chvalovský, M. Mägi and E. Lippmaa, J. Organometal. Chem., 51 (1973) C5.
6 Nguyen-Duc-Chuy, V. Chvalovský, J. Schraml, M. Mägi and E. Lippmaa, Coll. Czech. Chem. Commun., 40 (1975) 875.
7 J. Schraml, V. Chvalovský, M. Mägi and E. Lippmaa, Coll. Czech. Chem. Commun., 40 (1975) 879.
8 R.K. Harris and B.J. Kimber, Org. Magn. Reson., 7 (1975) 460.
9 J. Pola, Z. Papouskova and V. Chvalovský, Coll. Czech. Chem. Commun., 41 (1976) 239.
10 G. Englehardt, H. Jancke, M. Mägi, T. Pehk and E. Lippmaa, J. Organometal. Chem., 28 (1971) 293.
11 J. Schraml, Nguyen-Duc-Chuy and V. Chvalovský, Org. Magn. Reson., 7 (1975) 379.
12 C.G. Pitt, J. Chem. Soc., Chem. Commun. (1971) 816.
13 C.G. Pitt, J. Organometal. Chem., 61 (1973) 49.
14 J.B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp. 196—207.
15 P.E. Rakita, J.P. Srebro and L.S. Worsham, J. Organometal. Chem., 104 (1976) 27.
16 P.E. Rakita, L.S. Worsham and J.P. Srebro, Org. Magn. Reson., 8 (1976) 310.
17 V. Bažant, V. Chvalovský and J. Rathouský, "Organosilicon Compounds", Vol. 1, Academic Press, New York, 1965.
18 P.E. Rakita and L.S. Worsham, to be published.
19 G.A. Taylor and P.E. Rakita, Org. Magn. Res., 6 (1974) 644.
20 Yu.N. Luzikov, N.M. Sergeyev and Yu.A. Ustunyuk, Vestn. Mosk. Univ., 15 (1974) 109; Chem. Abstr., 81 (1975) 3155n.
21 W. Adcock, B.D. Gupta, W. Kitching, D. Doddrell and M. Geckle, J. Amer. Chem. Soc., 96 (1974) 7360.
22 W. Adcock, B.D. Gupta, W. Kitching and D. Doddrell, J. Organometal. Chem., 102 (1975) 297.
23 W.F. Reynolds, I.R. Peat, M.H. Freedman and J.R. Lyerla, Jr., Can. J. Chem., 51 (1973) 1857.
24 (a) D.M. Grant and B.V. Cheney, J. Amer. Chem. Soc., 89 (1967) 5315; (b) B.V. Cheney and D.M. Grant, ibid., 89 (1967) 5319.
25 S.H. Grover, J.P. Guthrie, J.B. Stothers and C.T. Tan, J. Magn. Reson., 10 (1973) 227.
26 G.L. Nelson, G.C. Levy and J.D. Cargioli, J. Amer. Chem. Soc., 94 (1972) 3089.
27 J. Lipowitz, J. Amer. Chem. Soc., 94 (1973) 1582.
28 A. Daneshrad, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 85 (1975) 35.
29 A.R. Bassindale, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 21 (1970) 91.