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^{13}C NMR STUDIES OF ORGANOSILANES

I. SUBSTITUENT-CHEMICAL-SHIFT PARAMETERS FOR PHENYLSILANES*

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Summary

The ^{13}C NMR spectra for a series of 38 phenylsilanes of the type $C_6H_5SiX_3$ ($X = CH_3$, Cl, C_6H_5, H, alkoxy) have been recorded and assigned. The phenyl resonances have been correlated in terms of a small number (five to nine) of empirical substituent-chemical-shift parameters. The *meta* and *para* resonances, which are highly correlated, exhibit a linear dependence on the nature of the substituents. The other two phenyl resonances show a more complex behavior, requiring second-order terms for successful correlation.

A general approach to the analysis and interpretation of a large variety of experimental data on chemical systems is the assumption that the behavior patterns for a homologous series of compounds can be described by the general equation 1:

$$P_n = P_o + \sum_i f_i \qquad (1)$$

where P_n is some property of the n-th compound, P_o the corresponding property of the reference compound, and the f_i's the factors which may influence the property in question [1]. This approach is a fundamental strategy for the understanding of molecular behavior and has lead to the successful correlation of diverse physical and chemical properties in numerous systems.

A noteworthy recent example of this approach is the application of equation 1 to ^{13}C NMR chemical shifts [2]. Successful correlations in terms of substituent-chemical-shift (SCS) parameters have been obtained for a number of organic systems including alkanes [3,4], substituted benzenes [5,6], alcohols [7], and others [2]. The situation with respect to heavier nuclei (particularly ^{29}Si and ^{119}Sn)

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is less clear. Correlations of ^{29}Si [8,9,10] and ^{119}Sn [8,11] resonances based on substituents have established general trends which can be empirically interpreted in terms of the electronegativity of the substituents, hybridization at the central atom, multiple bonding, and other factors. Correlations between the ^{29}Si resonances of phenyl- and benzyl-silanes have also been reported [10].

Organosilanes, as Group IV congeners of the hydrocarbons, are a logical class of compounds on which to attempt an extension of the SCS analysis of ^{13}C NMR spectra. It is reasonable to expect that useful results could be obtained, provided the appropriate factors (f_i's) are included in the analysis. We report here a study of the ^{13}C NMR spectra of a series of 38 phenylsilanes and an analysis of the data in terms of SCS parameters.

Experimental

General data

All preparations and manipulations were carried out in an atmosphere of purified nitrogen. Infrared spectra were recorded on liquid films or mineral oil mulls using a Perkin—Elmer 257 or 421 spectrophotometer. Proton NMR spectra were obtained with a Jeolco C60-HL spectrometer. Elemental analyses were performed by Chemalytics Inc., Tempe, Arizona. Analytically pure samples were obtained by GLPC separations using a Varian Aerograph Model 90-P3 chromatograph equipped with a thermal conductivity detector. Typical separations were carried out on a column (3/8" X 10') packed with 20% SE-30 on 60/80 Chromosorb W at 100-200°C with a flow rate of 30 ml/min.

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 transient responses was sufficient to obtain adequate signals for all carbon atoms. Samples were prepared as 20-40% w/w solutions in $CDCl_3$ containing 2-5% $CHCl_3$ as an internal reference. Insufficiently soluble samples were studied as saturated solutions, with an appropriate increase in the number of transients collected. Chemical shifts were recorded with respect to internal $CHCl_3$ and converted to the TMS scale using the relationship $\delta(CHCl_3) = 77.20$ ppm downfield from TMS. Positive shifts are reported downfield from TMS. Spectral reproducibility was better than 0.04 ppm for individual samples.

The chemical shift assignments were made by comparing the spectra from related compounds and correlating the systematic shifts due to slight differences in structure. The assignments showed a strong internal consistency and, where data were available in the literature, agreed with the reported values and assignments.

Samples of the chloro-, phenyl-, and hydro-silanes were obtained from Petrarch Systems, Levittown PA and used as received. The alkoxysilanes were prepared [12] from the corresponding chloro compounds by condensation with the appropriate alcohol in hexane or ether in the presence of pyridine, and purified by distillation. Isolated yields were typically 65-80%. For all new compounds the proton NMR and infrared spectra were in agreement with the expected structure. Boiling points and analytical data for the new compounds are presented below:

Methoxydimethylphenylsilane. 75-80°C/9 mmHg. Anal. Found: C, 64.82; H, 8.46. $C_9H_{14}SiO$ calcd.: C, 65.00; H, 8.49%.

Ethoxydimethylphenylsilane. 70°C/0.2 mmHg. Anal. Found: C, 66.41; H, 8.85. $SiC_{10}H_{16}O$ calcd.: C, 66.61; H, 8.94%.

Isopropoxydimethylphenylsilane. 50°C/0.05 mmHg. Anal. Found: C, 68.10; H, 9.29. $SiC_{11}H_{18}O$ calcd.: C, 67.98; H, 9.37%.

Methoxymethyldiphenylsilane. 108-14°C/0.5 mmHg. Anal. Found: C, 73.83; H, 7.09. $SiC_{14}H_{16}O$ calcd.: C, 73.63; H, 7.06%.

Ethoxymethyldiphenylsilane. 112°C/0.5 mmHg. Anal. Found: C, 74.53; H, 7.31. $SiC_{15}H_{18}O$ calcd.: C, 74.32; H, 7.48%.

n-Propoxymethyldiphenylsilane. 136°C/2.6 mmHg. Anal. Found: C, 74.90; H, 7.86. $SiC_{16}H_{20}O$ calcd.: C, 74.94; H, 7.86%.

n-Butoxymethyldiphenylsilane. 98-102°C/0.05 mmHg. Anal. Found: C, 75.55; H, 8.19. $SiC_{17}H_{22}O$ calcd.: C, 75.50; H, 8.20%.

n-Pentoxymethyldiphenylsilane. 124°C/0.05 mmHg. Anal. Found: C, 76.02; H, 8.46. $SiC_{18}H_{24}O$ calcd.: C, 76.00; H, 8.50%.

i-Propoxymethyldiphenylsilane. 89-94°C/0.05 mmHg. Anal. Found: C, 75.46; H, 7.86. $SiC_{16}H_{20}O$ calcd.: C, 74.94; H, 7.86%.

sec-Butoxymethyldiphenylsilane. 105°C/0.2 mmHg. Anal. Found: C, 75.49; H, 8.30. $SiC_{17}H_{22}O$ calcd.: C, 75.50; H, 8.20%.

iso-Butoxymethyldiphenylsilane. 98-102°C/0.05 mmHg. Anal. Found: C, 75.77; H, 8.21. $SiC_{17}H_{22}O$ calcd.: C, 75.50; H, 8.20%.

Methoxymethylphenylsilane. 40-43°C/1.4 mmHg. Anal. Found: C, 63.19; H, 8.14. $SiC_8H_{12}O$ calcd.: C, 63.10; H, 7.94%.

Ethoxymethylphenylsilane. 50-52°C/1.4 mmHg. Anal. Found: C, 64.71; H, 8.52. $SiC_9H_{14}O$ calcd.: C, 65.00; H, 8.29%.

iso-Propoxymethylphenylsilane. 44°C/1.2 mmHg. Anal. Found: C, 66.58; H, 8.75. $SiC_{10}H_{16}O$ calcd.: C, 66.61; H, 9.04%.

sec-Butoxymethylphenylsilane. 58°C/1.0 mmHg. Anal. Found: C, 68.17; H, 9.23. $SiC_{11}H_{18}O$ calcd.: C, 67.98; H, 9.33%.

Di-n-propoxydiphenylsilane. 136°C/0.005 mmHg. [lit. [13]. 182°C/15 mm Hg.].

Di-n-propoxymethylphenylsilane. 90°C/0.12 mmHg. Anal. Found: C, 65.90; H, 9.44 $SiC_{13}H_{22}O_2$ calcd.: C, 65.49; H, 9.30%.

Di-iso-propoxymethylphenylsilane. 34°C/0.05 mmHg. Anal. Found: 65.40; H, 9.13. $SiC_{13}H_{22}O_2$ calcd.: C, 65.49; H, 9.30%.

Calculations

Regression analyses and correlations including plots were performed on an IBM 360/65 computer using Statistical Analysis System (SAS) routines designed by A.J. Barr and J.H. Goodnight, North Carolina State University, Raleigh, North Carolina.

Results

^{13}C NMR spectra

The ^{13}C NMR spectra of 38 phenylsilanes of the type $C_6H_5SiX_3$ (X = CH_3, Cl, H, C_6H_5, OR; R = CH_3, C_2H_5, n-, iso-C_3H_7, n-, iso-, sec-C_4H_9, n-C_5H_{11}) have been recorded and assigned (Table 1). For this series of compounds the ranges of chemical shifts were: *ipso* * (140.33-127.97), *ortho* (136.44-132.99), *meta* (128.57-127.42) and *para* (132.73-128.79). For each compound the same order of *o*, *m*, and *p* signals was observed, viz. δ_{ortho} (downfield) $> \delta_{para} > \delta_{meta}$. Moreover, for the entire set, the ranges for these three resonances did not over-

TABLE 1

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

X_3 [a]	*ipso*	*ortho*	*meta*	*para*
Me_3	140.33(139.76)[b]	133.29(133.10)	127.77(127.75)	128.79(128.89)
Me_2Cl	136.15(136.25)	133.02(133.05)	128.05(128.03)	130.27(130.24)
$MeCl_2$	133.34(133.50)	132.99(132.99)	128.33(128.32)	131.60(131.59)
Cl_3	131.50(131.51)	133.10(132.93)	128.57(138.60)	132.73(132.93)
Me_2Ph	138.08(137.94)	134.13(134.16)	127.78(127.80)	129.05(129.12)
$MePh_2$	136.08(136.11)	135.25(135.22)	127.83(127.85)	129.35(129.34)
Ph_3 [c]	134.27(134.28)	136.44(136.28)	127.90(127.90)	129.61(129.57)
Me_2H	137.30(137.28)	133.96(133.59)	127.86(127.88)	129.16(129.26)
MeH_2	133.31(133.34)	134.84(134.54)	127.97(128.01)	129.49(129.64)
H_3	127.97(127.93)	135.83(135.94)	128.10(128.14)	129.78(130.01)
$PhCl_2$	131.88(131.68)	134.00(134.05)	128.31(128.37)	131.71(131.81)
Ph_2Cl [d]	133.06(132.60)	135.30(135.16)	128.14(128.13)	130.70(130.69)
Cl_2H	131.02(131.02)	133.26(133.48)	128.51(128.45)	132.24(131.96)
HPh_2	133.30(133.63)	135.78(135.71)	128.03(127.98)	129.78(129.72)
H_2Ph	131.41(131.51)	135.63(135.60)	128.08(128.06)	129.82(129.86)
PhMeCl	134.44(134.43)	133.97(134.10)	128.05(128.08)	130.46(130.46)
PhMeH	135.21(135.46)	134.78(134.65)	127.94(127.93)	129.46(129.49)
MeClH	133.36(133.77)	133.58(133.54)	128.22(128.16)	130.81(130.61)
Me_2OMe	137.30(137.51)	133.25(133.30)	127.70(127.63)	129.40(129.41)
Me_2OEt	137.91(138.07)	133.29(133.30)	127.69(127.63)	129.38(129.33)
Me_2O-i-Pr	138.40(138.64)	133.30(133.30)	127.60(127.63)	129.26(129.25)
MePhOMe	135.48(135.68)	134.05(134.36)	127.62(127.68)	129.55(129.64)
MePhOEt	136.08(136.25)	134.15(134.36)	127.68(127.68)	129.58(129.56)
MePhO-n-Pr	136.17(136.25)	134.14(134.36)	127.63(127.68)	129.50(129.56)
MePhO-n-Bu	136.18(136.25)	134.18(134.36)	127.67(127.68)	129.56(129.56)
MePhO-n-Pent	136.19(136.25)	134.22(134.36)	127.70(127.68)	129.59(129.56)
MePhO-i-Pr	136.70(136.81)	134.21(134.36)	127.65(127.68)	129.51(129.48)
MePhO-s-Bu	136.94(136.81)	134.33(134.36)	127.68(127.68)	129.54(129.48)
MePhO-i-Bu	136.29(136.25)	134.24(134.36)	127.71(127.68)	129.60(129.56)
MeHOMe	135.24(135.03)	133.59(133.79)	127.77(127.76)	129.90(129.78)
MeHOEt	135.75(135.59)	133.61(133.79)	127.75(127.76)	129.83(129.71)
MeHO-i-Pr	136.35(136.16)	133.67(133.79)	127.77(127.76)	129.79(129.63)
MeHO-s-Bu	136.46(136.16)	133.70(133.79)	127.74(127.76)	129.75(129.63)
$Ph(O\text{-}n\text{-}Pr)_2$	133.20(133.05)	134.76(134.55)	127.61(127.56)	129.95(130.00)
$Me(O\text{-}n\text{-}Pr)_2$	134.78(134.88)	133.79(133.49)	127.52(127.51)	129.64(129.77)
$Me(O\text{-}i\text{-}Pr)_2$	135.77(136.01)	133.78(133.49)	127.42(127.51)	129.44(129.61)
$Ph(O\text{-}n\text{-}Bu)_2$	133.24(133.05)	134.79(134.55)	127.62(127.56)	129.96(130.00)
MeHO-n-Pr	135.85(135.59)	133.66(133.79)	127.77(127.76)	129.85(129.71)
RMS deviation (ppm)	0.21	0.17	0.04	0.11

[a] Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pent = pentyl, Ph = phenyl. [b] Calculated values in parentheses. [c] 2 wt% in $CDCl_3$. [d] 5 wt% in $CCl_4/CDCl_3$ (1/1 by volume).

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* For the 1-carbon. From the Latin, ipse = he, himself; the very one; the selfsame.

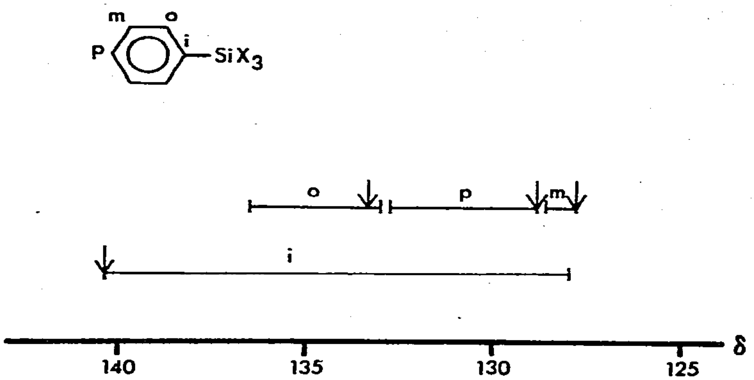

Fig. 1. Ranges of observed phenyl resonances for $C_6H_5SiX_3$ (X = CH_3, Cl, C_6H_5, H, alkoxy). Arrows denote locations of signals for $C_6H_5Si(CH_3)_3$.

lap each other (Fig. 1). The *ipso* resonances covered a range of over 12 ppm and spanned the regions in which the other three signals occurred. When sets of compounds were chosen so that the substituents on the silicon were systematically changed (e.g. successive substitution of CH_3 by H, (Fig. 2)), the four ring carbon resonances underwent regularly varying shifts. Thus, for example, successive replacement of CH_3 by H produced an upfield shift of the *ipso* resonance (~4 ppm per H), a downfield shift of the *ortho* resonance (~0.9 ppm per H), and smaller downfield shifts of the *meta* and *para* signals. These substituent shift effects were invariably linear at the *meta* and *para* positions for all pairs of substituents tested ($SiX_3 \rightarrow SiX_2Y \rightarrow SiXY_2 \rightarrow SiY_3$), but were significantly non-linear at the *ipso*

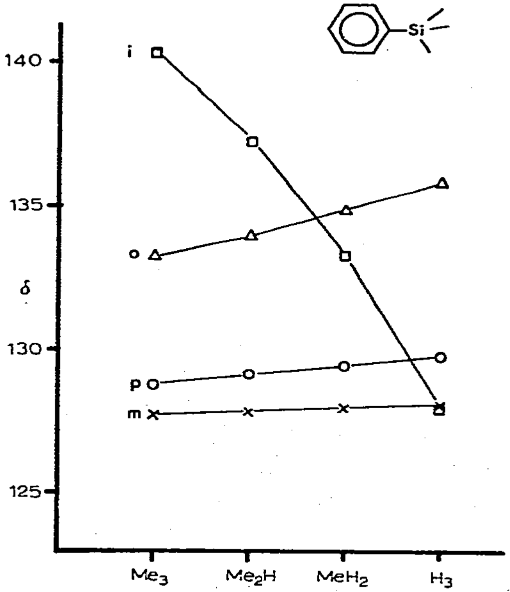

Fig. 2. Variations of the phenyl resonances upon successive substitution of H for CH_3 in C_6H_5 $Si(CH_3)_3$.

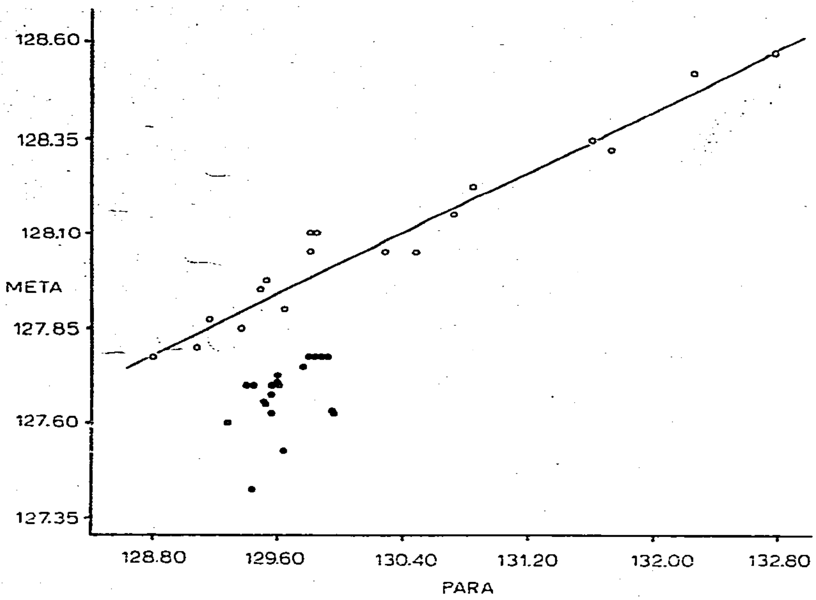

Fig. 3. Plot of the observed *meta* vs. *para* resonances. Solid circles = alkoxyphenylsilanes; open circles = non-alkoxyphenylsilanes.

and *ortho* positions for H, and at the *ipso* position for Cl and OR. For the alkoxy compounds, changes in the length and degree of substitution of the alkoxy carbon chain produced measurable shifts of the *ipso* and *para* resonances, marginally significant changes at the *ortho* position, and insignificant changes at the *meta* position.

Correlation diagrams of the observed phenyl resonances for the 38 compounds exhibited considerable scatter. There were no significant correlations between the observed resonances except for the pair *meta—para*. For all 38 compounds, the *meta—para* correlation coefficient was 0.830. For the sub-set of 18 non-alkoxy compounds the *meta—para* correlation was 0.973 (Fig. 3).

Regression analyses

The data for each ring carbon position (*i*, *o*, *m*, *p*) were analyzed separately using equation 2:

$$\delta_x^a = \mathrm{k}^a + \sum_{i=1}^{p} n_i \delta_i^a + \sum_{i=1}^{p} \sum_{j \geqslant i}^{p} n_{ij} \delta_{ij}^a \qquad (2)$$

where δ_x^a is the chemical shift of the a-th carbon (*i*, *o*, *m*, *p*) in the x-th compound, n_i the number of substituents of type i from the set of p substituents, δ_i^a the SCS parameter for a substituent of i-type, n_{ij} * the number of pairwise combinations of substituents i and j, δ_{ij}^a a second order SCS parameter, and k^a a constant. Phenyltrimethylsilane was chosen as a reference compound and

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* The second order, pairwise combination coefficients were defined as follows: If $i \neq j$, then $n_{ij} = (n_i)(n_j)$; If $i = j$, then $n_{ij} = (n_i)(n_i - 1)/2$.

TABLE 2

REGRESSION PARAMETERS[a]

	ipso	*ortho*	*meta*	*para*
k	139.76 ± 0.14	133.10 ± 0.10	127.75 ± 0.02	128.89 ± 0.06
δ(Cl)	—3.51 ± 0.13	—0.06 ± 0.05	0.28 ± 0.01	1.35 ± 0.03
δ(Ph)	—1.83 ± 0.06	1.06 ± 0.05	0.05 ± 0.01	0.23 ± 0.03
δ(H)	—2.48 ± 0.10	0.49 ± 0.08	0.13 ± 0.01	0.37 ± 0.13
δ(OR)	—2.25 ± 0.14	0.19 ± 0.06	—0.12 ± 0.01	0.52 ± 0.06
δ_β	0.56 ± 0.07	-	-	—0.08 ± 0.04
δ(H—H)	—1.47 ± 0.12	0.43 ± 0.09	-	-
δ(Cl—Cl)	0.76 ± 0.15	-	-	-
δ(OR—OR)	—1.50 ± 0.19	-	-	-
Multiple regression coefficient	0.996	0.979	0.990	0.992

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

$\delta^a(CH_3)$ and $\delta^a(CH_3—j)$ were defined as zero. A preliminary linear regression analysis (with all δ^a_{ij} = zero) on the 18 non-alkoxy compounds gave excellent agreement between observed and calculated chemical shifts for the *meta* and *para* resonances with four parameters (k, δ(Cl), δ(H), $\delta(C_6H_5)$). Equally satisfactory agreement (regression coefficient $\geqslant$0.99) was achieved for the *ortho* and *ipso* resonances by the addition of one (δ^o(H—H)) and two (δ^i(H—H) and δ^i(Cl—Cl)) second-order parameters, respectively, to the regression analysis. When the full data set was used, including 20 mono- and di-alkoxy phenyl silanes, one additional parameter δ^m(OR) and δ^o(OR) was sufficient to achieve excellent correlation of the *ortho* and *meta* resonances. Comparable agreement for the *para* signals was obtained using two parameters, δ^p(OR) and δ^p_β, the latter indicating the number of β substituents on the alkoxy carbon: Si—O—C—C_β—C_γ—C_Δ—. Likewise, a δ^i_β parameter and a second-order alkoxy parameter δ^i(OR—OR), in addition to the second-order hydrogen and chlorine coefficients, were needed to adequately predict the *ipso* resonances.

Attempts were made to find alternative second-order parameters for the *ipso* and *ortho* resonances. When the second-order coefficients were treated as quadratic terms in a power series expansion (i.e. when n_{ij} was defined as $(n_i) \times (n_j)$ for $i = j$), the agreement between calculated and observed values (as measured by the RMS deviation and correlation coefficient) was significantly poorer. In an attempted analysis using all pairwise combinations, the agreement was only marginally better even though the number of variables included in the analysis was considerably greater.

The final regression coefficients are given in Table 2 and the calculated chemical shifts are listed with the observed values in Table 1. For all four cases the correlation coefficient between the calculated and observed shifts was $\geqslant$0.98 and the RMS deviation of an individual data point was <5% of the range of observed resonances for that case. A plot of the calculated vs. observed values of the *ipso* resonances is given in Fig. 4.

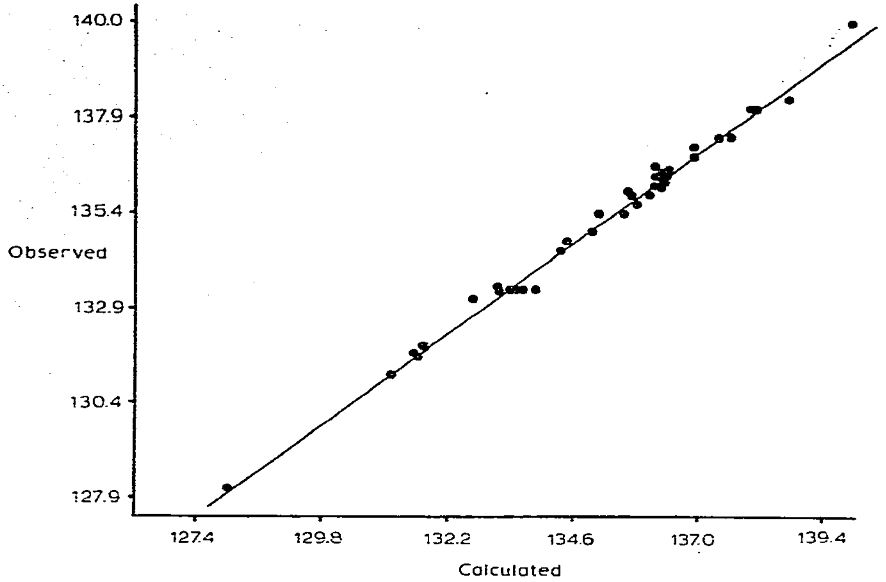

Fig. 4. Plot of calculated vs. observed values of *ipso* resonances. The solid line has unit slope and zero intercept.

Concentration and solvent effects

The effect of changes in concentration on the spectrum of phenyldimethylchlorosilane in $CDCl_3$ is given in Table 3. No significant shifts of the resonances were observed except at extremely high (i.e. $\geqslant$50 wt%) solute concentrations. Nor were any anomalous shifts noted for those compounds which, owing to low solubility, were studied in extremely dilute solution (e.g. $(C_6H_5)_4Si$, 2 wt% in $CDCl_3$; $(C_6H_5)_3SiCl$, 5 wt% in 1/1 $CCl_4/CDCl_3$). The nature of the solvent was shown to have a modest effect on the chemical shifts of the phenyl resonances of phenyltrimethylsilane (Table 4). A total shift range of about 1.5 ppm was observed as the solvent was varied from CCl_4 to toluene-d_8. Two observations were particularly noteworthy: (1) for a given solvent, the shifts of the *o*, *m*, and *p* resonances, compared to the values in $CDCl_3$, were essentially constant; and (2) the solvent shifts for the *ipso* resonance were uniformly 0.3-0.5 ppm more negative (i.e. further upfield) than the shifts for the other resonances in that solvent.

TABLE 3

CONCENTRATION DEPENDENCE OF THE ^{13}C PHENYL RESONANCES OF PHENYLDIMETHYLCHLOROSILANE

Concentration (wt%)[a]	*ipso*	*ortho*	*meta*	*para*
7	136.20[b]	133.05	128.06	130.30
15	136.19	133.06	128.07	130.31
24	136.15	133.02	128.05	130.27
50	136.07	132.99	128.03	130.24

[a] In $CDCl_3$. [b] ppm downfield from TMS, based on $CHCl_3$ = +77.20 ppm.; values ±0.04 ppm.

TABLE 4

SOLVENT DEPENDENCE OF THE ^{13}C PHENYL RESONANCES OF PHENYLTRIMETHYLSILANE

Solvent[a]	*ipso*	*ortho*	*meta*	*para*
$C_6D_5CD_3$	141.27[b]	134.54	129.05	130.04
	(+0.94)[c]	(+1.25)	(+1.28)	(+1.25)
$CO(CD_3)_2$	141.16	134.29	128.86	129.89
	(+0.83)	(+1.00)	(+1.09)	(+1.10)
C_6D_6	140.96	134.26	128.74	129.74
	(+0.63)	(+0.97)	(+0.97)	(+0.97)
$SO(CD_3)_2$	140.40	133.75	128.39	129.46
	(+0.07)	(+0.46)	(+0.62)	(+0.67)
CS_2	140.09	133.54	128.08	129.10
	(−0.24)	(+0.25)	(+0.31)	(+0.31)
$CDCl_3$	140.33	133.29	127.77	128.79
	(0.0)	(0.0)	(0.0)	(0.0)
CCl_4	139.63	132.94	127.49	128.51
	(−0.70)	(−0.35)	(−0.28)	(−0.28)
CCl_4	139.70[d]	133.02	127.58	128.59

[a] Solutions 20-25 wt% with 2-5 wt% $CHCl_3$ as internal reference. [b] In ppm downfield from TMS. [c] Solvent shift with respect to the corresponding resonance in $CDCl_3$. [d] Data from ref. 15.

As a test of the constancy of the solvent effect, the spectrum of phenylmethylsilane was recorded in C_6D_6. The observed shifts were *i* 134.13, *o* 135.85, *m* 128.98, and *p* 130.48 ppm. When these values were adjusted for the solvent shifts of C_6D_6 given in Table 4, the corrected values of 133.50, 134.88, 128.01, and 129. 51 ppm were in excellent agreement with values of 133.31, 134.84, 127.97 and 129.49 ppm observed for phenylmethylsilane in $CDCl_3$ (Table 1). In the absence of strong solute—solvent interactions [14], the effects of changes in solvent appear to be regular and predictable.

Discussion

The results clearly demonstrate that the ^{13}C NMR aromatic resonances of phenylsilanes can be readily and accurately predicted from a small set of empirical SCS parameters. The ratio of compounds correlated/parameters required varied from 4.2 (*ipso*) to 7.6 (*meta*), compared to a ratio of 2.7 (59 compounds/22 parameters) obtained by Lindemann and Adams in the successful correlation of the C_5 to C_9 paraffins [4]. Moreover the 38 compounds used in this study represent 32% of the set of 120 possible phenylsilanes containing CH_3, Cl, C_6H_5, H, and alkoxy with 0, 1, 2, or 3 β-carbons as substituents. This corresponds to compounds/parameter ratios of from 13.3 (*ipso*) to 24.0 (*meta*).

In order for SCS parameters to be generally valid, the limited data set from which they are derived must be representative (i.e. include a reasonable number of examples of all or most possible combinations of substituents). One test of the validity of the regression parameters is to note any variation of the parameters upon inclusion of additional compounds in the data set. In this study, trial regression analyses were performed with the sub-set of 18 non-alkoxy compounds, and the various δ(Cl), δ(Ph), and δ(H) parameters were derived. Significantly, no variation greater than twice the standard deviation of these parameters was noted when the 20 alkoxy compounds were included in the analysis. It is reasonable to conclude that SCS parameters derived from a partial data set would be valid for the complete set of compounds containing all possible combinations of those substituents.

In principle, the spectrum of each of the possible compounds in the complete set can be constructed from the regression parameters. This represents a "library" of spectral data useful for analytical purposes (e.g. the identification of unknown from their spectra by comparison with calculated spectra of all possible compounds containing certain substituents) *. This is a particularly promising application since each spectrum contains four ** independent pieces of data from the phenyl portion of the spectrum alone. Moreover, since the SCS parameters appear to be independent of concentration and solvent, the calculated spectra can be obtained for any reasonable set of conditions by use of appropriate solvent shift factors.

With any set of empirically derived parameters, it is important to attempt an interpretation of their values in chemical terms. It is not apparent at this stage that these data are amenable to such an interpretation. No correlation was observed between the values of the δ's at any ring position and the group electronegativity of the substituents. It should be noted that order of relative magnitude of the substituent effects ($i > o \sim p > m$) is qualitatively what might be expected if the influence of the substituents was transmitted through the phenyl ring via a π-type mechanism. On the other hand, the observed *meta* shifts are strongly correlated with the *para* shifts (Fig. 3), which suggests that resonance effects are not dominant at the *para* position.

The second-order terms are equally difficult to interpret. A successful correlation was achieved when the second order coefficients were included as pairwise combination terms, not as quadratic functions. Only homogeneous pairwise terms were significant in the final analysis. They cannot be readily ascribed to steric effects, since for the *ipso* resonance the signs on δ(Cl—Cl) and δ(OR—OR) are oppoosite. Moreover, second-order phenyl terms are not significant whereas second-order hydrogen parameters are required for both the *ipso* and *ortho* resonances.

Some possible significant correlations were noted between the ^{29}Si and ^{13}C resonances of 15 phenylsilanes for which ^{29}Si data were available in the literature. The results are summarized in Table 5. For each of the ring carbon positions, there was considerable scatter in the correlation between the ^{13}C and ^{29}Si resonances. In the case of the *ipso* and *para* signals, a good correlation was achieved when the 3 phenylsilanes with chloro substituents were excluded. A comparable level of agreement was obtained for the *ortho* resonances when the 3 di- and tri-alkoxy compounds were eliminated. Correlation of the *meta* signals was achieved only when both the chloro and polyalkoxy compounds were excluded.

It is clear that the lack of significant correlation at any ring position for all 15 compounds indicates that a complex set of factors is responsible for the ob-

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* A detailed treatment of this approach is the subject of a separate study.

** Three in the case of the non-alkoxy silanes where the *meta* and *para* resonances are highly correlated (Fig. 3).

TABLE 5

CORRELATION COEFFICIENTS FOR ^{29}Si and ^{13}C RESONANCES OF SELECTED PHENYLSILANES[a]

Compounds	*ipso*	*ortho*	*meta*	*para*	N^b
Complete set	0.631	0.520	0.466	0.229	15
Excluding 3 chlorophenylsilanes	0.948	0.328	0.120	0.817	12
Excluding 3 polyalkoxyphenylsilanes	0.486	0.862	0.134	0.362	12
Excluding 3 phenylchloro- and 3 phenyl(polyalkoxy)-silanes	0.934	0.812	0.937	0.722	9

[a] ^{29}Si data taken from refs. 9 and 10. ^{13}C data for $PhSi(OMe)_3$, $PhSiMe(OEt)_2$, and $PhSi(OEt)_3$ were calculated values using the regression parameters (Table 2). [b] Number of compounds.

served shifts. The *ipso* carbon, which is directly bonded to the silicon, might be expected to directly reflect substituent changes on the silicon. The slope of the correlation is positive (downfield ^{29}Si corresponds to downfield ^{13}C) but significant only when chloro substituents are excluded. Although it is appealing to suggest that the poor fit of the chloro compounds may be due to $p_\pi \rightarrow d_\pi$-interactions, other factors including inductive effects, neighboring group anisotropy and intramolecular dispersion interactions may also be important. It may be significant that at the *para* position, where these effects should be negligible, the slope of the correlation is negative (opposite that observed at the *ipso* carbon).

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