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CORRELATION OF HAMMETT σ CONSTANTS WITH NMR PARAMETERS FOR SUBSTITUTED PHENYLSILANES, PHENYLMETHYLSILANES AND PHENYLDIMETHYLSILANES

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SUMMARY

The ^{29}Si–H coupling constants and SiH chemical shifts have been determined for a series of substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes. Excellent correlations with almost identical ρ values, were found to exist between the coupling constants and the Hammett σ constants of the ring substituents for the three series. Treatment of the couplings within the framework of the Hammett–Taft equation gave new Taft σ^* constants for six substituted phenyl groups. The SiH chemical shifts were found to be much less sensitive to change in structure than $J(^{29}\text{Si–H})$. The ^{13}C–H coupling constants and chemical shifts of the methyl groups of substituted phenylmethylsilanes and phenyldimethylsilanes have also been measured and correlated by the Hammett σ constants. The ρ values obtained are compared with those of substituted phenyltrimethylsilanes reported by other workers.

INTRODUCTION

Yoder, Tuck and Hess[1] have recently shown that the methyl proton chemical shifts, as well as the methyl ^{13}C–H coupling constants, for a series of substituted toluenes, tert-butylbenzenes, *N,N*-dimethylanilines and anisoles are directly proportional to the Hammett σ constants for the *meta* and *para* substituents. This is to be expected since such NMR parameters must be related to the change in the electronic structures of molecules engendered by the presence of different substituents. A number of other workers[2–7] have also found similar examples of linear correlations between NMR data on substituted aromatics and substituent constants.

In view of our continuing interest in the chemistry of organosilicon hydrides[8], we have determined the ^{29}Si–H coupling constants and SiH chemical shifts for a series of *meta*- and *para*-substituted phenylsilanes, phenylmethylsilanes and phenyldimethylsilanes in order to correlate these data with the Hammett σ constants. The $SiCH_3$ proton chemical shifts and the methyl ^{13}C–H coupling constants for the two latter series of arylhydrosilanes are also reported and compared with the reported values for other structurally related compounds.

EXPERIMENTAL

Materials

Phenylsilane, phenylmethylsilane, phenyldimethylsilane, and their methyl and chloro derivatives, were prepared as described previously[8]. The *p*-methoxy and *p*-dimethylamino derivatives were prepared by the lithium aluminum hydride reduction of the corresponding aryltrichlorosilanes, arylmethyldichlorosilanes and aryldimethylsilanes which were obtained by reaction of the appropriate Grignard reagent in ether or THF solution with silicon tetrachloride, methyltrichlorosilane and dimethyldichlorosilane. The physical properties of the six hydrosilanes are tabulated in Table 1. In all cases final purification was achieved by preparative vapour phase chromatography. The purity of these hydrosilanes was shown to be greater than 99% by GLC analysis.

TABLE 1

PHYSICAL PROPERTIES OF SOME *p*-SUBSTITUTED ARYLHYDROSILANES ($YC_6H_4SiRR'H$)

Y	R	R'	B.p. [°C (mm)]	n_D^{20}	Calcd. (%)		Found (%)	
					C	H	C	H
p-$N(CH_3)_2$	H	H	81(5)[a]	[a]	63.51	8.66	64.11	8.98
p-OCH_3	H	H	177(760)[b]	1.5231[b]				
p-$N(CH_3)_2$	CH_3	H	110(16)	1.5614	65.39	9.15	66.39	9.42
p-OCH_3	CH_3	H	178(760)	1.5210	63.10	7.94	62.94	8.29
p-$N(CH_3)_2$	CH_3	CH_3	122(14)[c]	1.5465[c]				
p-OCH_3	CH_3	CH_3	107(26)[d]	1.5135[d]				

[a] M.p. 49–50°. [b] Lit.[9] b.p. 180° (739.5 mm), n_D^{25} 1.5251. [c] Lit.[10] b.p. 128° (15 mm), n_D^{20} 1.5468. [d] Lit.[11] b.p. 115° (41 mm), n_D^{20} 1.5139.

NMR measurements

NMR constants were determined from spectra obtained on a Varian Model A-60D high-resolution nuclear magnetic resonance spectrometer. Measurements of the coupling constants were made in the pure liquid phase. The ^{29}Si–H or ^{13}C–H coupling constants were evaluated from the satelite bands produced by the ^{29}Si or ^{13}C present in natural abundance, such bands being symmetrically disposed about the main SiH or CH proton signals. These values were obtained at 250 or 500 Hz sweep width with an estimated accuracy of at least ±0.3 Hz.

Chemical shifts were recorded at 500 Hz sweep width. All chemical shifts were measured in carbon tetrachloride (spectroquality grade) solution and the corrected values obtained by extrapolating measurements from three concentrations below 10% to infinite dilution.

RESULTS

All the NMR parameters determined in this study are compiled in Table 2. The coupling constants were obtained from measurements in neat liquids, while the

(*continued on p.* 85)

TABLE 2

NMR DATA FOR ARYLHYDROSILANES ($YC_6H_4SiRR'H$)[a]

Y	R	R'	$J(^{29}Si-H)$	$\delta(SiH)$	$J(^{13}C-H)$	$\delta(CH)$
p-$N(CH_3)_2$	H	H	−194.7	248.8		
p-OCH_3	H	H	−196.8	250.0		
p-CH_3	H	H	−197.3	250.2		
m-CH_3	H	H	−197.7	250.1		
H	H	H	−198.6	252.1		
p-Cl	H	H	−200.6	252.0		
m-Cl	H	H	−201.9	252.6		
p-$N(CH_3)_2$	CH_3	H	−189.3	255.5	121.1	20.5
p-OCH_3	CH_3	H	−191.5	257.3	121.4	22.3
p-CH_3	CH_3	H	−192.7	257.6	121.5	22.9
m-CH_3	CH_3	H	−193.0	257.2	121.5	23.6
H	CH_3	H	−193.7	259.3	121.6	24.7
p-Cl	CH_3	H	−195.7	258.7	121.6	24.9
m-Cl	CH_3	H	−196.7	259.0	122.1	26.0
p-$N(CH_3)_2$	CH_3	CH_3	−184.7	262.4	120.1	16.2
p-OCH_3	CH_3	CH_3	−186.4	263.6	120.4	17.6
p-CH_3	CH_3	CH_3	−187.8	263.8	120.3	18.2
m-CH_3	CH_3	CH_3	−187.7	263.2	120.5	18.8
H	CH_3	CH_3	−188.3	265.2	120.8	19.6
p-Cl	CH_3	CH_3	−190.3	264.6	121.0	19.6
m-Cl	CH_3	CH_3	−191.1	265.0	121.0	21.1

[a] Parameters are given in Hz; δ is by reference to TMS as an internal standard.

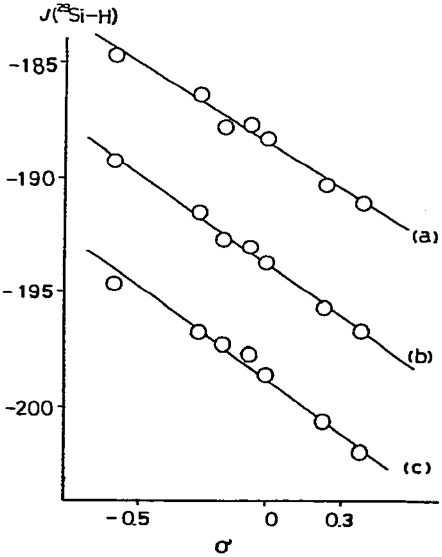


Fig. 1. Plots of $J(^{29}Si-H)$ values *vs.* σ for the three series: (a) phenyldimethylsilanes, (b) phenylmethysilanes and (c) phenylsilanes.

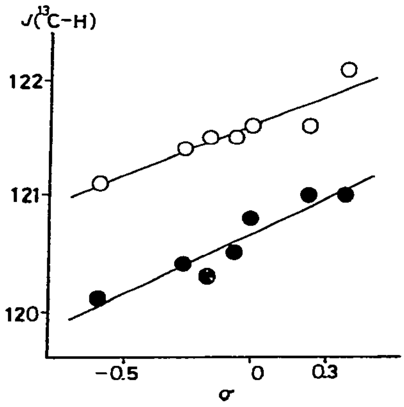
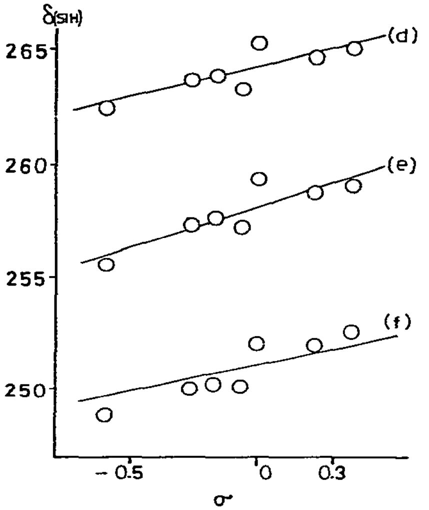


Fig. 2. Plots of methyl $J(^{13}C-H)$ values *vs.* σ for phenylmethylsilanes (open circles) and phenyldimethylsilanes (solid circles).



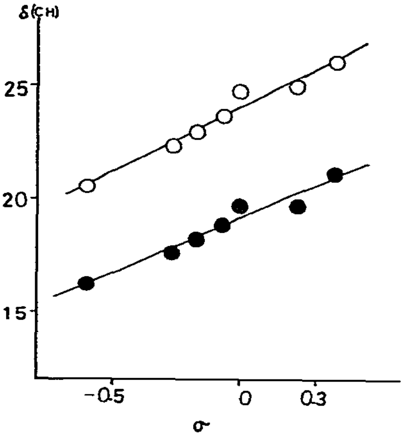


Fig. 3. Plots of δ(SiH) values *vs.* σ for the three series: (d) phenyldimethylsilanes (e) phenylmethylsilanes and (f) phenylsilanes.

Fig. 4. Plots of δ(CH) values *vs.* σ for phenylmethylsilanes (open circles) and phenyldimethylsilanes (solid circles).

TABLE 3

LEAST-SQUARE ANALYSIS CORRECTED PARAMETERS FOR NMR DATA[a]

Data	System		ρ	C	r
$J(^{29}Si\text{–}H)$	$YC_6H_4SiH_3$	σ	−7.41	−198.8	0.988
		σ^+	−2.95	−199.2	0.893
	$YC_6H_4SiH_2CH_3$	σ	−7.72	−193.8	0.997
		σ^+	−3.17	−194.3	0.963
	$YC_6H_4SiH(CH_3)_2$	σ	−6.72	−188.5	0.990
		σ^+	−2.74	−189.0	0.920
$J(^{13}C\text{–}H)$	$YC_6H_4SiH_2CH_3$	σ	0.86	121.6	0.928
		σ^+	0.36	121.7	0.872
	$YC_6H_4SiH(CH_3)_2$	σ	1.04	120.7	0.945
		σ^+	0.41	120.7	0.848
δ(SiH)	$YC_6H_4SiH_3$	σ	4.07	251.1	0.931
		σ^+	1.66	251.4	0.866
	$YC_6H_4SiH_2CH_3$	σ	3.62	258.1	0.881
		σ^+	1.61	258.4	0.893
	$YC_6H_4SiH(CH_3)_2$	σ	2.67	264.2	0.842
		σ^+	1.14	264.4	0.824
δ($SiCH_3$)	$YC_6H_4SiH_2CH_3$	σ	5.65	24.0	0.983
		σ^+	2.42	24.4	0.957
	$YC_6H_4SiH(CH_3)_2$	σ	4.82	19.1	0.977
		σ^+	2.05	19.4	0.946

[a] Values of ρ are given in Hz/σ or in Hz/σ^+ while those of C given in Hz.

chemical shifts were determined at infinite dilution from measurements in carbon tetrachloride solution.

The four kinds of NMR data obtained are plotted against the Hammett σ constants[12] in Figs. 1–4, yielding the respective straight-line relationship for each series. The slope (ρ), intercept (C) and correlation coefficient (r) were determined by the method of least squares and are given in Table 3. These values were also calculated using the σ^+ function derived by Brown–Okamoto[13]. Except for one case, all the data provide a better correlation with the ordinary σ constants than with the σ^+ constants.

DISCUSSION

The ^{29}Si–H coupling constants

The coupling constants presented in Table 2 exhibit the expected trend. In each series the presence of an electron-attracting group leads to an increase in absolute magnitude of the coupling constant, whereas an electron-donating group decreases it. For example, the ^{29}Si–H coupling constants for [4-(dimethylamino)phenyl]silane, phenylsilane and (3-chlorophenyl)silane are −194.7, −198.6 and −201.9 Hz, respectively. A similar increase in the magnitude of the directly-bound coupling constants has been noted in the methyl ^{13}C–H couplings for a series of substituted toluenes[1]. Although the magnitude of $J(^{13}\mathrm{C{-}H})$ has been shown to be related to the fraction of s character in the bonds between carbon and hydrogen[14], which is in turn related to the effective nuclear charge on the carbon atom[15], the magnitude of the ^{29}Si–H coupling constants for silicon compounds cannot be explained[16] in the simple terms used to account for the ^{13}C–H couplings. Nevertheless, the trend for the ^{29}Si–H couplings found in the present study is interesting and may suggest that, within a limited class of compounds, the magnitude of $J(^{29}\mathrm{Si{-}H})$ is approximately proportional to the degree of s character in the silicon hybrid orbital bonded to the hydrogen atom.

As seen immediately from Fig. 1 and Table 3, the correlation between $J(^{29}\mathrm{Si{-}H})$ and the usual Hammett σ constant is excellent for each series of arylhydrosilanes. A notable feature of the correlations is that the slopes for $J(^{29}\mathrm{Si{-}H})$ plots are appreciably greater than those for the $J(^{13}\mathrm{C{-}H})$ plots. Yoder *et al.*[1] have reported a ρ value of 1.7 Hz/σ for methyl $J(^{13}\mathrm{C{-}H})$ in substituted toluenes, while a ρ value of 7.4 Hz/σ for $J(^{29}\mathrm{Si{-}H})$ in substituted phenylsilanes, the silicon analogs of toluene, has been observed in this study. The greater structural dependence of $J(^{29}\mathrm{Si{-}H})$ in comparison to $J(^{13}\mathrm{C{-}H})$ suggests the possibility that the ^{29}Si–H coupling constants may provide a convenient and sensitive test of the substituent effects. Thus the successful correlation between the $J(^{29}\mathrm{Si{-}H})$ values for the three series of arylsilanes and the σ constant, which resulted in nearly identical ρ values, led us to investigate the polar effect of substituents on the $J(^{29}\mathrm{Si{-}H})$ values of hydrosilanes of the general formula $R_1R_2R_3$SiH, where the R's could be a phenyl (s), an alkyl (s) and a hydrogen (s). Available data taken from the literature[17,18] are listed in Table 4 and plotted in Fig. 5 against the sum of the Taft σ^* constants[19] for R_1, R_2 and R_3. The coupling constants were found from a least squares analysis to fit the equation

$$J(^{29}\mathrm{Si{-}H}) = -10.21\Sigma\sigma^* - 182.9$$

with a correlation coefficient of 0.994. It is thus possible to evaluate the polar substituent constants for the substituted phenyl groups employed in the present investiga-

TABLE 4

^{29}Si–H COUPLING CONSTANTS FOR SELECTED ALKYLPHENYLHYDROSILANES

Compound	$J(^{29}$Si–H) (Hz)	$\Sigma\sigma^*$	Ref.
$(C_2H_5)_3SiH$	179.2	−0.300	17
$(CH_3)_3SiH$	183.8	0.00	18
$(CH_3)_2SiH_2$	188.5	0.49	18
$C_6H_5(CH_3)_2SiH$	188.3	0.60	[a]
$CH_2I(CH_3)_2SiH$	191.4	0.85	17
CH_3SiH_3	194.6	0.98	18
$CH_2Br(CH_3)_2SiH$	193.2	1.00	17
$C_6H_5(CH_3)SiH_2$	193.7	1.09	[a]
$(C_6H_5)_2CH_3SiH$	194.0	1.20	17
$CH_2Cl(CH_3)SiH_2$	198.5	1.54	17
$C_6H_5SiH_3$	198.6	1.58	[a]
$CHCl_2(CH_3)SiH_2$	208.2	2.43	17

[a] The present work.

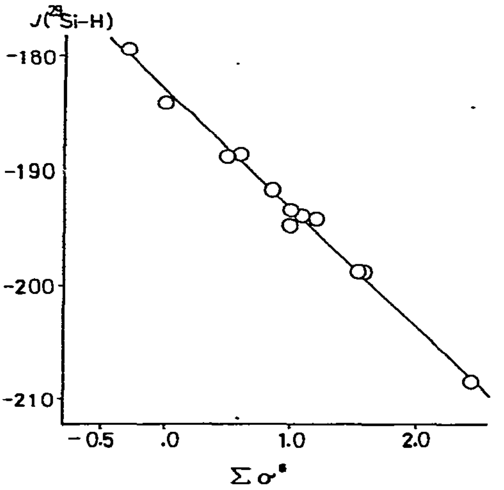


Fig. 5. Correlation of literature values of $J(^{29}$Si–H) for $R_1R_2R_3SiH$ with the sum of σ^* for R_1, R_2 and R_3.

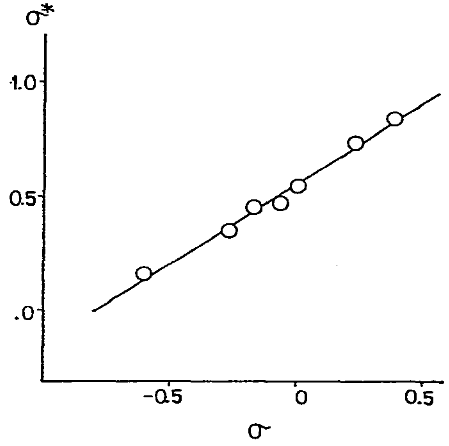


Fig. 6. Correlation between σ^* and σ.

tion through the use of this Hammett–Taft equation. As an example, consider the case of 4-tolylsilane for which $J(^{29}\text{Si–H}) = -197.3$. For such a value, $\Sigma\sigma^* = 1.410$, and since the other substituents present in the compound are two hydrogen atoms, the σ^* value for the 4-tolyl group will be

$$\sigma^*(4\text{-}CH_3C_6H_4) = 1.410 - 2 \times 0.49 = 0.430$$

The $J(^{29}$Si–H) values for 4-tolylmethylsilane and 4-tolyldimethylsilane have been similarly treated, yielding σ^* values of 0.470 and 0.480, respectively. As expected, these values are sufficiently similar with an average value of 0.460, to suggest that they

TABLE 5

POLAR SUBSTITUENT CONSTANTS (σ^*) FOR SUBSTITUTED PHENYL GROUPS

Group	σ^*	Probable error
p-$N(CH_3)_2C_6H_4$	0.163	±0.009
p-$CH_3OC_6H_4$	0.359	±0.008
p-$CH_3C_6H_4$	0.460	±0.010
m-$CH_3C_6H_4$	0.480	±0.002
p-ClC_6H_4	0.747	±0.008
m-ClC_6H_4	0.849	±0.016

correspond to the polar effect of a 4-$CH_3C_6H_4$ group. The σ^* values for other substituted phenyl groups can be calculated in a similar fashion and the results are listed in Table 5. Since these new σ^* constants have been obtained from a Hammett–Taft equation, they must be related to the original Hammett σ constants; the two sets of substituent constants are plotted against each other in Fig. 6 which exhibits a linear relationship with an excellent correlation coefficient of 0.995. The usefulness of the σ^* constants is also clearly shown by the straight-line relationship ($r=0.996$) illustrated in Fig. 7, where values of $J(^{29}Si–H)$ for 33 hydrosilanes (Tables 2 and 4) are plotted versus the sum of the σ^* constants for the three substituents on silicon. A more detailed account concerning the new σ^* constants derived in this way for substituted phenyl groups will be given elsewhere.

The results of the least squares analysis listed in Table 3 demonstrate yet another interesting point in that the $J(^{29}Si–H)$ values for the three series of arylhydrosilanes fail to provide a better correlation with the σ^+ constants. The present results provide little support for the $(p\rightarrow d)\pi$ back-bonding invoked by Freeburger and Spialter[7] to explain their $J(^{13}C–H)$ values for substituted phenyltrimethylsilanes. If such an interaction between a substituent and silicon were important, a better correlation with the σ^+ constants would have been observed.

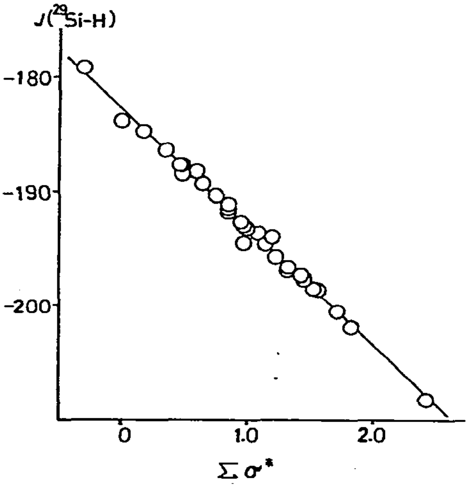
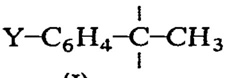


Fig. 7. Correlation of $J(^{29}Si–H)$ values for 33 hydrosilanes with $\Sigma\sigma^*$.

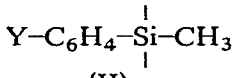
The methyl ^{13}C–H coupling constants

Examination of the effects of ring substituents on the $J(^{13}C\text{–}H)$ values for the methyl groups attached to the silicon atom for the two series of arylmethylsilanes (Table 2) shows that the expected trend *i.e.*, the greater the electron-withdrawing capacity of the substituent, the greater the coupling constant, occurs. A linear relationship between $J(^{13}C\text{–}H)$ and the substituent constants for each series is also exhibited in these cases as is shown in Fig. 2, the correlation being improved when the ordinary σ constants are employed in preference to the σ^+ constants (Table 3). From these results the ρ values for a series of arylmethylsilanes and aryldimethylsilanes are found to be 0.86 and 1.04 Hz/σ, respectively, being values comparable in magnitude with those for a series of substituted tert-butylbenzenes ($\rho = 1.03$ Hz/σ). This similarity in the structural dependence of the methyl $J(^{13}C\text{–}H)$ values for both carbon (I) and silicon (II) series indicates that similar substituent effects are transmitted with the same facility to the terminal methyl groups in both cases. This conclusion is consistent with an earlier observation of Sakurai and Ohtsuru[6] that the ρ values for the chemical shifts for tert-butylbenzenes (-5.38 Hz/σ) and phenyltrimethylsilanes (-5.86 Hz/σ) are nearly identical. Our $J(^{13}C\text{–}H)$ values are not consistent, however, with a similar set of recently reported values. Thus, Freeburger and Spialter[7] determined the methyl ^{13}C–H coupling constants for a series of 15 *meta*- and *para*-substituted phenyltrimethylsilanes and found that the data could not be accommodated by a single line, but that good correlations were obtained when *meta* and *para* compounds were treated separately. It is difficult to explain this discrepancy at this juncture and for this reason further work is apparently necessary on this particular point.



$\text{Y–C}_6\text{H}_4\text{–}\overset{|}{\underset{|}{\text{C}}}\text{–CH}_3$

(I)



$\text{Y–C}_6\text{H}_4\text{–}\overset{|}{\underset{|}{\text{Si}}}\text{–CH}_3$

(II)

Apart from this difficulty, however, it appears that the effects of substituted phenyl groups directly bonded to silicon on the methyl $J(^{13}C\text{–}H)$ values may also be tested in terms of the σ^* constants. Using the newly derived σ^* values listed in Table 5, a linear relationship may be established between the methyl $J(^{13}C\text{–}H)$ values for the investigated methylsilanes, $R_1R_2R_3SiCH_3$, and sum of the polar substituent con-

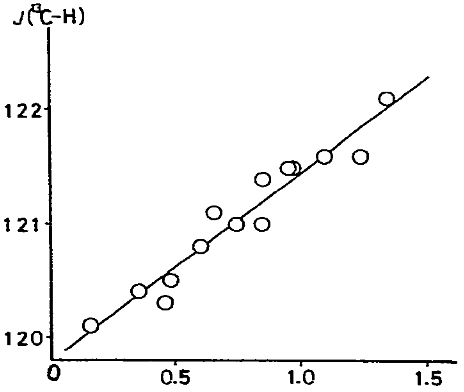


Fig. 8. Correlation of $J(^{13}C\text{–}H)$ values for phenylmethylsilanes and phenyldimethylsilanes with $\Sigma\sigma^*$

stants for the three groups (R_1, R_2 and R_3) on silicon (Fig. 8). The slope of the line shown in this Figure is equal to 1.67 Hz/σ^* with a correlation coefficient of 0.966. The existence of a Hammett–Taft correlation of this type provides further support for the consistency of the σ^* values for the substituted phenyl groups calculated in the preceding paragraph.

Chemical shifts

All the chemical shift values listed in Table 1 were measured at several concentrations in carbon tetrachloride and extrapolated to infinite dilution. Chemical shifts for silyl hydrogens for the hydrosilanes employed in the present study are again linearly related to the Hammett σ constants for each series (Fig. 3 and Table 2). The relationships involving the SiH chemical shift are, however, somewhat poorer than those for the other quantities, and the use of the σ^+ values does little to improve the linearity. The rather poor correlations of δ(SiH) with the substituent constants are presumably a consequence of some anisotropy effects in the chemical shift data.

The ρ values for the SiH chemical shift correlations lie in the range 2.67 to 4.07 Hz/σ. In contrast, much higher ρ values have been reported for the CH chemical shift correlations: Marcus *et al.*[2] obtained a value of $\rho = 12.8$ Hz/σ for α-hydrogens in substituted toluenes, while Williamson *et al.*[3] found that $\rho = 12.1$ Hz/σ for substituted ethylbenzenes. The rather small ρ values which are observed for the silyl hydrogens in the present series of compounds clearly show that the SiH shielding is less sensitive to changes in molecular structure than the CH shielding.

Linear relationships have also been found for the chemical shifts of the Si–CH_3 hydrogens for the two series of methylsilanes studied and the corresponding Hammett σ constants (Fig. 4). As shown in Table 3, slopes of 5.65 and 4.82 Hz/σ, respectively, have been obtained for the arylmethylsilanes and for the aryldimethylsilanes. These values are believed to be of the correct magnitude, since Sakurai and Ohtsuru[6] have reported a ρ value of 5.86 Hz/σ for substituted phenyltrimethylsilanes from a least squares analysis of their results. More recently, two groups of workers[7,20] have reported ρ values ranging between 3.99 and 6.86 for the same series of compounds.

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