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^{29}Si CHEMICAL SHIFTS

I. ADDITIVE RELATIONS IN ALKYLHALOSILANES

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Summary

^{29}Si NMR chemical shifts of simple alkylhalosilanes have been shown to follow an additive relation with first and second order coefficients. Grant and Paul's method is extended to ^{29}Si NMR and 175 pieces of data are fit to 32 dependent variables with a correlation of 0.994 and a standard error of 7.67 ppm. The relative importance of the diamagnetic term in the shielding expression is discussed.

Introduction

There have been considerable efforts to correlate ^{13}C NMR chemical shifts to chemical structure. The most successful empirical method is that due to Grant and Paul [1]. They found that ^{13}C chemical shifts of haloalkanes could be fit to an equation of the form

$$\delta = B + \sum_{i} A_i + \sum_{i \neq j} C_{i,j} \tag{1}$$

where B is the chemical shift of methane. The A_i's are first order constants linear in the number and type of substituents bound to the carbon atom of interest. The $C_{i,j}$'s are second order constants representing the interactions between bound substituents, and the summations are over all atoms in the molecule. Only first order constants are needed to fit alkanes [1]. Litchman and Grant included second order constants for haloalkanes [2]. Others included

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third order constants [3] to improve the fit of haloalkanes, in particular bromo- and iodo-alkanes, however third order constants tend to overspecify the data.

The factors influencing ^{29}Si NMR chemical shifts are still not well understood. However, there is now a large enough body of data available in the literature to make an empirical approximation both feasible and useful. The basic trends of ^{29}Si chemical shifts have been observed and interpreted by many workers. Scholl, Maciel and Musker [4] attempted to explain the trends in terms of simple additive constants. They only considered alkylsilanes covering a chemical shift range of about 20 ppm and, as pointed out by Lippmaa, Magi, Engelhardt et al. [5] their limited success was due to a fortuitous choice of compounds. Ernst, Spialter, Buell and Wilhite [6] observed a parabolic dependence of the chemical shifts of alkylhalosilanes on the total electronegativity of the substituents. Their results tend to indicate that an additive but not linear relation should exist between the number of substituents and the chemical shift. The nonlinearity of ^{29}Si chemical shifts have been pointed out in a series of papers by Schraml and Engelhardt [7—11]. This is usually attributed to steric and $(p—d)\pi$ bonding. The same authors have noted [12,13] that steric effects are greater when through an oxygen linkage.

A number of authors have used more theoretical arguments to calculate the chemical shift [6,14,15]. For the most part Pople's equation has been used but with limited success due to the complexity of the terms involved. In Pople's equation the chemical shift is expanded into diamagnetic and paramagnetic effects which are further expanded into local and long range effects. It has generally been suggested that local paramagnetic effects dominate [16]. The validity of ignoring local diamagnetic effects is questionable, and the general use of average excitation energies and neglect of the *d*-orbital term raises further questions. It is generally agreed that average excitation energies are not adequate [17] and the $(p—d)\pi$ bonding plays an important role in the chemistry of silicon compounds. Engelhardt [15] calculated a paramagnetic term relative to a hypothetical nonpolar molecule. Harris [16] points out that this method is in general not valid and indeed predicts trends of halosilanes incorrectly. Harris [17] extended Grant and Paul's method [1] for ^{13}C NMR to ^{29}Si, and was able to correctly predict the chemical shift of silane from data of only 4 other compounds. We have extended Harris' method to include interaction coefficients and applied this to 175 pieces of data, representing 114 compounds, including simple alkylhalosilanes.

Results and discussion

We fitted 175 pieces of data from the literature, representing multiple measurements on 114 different compounds to equation 1. A least squares multiple regression was performed which yielded the results listed in Tables 1 and 2.

From Table 1 the coefficient of multiple correlation is 0.994 or very nearly 1.0 and the standard error of estimation is 7.67 ppm or 2% of the chemical shift range studied. A plot of the calculated chemical shift vs. the experimental chemical shift is given in Fig. 1. This shows the excellent fit given by this method for the compounds studied.

Table 3 list some first and second order coefficients for both ^{13}C and ^{29}Si.

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TABLE 1

COEFFICIENTS (ppm) FROM THE MULTIPLE LINEAR REGRESSION OF ^{29}Si CHEMICAL SHIFTS (See eq. 1)

$A_{C(1)}$	18.88	$C_{(C(1),C(1))}$	0.37	$C_{(O,O)}$	—10.21
$A_{C(2)}$	—0.42	$C_{(C(1),C(2))}$	0.44	$C_{(F,F)}$	—23.69
$A_{C(3)}$	—1.21	$C_{(C(1),O)}$	3.31	$C_{(F,Cl)}$	—15.03
$A_{C(4)}$	2.01	$C_{(C(1),Ph)}$	0.01	$C_{(F,Br)}$	—13.35
A_{O}	13.31	$C_{(C(1),Vi)}$	0.33	$C_{(Cl,Cl)}$	—14.54
A_{Ph}	11.73	$C_{(C(1),F)}$	5.02	$C_{(Cl,Br)}$	—17.54
A_{Vi}	8.12	$C_{(C(1),C(1))}$	2.81	$C_{(Cl,I)}$	—26.73
A_{F}	23.12	$C_{(C(1),Br)}$	4.04	$C_{(Br,Br)}$	—22.90
A_{Cl}	34.84	$C_{(C(1),I)}$	6.20	$C_{(Br,I)}$	—36.88
A_{Br}	29.78	$C_{(Ph,Ph)}$	2.67	$C_{(I,I)}$	—52.43
A_{I}	11.11	$C_{(Vi,Vi)}$	2.67		

B —71.65 ppm

Coefficient of determination (r^2) = 0.9874

Coefficient of multiple correlation = 0.9937

Standard error of estimation 7.67 ppm

TABLE 2

CHEMICAL SHIFT DATA AND CALCULATED VALUES FROM COMPOUNDS USED IN THE CALCULATION OF THE COEFFICIENTS IN TABLE 1 (All chemical shifts are reported downfield from TMS)

Compound	Shift	Compound	Shift
SiI_4	—341.78	SiH_2I_2	—101.86
	—351.7(13)		—99.6(20)
	—346.2(18)	$SiBrICl_2$	—101.04
$SiBrI_3$	—276.48		—98.9(19)
	—280.1(19)	$SiBr_4$	—89.95
$SiClI_3$	—240.96		—93.6(18)
	—245.9(19)		—92.7(19)
$SiBr_2I_2$	—212.73	$Si(OMe)_4$	—87.37
	—212.3(19)		—79.2(26)
$SiHI_3$	—195.60		—79.1(27)
	—175.9(20)	$Si(OEt)_4$	—86.22
$SiBrClI_2$	—182.00		—83.5(24)
	—181.9(19)		—82.4(25)
$SiMeI_3$	—158.13	$SiBrF_3$	—83.61
	—144.0(20)		—83.5(22)
$SiCl_2I_2$	—153.56		—82.4(23)
	—151.5(19)	$SiClF_3$	—83.59
$SiIBr_3$	—150.56		—82.8(22)
	—149.5		—81.7(23)
$SiClIBr_2$	—124.61		—82.4(8)
	—122.8(19)	$Si(OH)_4$	—79.68
SiF_4	—121.29		—73.3(19)
	—117.4(21)	$SiHF_3$	—73.35
	—113.6(22)		—77.8(20)
	—110.1(22)	$SiPh(OEt)_3$	—55.54
	—109.0(18)		—60.5(24)
SiH_4	—71.65		—59.4(33)
	—93.1(31)		—58.4(34)
	—91.9(19)	SiF_2Cl_2	—54.06
$SiClBr_3$	—68.79		—56.1(22)
	—69.8(19)		—55.0(23)
$SiFBr_3$	—67.94	$SiMeH_3$	—52.78
	—68.1(22)		—65.2(31)
	—67.0(23)		

TABLE 2 (continued)

Compound	Shift	Compound	Shift
$SiH(OEt)_3$	—67.26	$SiHBr_3$	—51.02
	—59.5(34)		—43.4(20)
$SiBr_2F_2$	—65.83	$SiCl_2Br_2$	—50.00
	—67.4(23)		—50.7(19)
$SiH(OMe)_3$	—63.63	SiH_2F_2	—49.09
	—54.9(35)		—28.5(20)
$SiPhF_3$	—61.62	$SiFH_3$	—48.53
	—76.2(28)		—17.4(20)
	—73.2(29)	SiH_2Ph_2	—45.53
	—72.7(30)		—34.5(24)
SiH_3I	—60.54		—33.6(33)
	—83.3(20)		—33.2(32)
$SiPhH_3$	—59.92	$SiBrH_3$	—41.87
	—61.5(24)		—49.0(36)
	—60.1(32)		—48.5(20)
	—59.9(33)	$Si(OMe)_2Ph_2$	—29.97
$SiVi(OEt)_3$	—59.14		—29.4(35)
	—60.3(7)	$SiPh_2(OH)_2$	—29.12
$SiMeF_3$	—39.42		—32.4(39)
	—55.7(20)	$SiHPh_3$	—28.47
	—51.8(22)		—22.5(37)
$SiMe_2I_2$	—38.94		—17.8(35)
	—33.6(38)		—17.8(32)
$SiMe(OEt)_3$	—37.14	$SiHMePh_2$	—26.64
	—45.5(24)		—19.5(35)
	—44.5(9)	$SiVi_4$	—23.13
	—44.2(25)		—22.5(24)
$SiClH_3$	—36.81	$SiPh_2F_2$	—22.97
	—36.1(31)		—31.0(28)
SiH_2Br_2	—34.99		—30.5(35)
	—30.3(20)	$SiHPhMe_2$	—21.79
$SiBrCl_3$	—33.58		—17.2(4)
	—34.3(19)	$SiMeBr_3$	—20.02
$SiMe_2H_2$	—33.53		—19.2(18)
	—41.5(24)		—18.2(38)
	—37.3(31)	$SiCl_4$	—19.52
$SiMe(OEt)_3$	—33.50		—20.0(19)
	—41.4(37)		—19.9(31)
	—39.8(27)		—18.5(12)
$SiFCl_3$	—32.70		—16.5(11)
	—33.2(22)	$SiPh_4$	—8.75
	—32.1(23)		—15.2(35)
$SiPh_2(OEt)_2$	—32.40		—13.9(32)
	—34.5(24)	$SiMePhF_2$	—8.44
$SiMeVi_3$	—19.41		—12.4(29)
	—20.6(14)	$SiMe_2Ph_2$	—7.38
SiH_2Cl_2	—16.51		—9.4(37)
	—11.0(37)		—8.4(35)
$SiH(n\text{-}Pr)_3$	—14.90	$Si(OEt)ViMe_2$	—5.58
	—8.5(18)		2.7(7)
	—8.1(17)	$SiMe_2(OEt)_2$	—5.39
$SiHMe_3$	—13.92		—6.1(9)
	—16.3(13)		—5.7(25)
	—15.5(31)	$SiFPh_3$	—5.35
$SiMe_2Vi_2$	—13.31		—4.7(12)
	—13.7(4)	$SiViMe_3$	—4.82
$SiH(s\text{-}Bu)_3$	—12.24		—7.6(40)
	—14.7(18)		—6.8(4)
$SiMeViF_2$	—11.73	$SiHPhCl_2$	—4.78
	—13.4(7)		—2.1(35)

TABLE 2 (continued)

Compound	Shift	Compound	Shift
$SiHEt_3$	−11.26	$SiEtViMe_2$	−3.93
	0.2(17)		−4.4(7)
$SiHClPh_2$	−10.69	$SiMeViEt_2$	−3.04
	−5.4(35)		−2.3(7)
$SiMePh_3$	−9.57	$SiMe_2Et_2$	8.70
	−11.9(37)		5.3(28)
$SiH(n\text{-}Bu)_3$	−8.86	$Si(OEt)Me_3$	9.00
	−6.7(18)		13.5(9)
	−6.6(17)		14.5(25)
$SiViCl_3$	−2.62	$SiMe_2F_2$	9.10
	−3.5(7)		8.8(22)
$SiMe_2(OMe)_2$	−2.97	$SiPh_2Cl_2$	9.61
	−2.5(41)		6.2(32)
	−1.6(27)		6.3(28)
$SiPhMe_3$	−2.17	SiF_2Et_2	10.00
	−5.1(37)		0.5(33)
	−4.5(6)	$SiMeEt_3$	10.02
	−4.4(13)		6.5(36)
$SiViEt_3$	−2.16	$Si(OMe)Me_3$	10.22
	−1.7(7)		17.2(4)
$SiPhMe(n\text{-}Bu)_2$	−1.21		17.8(27)
	−1.7(21)	$SiEt_4$	11.35
$SiPhCl_3$	0.98		8.4(36)
	5.3(28)		8.7(38)
$SiMeFPh_2$	1.50		8.9(16)
	7.7(18)	$SiPhFMe_2$	11.37
$SiMe_4$	6.06		19.8(29)
	0.0	$Si(s\text{-}Bu)Et_3$	11.46
$SiClPh_3$	6.37		8.2(21)
	1.2(39)	$SiFMe_3$	24.26
	1.2(35)		30.5(42)
$SiEtMe_3$	7.38		31.9(6)
	1.6(36)		32.0(16)
$Si(n\text{-}Bu)Et_3$	12.15		35.4(35)
	6.2(21)	$SiBrMe_3$	27.98
$Si(OMe)Et_3$	12.87		26.2(16)
	18.8(4)		25.4(38)
$SiClViMe_2$	15.70	$SiF(n\text{-}Bu)_3$	29.32
	16.7(6)		28.8(18)
$SiCl_2ViMe$	16.43	$SiClMe_3$	29.34
	16.5(7)		30.2(38)
$SiMeCl_3$	16.55		30.3(16)
	12.2(11)		32.5(42)
	12.5(38)	$SiClEt_3$	31.99
$SiPhClMe_2$	18.66		36.0(35)
	19.9(29)	$SiCl_2Me_2$	32.83
$SiMe_2Br_2$	19.29		32.2(38)
	19.2(16)		
	19.9(38)		
$SiPhMeCl_2$	19.72		
	17.9(29)		
$SiF(n\text{-}Pr)_3$	23.28		
	28.8(18)		

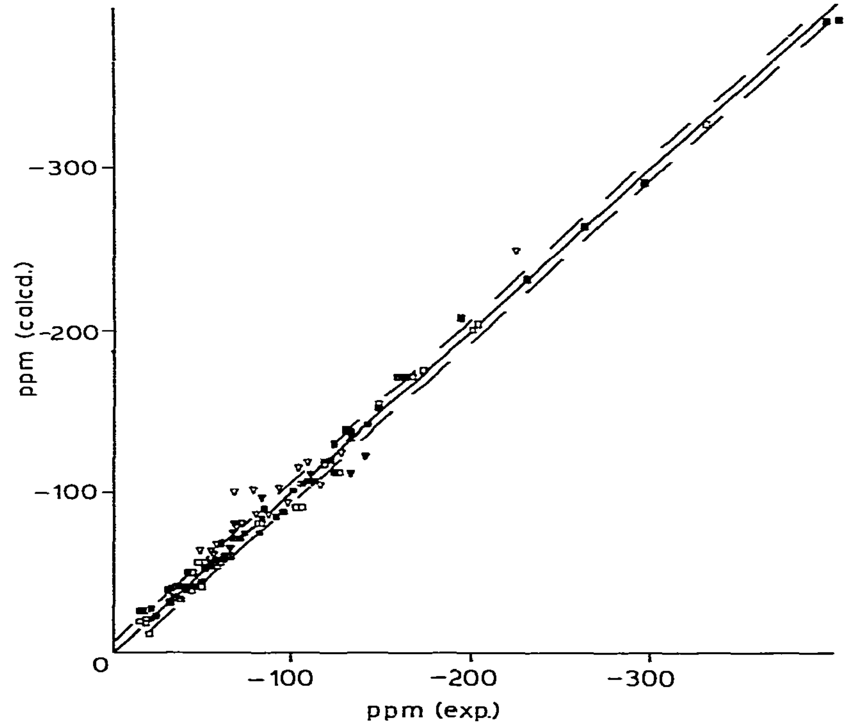


Fig. 1. Comparison of calculated and experimental chemical shifts. The broken lines are drawn one standard deviation away from the solid line which passes through the origin with a slope of +1. Silanes with directly bonded protons are shown as triangles as opposed to squares, and are most affected by the diamagnetic term which was not considered.

The ^{13}C coefficients were taken from Somoyajulu's study [3] in which third order coefficients were also considered. However, general trends can still be seen, and the values for ^{13}C and ^{29}Si are comparable. It is interesting that the first order coefficient least likely to $(p-d)\pi$ bond displays the largest

TABLE 3

COEFFICIENTS FROM THIS WORK AND FROM A SIMILAR STUDY BY SOMAYAJULU ON ^{13}C CHEMICAL SHIFTS. (Both studies are referenced to TMS, increasing to lower field)

Parameter	^{29}Si (ppm)	^{13}C [a] (ppm)
first order		
A_{Cl}	34.84	35.66
A_{Br}	29.78	26.48
A_{I}	11.11	0.79
second order		
$C_{(Cl,Cl)}$	−14.54	−5.99
$C_{(Cl,Br)}$	−17.54	−12.65
$C_{(Br,Br)}$	−22.90	−20.37
$C_{(I,I)}$	−52.43	−46.73

[a] Taken from Somayajulu [3].

variance. A possible explanation might be derived from an electronegativity viewpoint. The C—I bond is almost purely covalent ($X_C - X_I = 0$), while that of Si—I is still somewhat ionic ($X_{Si} - X_I = 0.7$) implying that iodine causes more deshielding of the silicon nuclei than the carbon, resulting in a greater upfield shift for silicon and a more negative first order parameter. For the second order coefficients, however, the order is as expected, the $C_{(Cl,Cl)}$ coefficient varies greatest which may be attributed to $(p—d)\pi$ bonding. This is in agreement with the assumption that $(p—d)\pi$ bonding is a nonlinear effect.

If one assumes that the second order coefficients are a function of steric effects only, a straight line graph should be obtained for $C_{(X,X)}$ of halogen X vs. the atomic radius of X. This is shown in Fig. 2 for the halogens. It is seen that $C_{(F,F)}$ does not fall on a line described by the other three coefficients. If $C_{(F,F)}$ is projected onto the line an atomic radius of 1.1 Å is assigned to it. This corresponds to a 69% ionic character given a covalent radius of 0.68 Å. Pauling [43] gives a 70% ionic character to this bond from electronegativity calculations which is in good agreement.

Figure 1 shows that all compounds which deviate by more than 1.5 standard errors contain directly bonded protons. This leads one to conclude that the diamagnetic shielding term which has been previously ignored is apparently important for qualitative studies. Pople's expression for shielding (neglecting ring cur-

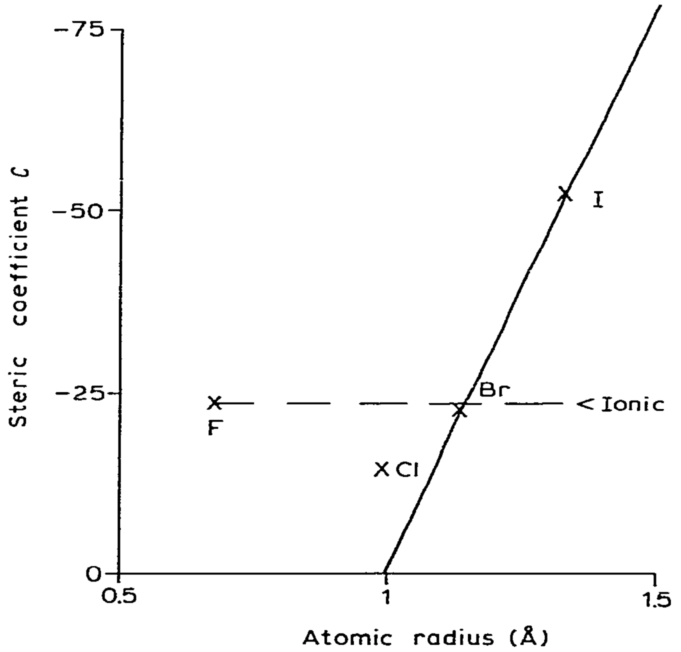
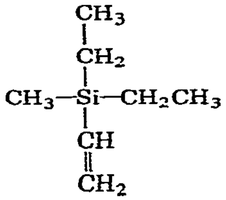


Fig. 2. Plotted is the steric coefficient $C_{(X,X)}$ of halogen X vs. the covalent atomic radius of X, one would expect a straight line if the effect is truely steric in nature. Pauling [43] has shown that the atomic radius may be simply related to the percent ionic character of a bond, we assume then that this may explain the discrepancies of the plot. Since I and Br are very nearly covalently bonded to Si a solid line has been drawn through them and a broken line connects the covalent and ionic radii of F. From their intersection an ionic character of 69% for the Si—F bond is calculated in good agreement with the 70% quoted by Pauling. Notice that Cl is also slightly ionic as would be expected.



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3{-}Si{-}CH_2CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

$$\delta = B + A_{(\mathrm{Vi})} + 3A_{\mathrm{C(1)}} + 2A_{\mathrm{C(2)}} + 3C_{(\mathrm{C(1)},\mathrm{C(1)})} + 6C_{(\mathrm{C(1)},\mathrm{C(2)})} + 3C_{(\mathrm{C(1)},\mathrm{Vi})}$$
$$= -2.99 \text{ ppm}$$

Fig. 3. A sample calculation of the chemical shift of methyldiethylvinylsilane using the coefficients given in this paper. Lippmaa [7] reports a chemical shift of —2.3 ppm for this compound. (Vi = vinyl).

rents and long range effects) may be written as:

$$\sigma = \frac{\mu_0 e^2}{12\pi m} \langle 0 | \sum_i r^{-1}{}_i | 0 \rangle - \frac{\mu_0 e^2 \hbar^2}{8\pi m^2 \, \Delta E} [\langle r^{-3} \rangle_p Q_p + \langle r^{-3} \rangle_d Q_d]$$
$$= \sigma_{\mathrm{dia}} + \sigma_{\mathrm{par}}$$

which has been taken from Harris [16]. Note that the paramagnetic term only includes *p* and *d* type orbitals, *s*-type atomic orbitals are dealt with in the diamagnetic term. By assuming that protons do not interact at all and that their electron density does not contribute to ^{29}Si chemical shifts we have considered only the paramagnetic term. The diamagnetic shielding term is usually credited with a 0—20 ppm influence on the chemical shift which is just the range of errors in our method. We are presently investigating the effects of the diamagnetic term on ^{29}Si chemical shifts.

Note that simply including another linear term to account for proton electron density will not accomplish anything since this only shifts the reference point to a hypothetical silicon atom. Further interactions, involving protons, should be included to account for the diamagnetic term.

In conclusion we feel that this method provides a fairly accurate and general method for calculating ^{29}Si chemical shifts. A review of other successful empirical methods for calculating ^{29}Si chemical shifts is given by Marsmann in a recent review article [44]. An example of the use of this method is given in Fig. 3. In addition it is probable that this method is applicable to still other nuclei.

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