

THE DETERMINATION OF A π -SIGMA CONSTANT FOR SUBSTITUENTS ATTACHED TO SILICON

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Summary

The proton, ^{13}C , and ^{29}Si chemical shifts and the ^{13}C - ^1H coupling constants of a series of compounds of the type $(\text{CH}_3)_3\text{SiX}$ were measured and correlated with inductive and resonance σ constants. In order to provide a comparison with a homologous series in which π -bonding is absent, shifts and coupling constants were obtained for the t-butyl series, $(\text{CH}_3)_3\text{CX}$. Only the coupling constants gave significant correlations with σ_1 . A series of σ constants, presumably reflective of the amount of π -bonding, were obtained from the deviations from the J vs. σ_1 plot. The magnitudes of these values indicate that oxygen is a better π -donor than nitrogen and chlorine.

Introduction

Although the concept of π -bonding to silicon has been attacked from many quarters, particularly via quantum-mechanical calculations that approximate various physical and chemical characteristics of silicon compounds without the inclusion of d orbitals in the basis set, it remains a valuable, simple rationalization for a variety of properties of silicon, phosphorus, and sulfur compounds [1]. In spite of an appeal that has endured for about three decades, there have been no attempts to provide a quantitative measure of the extent to which substituents interact with a π -acceptor site. This measure is most easily obtained and used in the form of a substituent constant of the Hammett type. The present study is an attempt to formulate a set of σ constants for π -interactions with the most common π -acceptor site, the $\text{Si}(\text{CH}_3)_3$ group. We will henceforth refer to this constant as σ_π .

NMR chemical shifts and coupling constants are easily measured characteristics of a compound and, more importantly, have been amply correlated with the electronic effects of substituents. The NMR parameter that most accurately reflects the electronic effects of substituents is probably the coupling constant, particularly the ^{13}C - ^1H one-bond constant [2]. This coupling constant has been shown to

correlate strongly with the Hammett constant for *meta* and *para* substituents in a large variety of substituted aromatics [3]. Dual parameter correlations with $J(^{13}\text{C}-^1\text{H})$ have also been very successful [4]. We have therefore chosen to measure proton, ^{13}C , and ^{29}Si chemical shifts and $^{13}\text{C}-^1\text{H}$ coupling constants of the $\text{Si}(\text{CH}_3)_3$ group in a variety of substituted trimethylsilanes. In order to compensate for electronic or magnetic effects that might not be indicative of π -bonding, these parameters were also measured for a set of similar $\text{C}(\text{CH}_3)_3$ homologs.

Experimental

All compounds were obtained commercially and were more than 95% pure as indicated by their proton spectra. Coupling constants were obtained on 50% solutions in dry CH_2Cl_2 in 10 mm NMR tubes. Chemical shifts were obtained in 25% solutions in dry CH_2Cl_2 with TMS as an internal standard. An inner coaxial tube filled with acetone- d_6 was used as a lock solvent. Spectra were obtained on a JEOL FX 90-Q using the following acquisition parameters for ^{29}Si : observation frequency, 17.75 MHz; pulse width, 13 μs ; frequency width, 5000 Hz; pulse delay, 15 s; points, 16 k. $^{13}\text{C}-^1\text{H}$ coupling constants were obtained from the coupled ^{13}C spectra obtained with the following parameters: observation frequency, 22.49 MHz; pulse width, 8 μs ; frequency width, 600 Hz; pulse delay, 10 s; points, 32k. σ_I and σ_R values were obtained from ref. 5. Regression analyses were performed with Statworkstm.

Results and discussion

All chemical shifts and coupling constants are reported in Table 1. All values are in all cases in good agreement with those that have been reported in the literature.

TABLE 1
CHEMICAL SHIFTS AND $^{13}\text{C}-^1\text{H}$ COUPLING CONSTANTS FOR $(\text{CH}_3)_3\text{SiX}$ AND $(\text{CH}_3)_3\text{CX}$ ^a

X	$(\text{CH}_3)_3\text{SiX}$			$(\text{CH}_3)_3\text{CX}$			
	$J(^{13}\text{C}-^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^{29}\text{Si})$	$J(^{13}\text{C}-^1\text{H})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^{13}\text{C}_q)$
CH_3	118.1	0	0	124.0	0	31.71	28.24
Cl	120.6	3.28	31.27	127.5	1.61	34.59	67.74
Br	121.3	4.20	27.53	127.5	1.78	36.54	63.09
ClCH_2	119.3	-3.06	2.91	125.7	0.10	27.17	33.02
Cl_2CH	120.6	-4.09	10.34				
HOCH_2	119.0	-3.44	-11.69	124.7	0.89	26.25	32.83
C_6H_5	119.2	-1.11	-4.11	125.5	1.31	31.48	34.83
CH_3O	118.1	-1.00	18.27	125.1	1.14	27.14	72.73
$\text{C}_6\text{H}_5\text{O}$	118.8	0.22	19.23				
CH_3S	120.1	0.27	16.80				
CH_3CO_2	119.6	-0.26	22.77	126.7	1.42	22.56	80.18
CN	121.7	-1.76	-11.28	129.0	1.34	28.95	92.82
$(\text{CH}_3)_2\text{N}$	117.9	-1.52	7.30				
CH_3NH				124.4	0.63	29.96	

^a Chemical shifts in ppm relative to TMS; coupling constants in Hz; C_q is quaternary carbon.

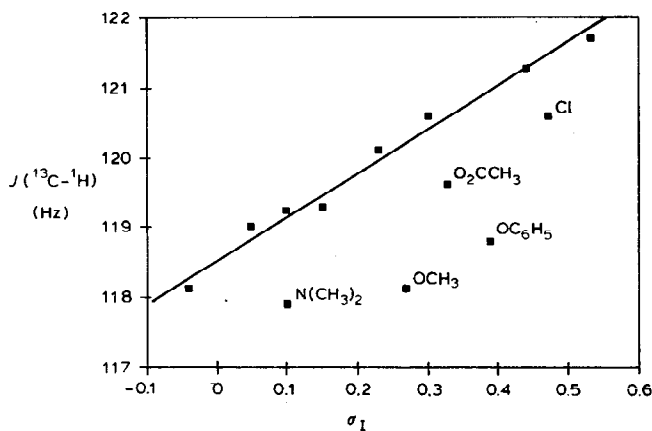


Fig. 1. Plot of $J(^{13}\text{C}-^1\text{H})$ vs. σ_I for $(\text{CH}_3)_3\text{SiX}$.

Because the substituents were expected to affect the coupling constants and chemical shifts by both the inductive effect and π -interactions, all parameters were correlated with σ_I and σ_R in simple and multiple regressions. The best correlations were obtained between the coupling constants and σ_I for both the silicon and carbon series. Chemical shifts generally did not correlate well with σ_I ; only the ^{29}Si chemical shifts for the trimethylsilyl series produced correlations with $r > 0.9$ (when $\text{X} = \text{CN}$ was excluded). Multiple regressions with σ_I and σ_R were not significantly better than the single independent variable correlations, and no correlations with σ_R were good.

The plot of $J(^{13}\text{C}-^1\text{H})$ vs. σ_I for the silicon series is shown in Fig. 1. The correlation using all 13 points produces a correlation coefficient of 0.74. Inspection of the residuals shows, however, that the omission of five points significantly improves the correlation. The straight line in Fig. 1 is the line that results after the points for Cl , CH_3O , $\text{C}_6\text{H}_5\text{O}$, CH_3CO_2 and $(\text{CH}_3)_2\text{N}$ have been omitted from the regression. The least-squares equation for this relation is $J = 6.263\sigma_I + 118.54$ with a correlation coefficient of 0.992 and an F -value of 385. Clearly, the 8 substituents that constitute this straight line exhibit an excellent correlation of σ_I with the coupling constant. It is probable, therefore, that π -bonding is absent, constant, is proportional to σ_I , or can not be detected for these substituents. Because of the variety of different types of substituents is not likely that π -bonding is constant or proportional to σ_I .

Moreover, the substituents that deviate from the line are those to which π -bonding is generally attributed (all have lone pairs of electrons on second or third period atoms). Thus, it likely that π -bonding does influence the magnitude of the coupling constant by supplying additional electron density at the silicon thereby lowering the coupling constant. Substituents that fit the line very likely do not interact via π -bonding with the trimethylsilyl silicon.

Figure 2 shows the correlation of $J(^{13}\text{C}-^1\text{H})$ with σ_I for the *t*-butyl series. For all 10 points the correlation coefficient is 0.94; the equation for the straight line is $J = 7.703\sigma_I + 124.16$ with an F -level of 60.0. Although the correlation can be improved by removing the points for CH_3O , NHCH_3 , and CN , the residuals for

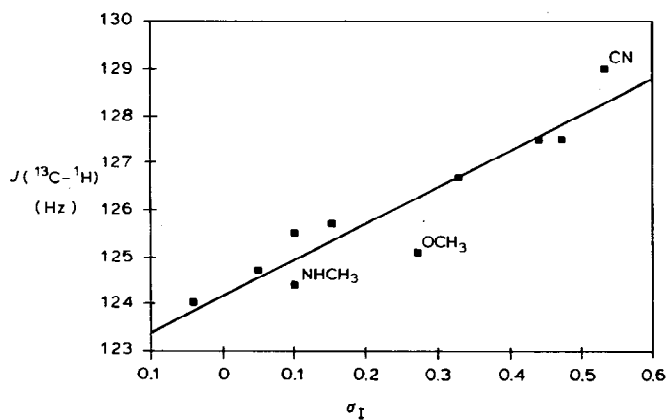


Fig. 2. Plot of $J(^{13}\text{C}-^1\text{H})$ vs. σ_I for $(\text{CH}_3)_3\text{CX}$.

these points is not as large as those for the silicon series. Thus, in a system where π -interactions are absent, the correlation of the coupling constant with σ_I is reasonably good. It is true that two of the "deviant" substituents are the same as (or similar to) those to which π -bonding was attributed in the silicon series. Thus, some electronic or magnetic effect other than π -bonding is causing a small deviation in the *t*-butyl series*. We chose, however, to ignore these deviations and use as σ_π values those calculated from the silicon plot shown in Fig. 1.

The magnitude of the π -interaction with silicon can be obtained by calculating the σ constant necessary to obtain a fit with the J vs. σ_I line using the equation above. σ_π , then, is a measure of how much the substituent deviates from this line and is obtained by subtracting σ_I for the substituent from the calculated value of σ . σ_π values calculated in this way are: Cl, -0.14 ; CH_3O , -0.34 ; $\text{C}_6\text{H}_5\text{O}$, -0.35 ; CH_3CO_2 , -0.17 ; $(\text{CH}_3)_2\text{N}$, -0.20 . The negative sign is indicative of electron release and the relative magnitudes of the values are indicative of the amount of π -bonding.

According to the magnitude of the σ_π values, methoxy is a better π -donor than chloro and the dimethylamino group. Although the relative donor abilities of oxygen and chlorine is not unexpected, the greater donor ability of oxygen relative to nitrogen is surprising in view of the generally more dramatic effects of silicon on the structure and reactivity of amines and amides. The smaller value for the CH_3CO_2 group relative to CH_3O is presumably a result of inductive and resonance electron withdrawal by the carbonyl from the oxygen attached to silicon.

* In order to correct σ_π for this effect, a " σ_π " for these substituents could be calculated as described above and a corrected σ_π for the silicon substituents then obtained by subtraction. The " σ_π " values for the carbon series are: NHCH_3 , -0.12 ; OCH_3 , -0.18 ; CN , 0.14 . Assuming similar electronic effects for the NHCH_3 and $\text{N}(\text{CH}_3)_2$ substituents and the OCH_3 and OC_6H_5 substituents, the set of corrected σ_π constants is: Cl, -0.14 ; OCH_3 , -0.16 ; OC_6H_5 , -0.17 ; $(\text{CH}_3)_2\text{N}$, -0.08 ; O_2CH_3 , -0.17 .

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