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AN NMR INVESTIGATION OF THE TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH SILICON

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SUMMARY

The proton NMR spectra of five triphenylsilyl derivatives ($-OH$, $-OCH_3$, $-H$, $-Cl$, $-F$) have been analyzed exactly in terms of chemical shifts and coupling constants. Varying substituents on silicon appears to have little effect on the π-interaction between silicon and the phenyl rings. However, substituents do affect the sigma electron framework of the phenyl rings as evidenced by the correlation between $J(H_o\text{–}H_m)$ and the electronegativity of the substituent.

INTRODUCTION

The role of $(p \rightarrow d)\pi$ bonding between silicon, germanium, tin, lead, and carbon has been the subject of extensive investigation[1-3]. Comparison of the trends observed in several spectroscopic investigations of group IV compounds have led to the conclusion that the relative order of participation in π-bonding is $Si > Ge > Sn > Pb$[4-6]. In the majority of the previous investigations, a series of compounds have been examined in which the group IV atom has been varied while the substituents have been held constant. However, recently it was reported[7] that there was significant variation with substituent in the NMR spectra of compounds of the type $PhSiX_3$. In an investigation of the NMR spectra of triphenyl group IV lithium compounds[8], it was also observed that the NMR parameters for the phenyl rings were slightly different from those observed for other triphenylsilyl compounds.

As a continuation of our previous investigations of organosilanes[8,9], it seemed worthwhile to investigate the triphenylsilyl compounds in detail. We wish to report here the complete analysis of the proton NMR spectra of five triphenylsilyl derivatives (OH, OCH_3, H, Cl, F). The parameters (chemical shifts and coupling constants) are discussed in relation to the effect of substituents on the interaction between the phenyl rings and silicon in these compounds.

EXPERIMENTAL

Triphenylmethoxysilane was prepared according to a literature procedure[10]. All other silicon compounds were obtained from Peninsular ChemResearch and were used without further purification. Samples were made up gravimetrically to

5 mole % in diethyl ether containing 2 % tetramethylsilane as an internal reference and lock signal source. All samples were degassed and sealed under vacuum.

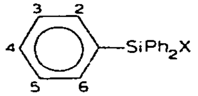
Proton NMR spectra were obtained on a Varian Associates HA-100 spectrometer operating in the field-sweep mode with a probe temperature of 29°. Calibration of the spectra was accomplished by utilizing the frequency difference network. Line positions used in the calculation of the chemical shifts and coupling constants were the average of four separate measurements. A sweep-rate of 0.05 Hz/sec was used.

RESULTS AND DISCUSSION

The spectrum of triphenylfluorosilane was analyzed as an AA'BB'CX system. The remainder of the spectra were of the AA'BB'C type. Although the signals from the *ortho*-protons of triphenylsilane were broadened slightly, no coupling between the ring protons and the proton on silicon could be detected. All spectra were analyzed in terms of chemical shifts and coupling constants using the computer program LAOCN3[11]. The results are presented in Table 1. Calculated probable errors for the parameters were always less than 0.05 Hz.

TABLE 1

NMR PARAMETERS FOR SOME SUBSTITUTED TRIPHENYLSILANES



X	ν_2[a]	ν_3	ν_4	J_{23}[b]	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}
OH	7.560	7.248	7.248	7.43	1.39	0.71	1.30	7.51	1.22
OCH_3	7.573	7.282	7.325	7.43	1.42	0.71	1.31	7.53	1.26
H	7.512	7.275	7.309	7.67	1.18	0.76	1.23	7.52	1.08
Cl	7.589	7.314	7.373	7.52	1.34	0.68	1.40	7.59	1.21
F[c]	7.588	7.321	7.389	7.32	1.41	0.80	1.39	7.59	1.21

[a] In ppm downfield from internal TMS. [b] In Hz. [c] $J(H_2\text{–}F) = -0.07$ Hz; $J(H_3\text{–}F) = 0.52$ Hz; $J(H_4\text{–}F) = -0.22$ Hz.

Our primary concern in this investigation was to determine the transmission of substituent effects through silicon to a π-system. Since *para*-proton chemical shifts are related to the electron density of the attached carbon[12], we have used the *para*-proton chemical shift as an indication of the transmission of resonance or π-effects through silicon. Factors other than resonance effects such as electric field and magnetic anistropy influence the *meta*- and *ortho*-proton shifts. The effect of substituents on the coupling constants of monosubstituted benzenes has recently been determined[13–15]. A correlation between the electronegativity of the substituent and the *ortho–meta* coupling constant has been established[13]. Furthermore, it has been suggested that substituents influence the *ortho–meta* coupling constant in monosubstituted benzenes primarily through a perturbation of the sigma electrons (inductive effect)[13]. Therefore, an indication of the effect of substituents on the inductive effect of silicon may be obtained from the *ortho–meta* coupling constants (J_{23}) of the triphenylsilyl derivatives.

The *para* protons of the triphenylsilyl derivatives are shielded with substituent in the order OH > H > OCH_3 > Cl > F (Table 1). With the exception of $-OCH_3$, this is the order expected based on the resonance effect of the substituents. However, the range of *para*-proton shifts is small. In fact the range of all proton shifts with substituent is only 0.08 ppm (Table 1). Previous investigations of the NMR spectra of phenyl substituted group IV compounds have also shown that the range of *para*-proton chemical shifts is small[6,7]. We do not believe that this variation is large enough to develop a discussion of the transmission of the π-effects through silicon. While the expected trends are present, it appears that chemical shifts are not well suited for such studies.

It appears that coupling constants are more responsive than chemical shifts to changing substituents on silicon. Of the six coupling constants characteristic of the phenyl ring, only J_{23} exhibits a regular variation with substituent (Table 1). The decreasing trend of J_{23} with increasing electronegativity of the substituent (Fig. 1) is similar to the effect of substituents on the *cis* coupling constant in vinyl derivatives[16]. Castellano and co-workers have shown that in monosubstituted benzenes and *N*-substituted pyridines, J_o increases with increasing electronegativity of the substituent[17]. Comparison of these data with similar data for monosubstituted ethylenes and butadienes led to the conclusion that the effect of substituents on vicinal coupling constants alternates depending on the number of bonds separating the H–C–C–H fragment and the substituent. Considering that the substituent is three bonds removed from the H–C–C–H in the triphenylsilyl derivatives, the decrease in J_{23} with increasing electronegativity of the substituent is the predicted trend based on the alternation effect. That the range of J_{23} is smaller than that observed for monosubstituted benzenes (0.35 Hz *vs.* 0.80 for identical substituents) may be taken as further evidence for the effect of substituents on vicinal coupling constants occurring primarily through in-

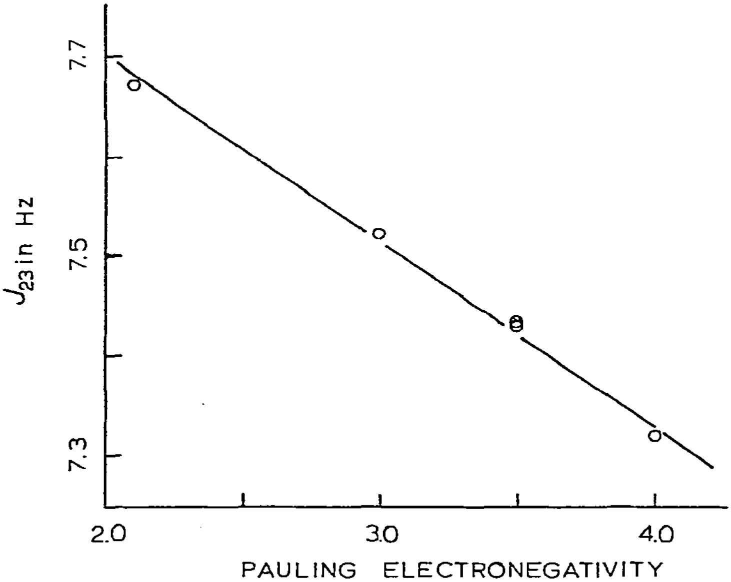


Fig. 1. A plot of J_{23} *vs.* the Pauling electronegativity of the substituent.

ductive effects since this effect should diminish rapidly with increasing separation of the substituent and the H–C–C–H fragment.

In conclusion, it appears that the effect of varying substituents on silicon on the $(p\rightarrow d)\pi$ interaction between silicon and a π-system is small. The inductive effect of substituents transmitted through silicon to a π-system follows previously established trends. It should be interesting to compare these results with similar data for the corresponding carbon systems where the substituent is three bonds removed from the H–C–C–H fragment. Such investigations are presently underway.

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