

NOTE

CORRELATION OF Si-H INFRARED STRETCHING FREQUENCIES

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Three previous accounts of the correlation of the stretching frequencies of Si-H bonds with parameters characteristic of the other substituents at the silicon atom have appeared in the literature. Smith and Angelotti¹ have demonstrated that for silanes of the type R_3SiH , where $R \neq H$, a good correlation exists between the observed frequencies and a series of empirical constants, E values, which indicates that the substituent effects are additive. Subsequently Thompson² suggested that a direct correlation of the observed frequencies with the sum of the Taft inductive constants, $\Sigma\sigma^*$, for the other substituents was possible. A similar correlation has also been reported by Ponomarenko and Egorov³.

The object of this note is to point out that significant deviations occur in a simple correlation of the observed data with $\Sigma\sigma^*$ from which it is apparent that the inductive influences of the substituents are not solely responsible for the observed variations. Fig. 1 shows the good correlation which exists between the Si-H stretching

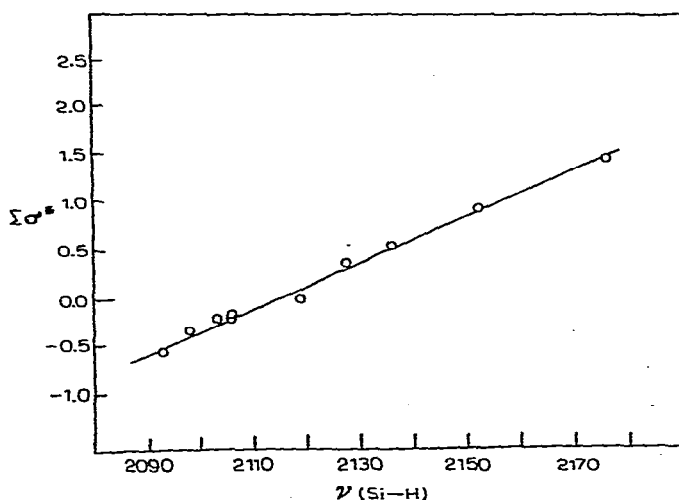


Fig. 1. Plot of $\Sigma\sigma^*$ vs. the Si-H stretching frequency for alkylsilanes.

frequencies of alkylsilanes and $\Sigma\sigma^*$. However, a similar plot for silanes of the type, $\text{Me}_n\text{R}_{3-n}\text{SiH}$, where $n=0, 1, 2$ and 3 , and $\text{R}=\text{OMe}, \text{Cl}, \text{F}, \text{Ph}$ and NMe_2 , shown in Fig. 2, indicates that the slope of the plot for each substituent, R , varies considerably

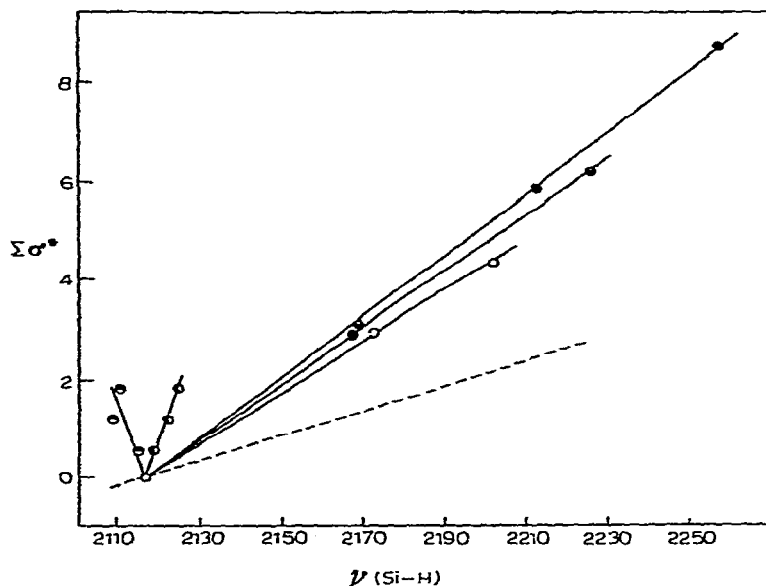


Fig. 2. Plot of $\Sigma\sigma^*$ vs. the Si-H stretching frequency for silanes of the type $\text{Me}_n\text{R}_{3-n}\text{SiH}$. ----- indicates line established for alkylsilanes. $\text{R}=\text{F}$ (◐), Cl (◑), OMe (○), Ph (◒) and NMe_2 (◔).

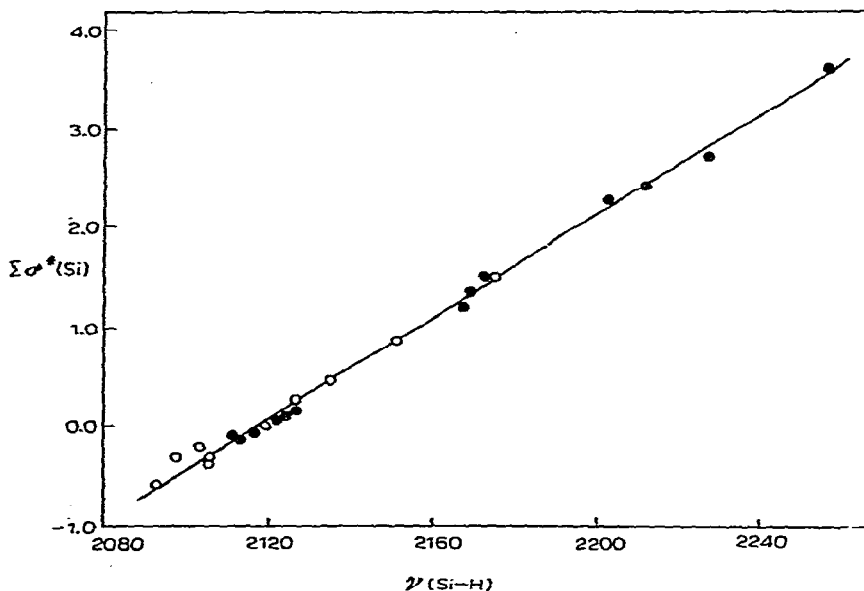


Fig. 3. Plot of $\Sigma\sigma^*(\text{Si})$ vs. the Si-H stretching frequency for alkylsilanes (○) and silanes of the type $\text{Me}_n\text{R}_{3-n}\text{SiH}$ (●).

with the nature of R. In the case, for example, of the dimethylamino-group, as noted previously for tris(dimethylamino)silane⁴, replacement of the methyl groups by the dimethylamino results in a decrease in the observed frequency, whereas an increase is predicted by the inductive constants.

A correlation of the data in Fig. 2 can be achieved by adjustment of the σ^* factors for the R substituents by subtracting an empirical constant, δ , to give a $\sigma^*(\text{Si})$ factor for each substituent:

$$\sigma^*(\text{Si}) = \sigma^* - \delta$$

A plot of observed frequencies as a function of $\Sigma\sigma^*(\text{Si})$ is given in Fig. 3. A good correlation is obtained for both silanes with R substituents and alkylsilanes*. For the latter it is assumed that $\sigma^*(\text{Si}) = \sigma^*$. The numerical data appropriate to Figs. 1-3 is given in Tables 1-3.

TABLE 1

| Compound | $\Sigma\sigma^*$ | $\nu(\text{Si-H})$ | Ref. |
|---|------------------|--------------------|------|
| Me_3SiH | 0.00 | 2118 | 5 |
| Me_2SiH_2 | 0.49 | 2135 | 1 |
| SiH_4 | 1.47 | 2175 | 6 |
| Et_2MeSiH | -0.20 | 2103 | 1 |
| Et_3SiH | -0.30 | 2097 | 1 |
| $n\text{-Pr}_2\text{SiH}_2$ | 0.26 | 2127 | 7 |
| $n\text{-C}_6\text{H}_{13}\text{SiH}_3$ | 0.85 | 2152 | 7 |
| $n\text{-Pr}_3\text{SiH}$ | -0.345 | 2105 | 8 |
| $\text{iso-Pr}_3\text{SiH}$ | -0.57 | 2092 | 8 |
| $n\text{-Bu}_3\text{SiH}$ | -0.39 | 2105 | 8 |

TABLE 2

| Group | σ^* | δ | $\sigma^*(\text{Si})$ |
|----------------|------------|----------|-----------------------|
| H | 0.49 | 0.00 | 0.49 |
| Me | 0.00 | 0.00 | 0.00 |
| Cl | 2.90 | 1.70 | 1.20 |
| F | 3.10 | 1.75 | 1.35 |
| OMe | 1.45 | 0.70 | 0.75 |
| Ph | 0.60 | 0.55 | 0.05 |
| NMe_2 | 0.60 | 0.65 | -0.05 |

TABLE 3

| Compound | $\Sigma\sigma^*$ | $\Sigma\sigma^*(\text{Si})$ | $\nu(\text{Si-H})$ | Ref. |
|---------------------------------------|------------------|-----------------------------|--------------------|------|
| Me_2ClSiH | 2.90 | 1.20 | 2168 | 1 |
| MeCl_2SiH | 5.80 | 2.40 | 2213 | 1 |
| Cl_3SiH | 8.70 | 3.60 | 2258 | 1 |
| Me_2FSiH | 3.10 | 1.35 | 2169 | 9 |
| MeF_2SiH | 6.20 | 2.70 | 2227 | 1 |
| $\text{Me}(\text{OMe})_2\text{SiH}$ | 2.90 | 1.50 | 2173 | 9 |
| $(\text{OMe})_3\text{SiH}$ | 4.35 | 2.25 | 2203 | 1 |
| Me_2PhSiH | 0.60 | 0.05 | 2120 | 1 |
| MePh_2SiH | 1.20 | 0.10 | 2124 | 1 |
| Ph_3SiH | 1.80 | 0.15 | 2126 | 1 |
| $\text{Me}_2(\text{NMe}_2)\text{SiH}$ | 0.60 | -0.05 | 2117 | 9 |
| $\text{Me}(\text{NMe}_2)_2\text{SiH}$ | 1.20 | -0.10 | 2110 | 9 |
| $(\text{NMe}_2)_3\text{SiH}$ | 1.80 | -0.15 | 2112 | 9 |

The significance of the empirical constant, δ , is a matter of speculation. The deviations from a simple correlation with the inductive constants are consistent with the presence of $d_{\pi-p_{\pi}}$ back donation and the numerical values of δ would suggest

* This would be expected in view of the success of Smith and Angelotti's correlation⁴.

(Si-R) π -bond orders decreasing in the sequence Me_2N , $\text{Ph} > \text{F}$, Cl , $\text{OMe} > \text{H}$ or alkyl.

Recently alkoxychlorosilanes of the type $\text{R}_n\text{Cl}_{3-n}\text{SiH}$, where $\text{R} = \text{OMe}$ or OEt and $n = 1$ or 2 , have been shown to have abnormally high Si-H stretching frequencies compared to those predicted by a correlation with the Taft inductive substituent constants¹⁰. While these deviations cannot be accounted for by the previous correlations¹⁻³, with the present approach they could be rationalised in terms of a small decrease in $d_{\pi-p_{\pi}}$ back donation (lowering of δ) due to competition for the d orbitals of silicon by the chloro and alkoxy substituents. This type of competition has been tentatively proposed in a number of cases to explain anomalous reactivities and spectra of organosilicon compounds¹¹. Clearly, if specific interactions of this type occur, a general correlation of observed Si-H stretching frequencies with substituent parameters is not possible and it is unlikely that a consistent scale of $\sigma^*(\text{Si})$ constants for substituent effects at silicon centres can be devised.

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