View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

# Proton Magnetic Resonance Spectra of Di- and Trisubstituted Derivatives of Methylsilane

By E. A. V. Ebsworth* and S. G. Frankiss†

*Received* 26*th January* 1967

The proton magnetic resonance spectra of 23 di- and tri-substituted derivatives of methylsilane are reported. The α-proton chemical shifts in these compounds are generally non-additive properties of the α-substituents. The deviations from additivity are largest for highly electronegative or bulky substituents. In contrast, the β-proton chemical shifts are generally additive properties of the α-substituents, though deviations from additivity are observed for the fluorides. The factors affecting the β-proton chemical shifts are discussed. The directly bound β(C,H) and α(Si, H) and vicinal (H, H) coupling constants are approximately additive properties of the least electronegative substituents. The vicinal (H, H) coupling constants in substituted methylsilanes generally decrease with increasing substituent electronegativity. The geminal (Si, H) coupling constants are rather insensitive to change of substituent.

In an earlier paper [1] in this series,[2] similarities were found between the proton chemical shifts and nuclear spin-spin coupling constants in silyl and monomethylsilyl compounds and related alkyl compounds. For example, $\tau(\mathrm{Si\underset{\sim}{H}XYZ})$ increases with $\tau(\mathrm{C\underset{\sim}{H}XYZ})$ for many substituents, and the vicinal (H,H) coupling constants in $CH_3SiH_2X$ and $CH_3CH_2X$ are linear functions of the electronegativity of X. The study of dimethylsilyl and trimethylsilyl compounds and some disubsituted derivatives of methylsilane that is reported here forms part of an attempt to determine whether these correlations extend to more heavily substituted methylsilanes. In addition, it was hoped that this study would provide extensive data concerning the effect of α-substitution on the *β*-proton chemical shifts and *β*(C,H) coupling constants in substituted methylsilanes. These effects are small and so it is important that environmental effects should be minimized. Measurements for the three methylsilanes, methyldichlorosilane, dimethylchlorosilane and the trimethylsilyl derivatives are included because the data for these compounds that have already been published [3-5] were not obtained under conditions that were used in the study of silyl [6] and monomethylsilyl [1] compounds.

## EXPERIMENTAL

Dimethylsilane,[7] dimethylsilyl iodide [8] and fluoride,[9] bis(dimethylsilyl) sulphide,[8] trimethylsilyl iodide,[10] bromide [11] and fluoride,[12] bis(trimethylsilyl) sulphide [11] and methyldiiodosilane [13] were prepared by previously reported methods. Dimethylsilyl chloride and bis(dimethylsilyl) ether were prepared by the reaction between dimethylsilyl iodide with mercuric chloride and water, respectively. The vapour-phase reaction between dimethylsilyl iodide and ammonia gave a 65 % yield (based on the amount of iodide taken) of bis(dimethylsilyl)amine, and a 12 % yield of tris(dimethylsilyl)amine. Dimethylsilyl bromide was prepared in 75 % yield from the reaction between dimethylsilyl iodide and silver bromide. Methyldichlorosilane, methyldibromosilane (a new compound) and methyldifluorosilane were prepared by the reaction between methyldiiodosilane and mercuric chloride, silver bromide and antimony trifluoride, respectively (the yields, based on the amount of iodide taken, were 90, 65 and 50 %, respectively). A small quantity of 1,1′-dimethyl-1,1′-difluorodisiloxane (also a new compound) was obtained (in 15 % yield) as a

---

* University Chemical Laboratory, Lensfield Road, Cambridge.
† William Ramsay and Ralph Forster Laboratories, University College, London W.C.1.

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

by-product in the preparation of methyldifluorosilane. Trimethylsilyl chloride, hexamethyldisiloxane, bis(trimethylsilyl)amine and tetramethylsilane were obtained from Hopkin and Williams, and were purified by low-temperature bulb-to-bulb distillation.

The purity of the compunds was determined by vapour density and, where relevant data were available, vapour pressure measurements. The samples of dimethylsilyl iodide and bromide, bis(dimethylsilyl)amine and tris(dimethylsilyl)amine contained about 5 % of the respective trimethylsilyl compound, but these impurities did not complicate the analysis of the spectra.

All the compounds except tris(dimethylsilyl)amine and 1,1′-dimethyl-1,1′-difluorodisiloxane were studied in the liquid phase in concentrated (*ca.* 90 % by volume) and in dilute (*ca.* 10 %) solution, using tetramethylsilane (for the study of methyldibromosilane) and cyclohexane (for the remaining compounds) as solvent and internal reference. As only limited amounts of tris(dimethylsilyl)amine and 1,1′-dimethyl-1,1′-difluorodisiloxane were available, they were studied as dilute (*ca.* 15 and 30 %, respectively) solutions in cyclohexane. No lines were observed in the spectra which could be attributed to impurities in the solvents. The samples were held in 5 mm ext. diam. Pyrex tubing.

Most of the spectra were recorded using a Varian Associates V4300B spectrometer operating at 40 Mc/sec. The spectra of tri- and tetramethylsilane, trimethylsilyl bromide and bis(trimethylsilyl) sulphide were obtained on a Varian A-60 spectrometer.

## RESULTS

The spectra were satisfactorily analyzed by a first-order treatment. A summary of the results is given in tables 1 and 2. Each value is the mean of at least 8 (and

TABLE 1.—PROTON CHEMICAL SHIFTS AND DILUTION SHIFTS IN SOME DERIVATIVES OF METHYLSILANE

| compound | $\tau\overset{\circ}{\mathrm{C}}\underset{\sim}{\mathrm{H}}$ [a] ±0·01 | $\mathrm{C}\underset{\sim}{\mathrm{H}}$ diln.[b] shift p.p.m. ±0·02 | $\tau\overset{\circ}{\mathrm{S}}\mathrm{i}\underset{\sim}{\mathrm{H}}$ [a] ±0·01 | $\mathrm{Si}\underset{\sim}{\mathrm{H}}$ diln.[b] shift p.p.m. ±0·02 |
|---|---|---|---|---|
| $CH_3SiHF_2$ | 9·68 | 0·04 | 5·24 | −0·01 |
| $CH_3SiHCl_2$ | 9·24 | −0·04 | 4·48 | −0·07 |
| $CH_3SiHBr_2$ | 8·91 | −0·03 | 4·39 | −0·08 |
| $CH_3SiHI_2$ | 8·37 | −0·08 | 4·96 | −0·16 |
| $(CH_3SiHF)_2O$ | 9·73[c] | *e* | 5·26[c] | *e* |
| $(CH_3)_2SiH_2$ | 9·89 | 0·02 | 6·19 | 0·02 |
| $(CH_3)_2SiHF$ | 9·74 | 0·00 | 5·17 | 0·02 |
| $(CH_3)_2SiHCl$ | 9·56 | −0·03 | 5·14 | −0·01 |
| $(CH_3)_2SiHBr$ | 9·43 | −0·09 | 5·20 | −0·04 |
| $(CH_3)_2SiHI$ | 9·17 | −0·09 | 5·28 | −0·08 |
| $[(CH_3)_2SiH]_2O$ | 9·85 | 0·00 | 5·27 | 0·00 |
| $[(CH_3)_2SiH]_2S$ | 9·63 | −0·02 | 5·30 | −0·01 |
| $[(CH_3)_2SiH]_2NH$ | 9·82 | −0·01 | 5·44 | −0·02 |
| $[(CH_3)_2SiH]_3N$ | 9·82[d] | *e* | 5·43[d] | *e* |
| $(CH_3)_3SiH$ | 9·94 | 0·01 | 6·01 | −0·01 |
| $(CH_3)_3SiF$ | 9·83 | 0·02 | | |
| $(CH_3)_3SiCl$ | 9·63 | −0·03 | | |
| $(CH_3)_3SiBr$ | 9·49 | −0·05 | | |
| $(CH_3)_3SiI$ | 9·27 | −0·08 | | |
| $[(CH_3)_3Si]_2O$ | 9·94 | 0·00 | | |
| $[(CH_3)_3Si]_2S$ | 9·69 | −0·02 | | |
| $[(CH_3)_3Si]_2NH$ | 9·95 | 0·01 | | |
| $(CH_3)_4Si$ | 10·00 | 0·01 | | |

Isotope shifts $\Delta\tau\mathrm{C}\underset{\sim}{\mathrm{H}}(^{13}\mathrm{C}\text{-}^{12}\mathrm{C})$, $\Delta\tau\mathrm{Si}\underset{\sim}{\mathrm{H}}(^{29}\mathrm{Si}\text{-}^{28}\mathrm{Si})$ and $\Delta\tau\mathrm{C}\underset{\sim}{\mathrm{H}}(^{29}\mathrm{Si}\text{-}^{28}\mathrm{Si})$ are in the range (±0·006)±0·010 in all cases measured (using the 40 Mc/sec spectrometer). The following more significant isotope shifts were measured using the 60 Mc/sec spectrometer:

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

| compound | concentration % v/v in cyclohexane | $\Delta\tau C\underset{\sim}{H}(^{13}C-^{12}C)$ ±0·001 | $\Delta\tau Si\underset{\sim}{H}(^{29}Si-^{28}Si)$ ±0·001 | $\Delta\tau C\underset{\sim}{H}(^{29}Si-^{28}Si)$ ±0·002 |
|---|---|---|---|---|
| $(CH_3)_3SiH$ | 100 | +0·003 | +0·000(3) | +0·002 |
| $(CH_3)_3SiBr$ | 90 | +0·004 | | +0·002 |
| $(CH_3)_3SiI$ | 100 | +0·004 | | *e* |
| $(CH_3)_3SiI$ | 50 | +0·002 | | *e* |
| $[(CH_3)_3Si]_2S$ | 90 | +0·003 | | +0·001 |

[a] $\tau°$ are $\tau$ values extrapolated to infinite dilution in cyclohexane or tetramethylsilane. $\tau°$ (cyclohexane) = 8·556.

[b] diln. shift = $\delta$ (pure compound—infinitely dilute compound). Cyclohexane was used as the solvent for all compounds except $CH_3SiHBr_2$, for which tetramethylsilane was used.

[c] $\tau$ values for 30 % by volume solution in cyclohexane.

[d] $\tau$ values for 15 % by volume solution in cyclohexane.

[e] not measured.

TABLE 2.—(C, H), (Si, H) AND (H, H) COUPLING CONSTANTS IN SOME DERIVATIVES OF METHYLSILANE

| compound | $\lvert J_{CH}\rvert$, c/sec | $\lvert J_{SiH}\rvert$, c/sec | $\lvert J_{\mathrm{gem}}^{\mathrm{SiH}}\rvert$, c/sec | $\lvert J_{\mathrm{vic}}^{\mathrm{HH}}\rvert$ [a], c/sec |
|---|---|---|---|---|
| $CH_3SiHF_2$ | 121·3 ±0·3 | 273·1 ±0·8 | 7·8 ±0·2 | 1·22 ±0·03 |
| $CH_3SiHCl_2$ | 124·2 ±0·4 | 280·8 ±0·2 | 8·2 ±0·2 | 2·29 ±0·06 |
| $CH_3SiHBr_2$ | 125·1 ±0·5[c] | 280·8 ±0·7[c] | 8·0 ±0·2 | 2·52 ±0·08 |
| $CH_3SiHI_2$ | 126·4 ±0·3 | 271·6 ±0·6[c] | *d* | 2·94 ±0·06 |
| $(CH_3SiHF)_2O$ | 120·2 ±0·6[b] | 261·1 ±1·0[c] | 7·9 ±0·2 | 1·34 ±0·08 |
| $(CH_3)_2SiH_2$ | 120·7 ±0·4 | 188·6 ±0·4[c] | 6·8 ±0·2 | 4·17 ±0·05 |
| $(CH_3)_2SiHF$ | 120·0 ±0·3 | 215·8 ±0·3 | 7·4 ±0·2 | 2·69 ±0·07 |
| $(CH_3)_2SiHCl$ | 121·8 ±0·2 | 222·8 ±0·3 | 7·6 ±0·1 | 3·09 ±0·08 |
| $(CH_3)_2SiHBr$ | 122·4 ±0·3 | 225·0 ±0·7[c] | 7·3 ±0·4 | 3·20 ±0·07 |
| $(CH_3)_2SiHI$ | 123·1 ±0·2 | 224·8 ±0·3 | 7·3 ±0·2 | 3·41 ±0·06 |
| $[(CH_3)_2SiH]_2O$ | 118·8 ±0·3 | 205·2 ±0·2 | 7·2 ±0·2 | 2·80 ±0·07 |
| $[(CH_3)_2SiH]_2S$ | 121·4 ±0·3 | 207·6 ±0·3 | 7·4 ±0·2 | 3·41 ±0·05 |
| $[(CH_3)_2SiH]_2NH$ | 119·5 ±0·3 | 193·6 ±0·4 | 6·9 ±0·2 | 3·35 ±0·09 |
| $[(CH_3)_2SiH]_3N$ | 119·3 ±0·4[b] | *d* | 7·0 ±0·1 | 3·31 ±0·10 |
| $(CH_3)_3SiH$ | 119·2 ±0·1 | 184·1 ±0·2 | 6·8 ±0·4 | 3·65 ±0·02 |
| $(CH_3)_3SiF$ | 118·9 ±0·4 | | 7·3 ±0·2 | |
| $(CH_3)_3SiCl$ | 120·5 ±0·4 | | 7·4 ±0·3 | |
| $(CH_3)_3SiBr$ | 121·2 ±0·1 | | 7·1 ±0·1 | |
| $(CH_3)_3SiI$ | 121·8 ±0·2 | | 7·4 ±0·1 | |
| $[(CH_3)_3Si]_2O$ | 117·9 ±0·3 | | 7·0 ±0·1 | |
| $[(CH_3)_3Si]_2S$ | 120·2 ±0·1 | | 6·8 ±0·1 | |
| $[(CH_3)_3Si]_2NH$ | 118·0 ±0·3 | | 7·0 ±0·1 | |
| $(CH_3)_4Si$ | 118·2 ±0·1 | | 6·9 ±0·1 | |

[a] mean of 50-150 measurements. No significant dependence of $\lvert J_{\mathrm{vic}}^{\mathrm{HH}}\rvert$ on concentration was observed.

[b] low-field satellites not observed
[c] high-field satellites not observed
} calculated assuming the appropriate isotopic shift to be zero.

[d] not measured.

usually 12) separate determinations. The quoted errors are the calculated mean errors plus (for $\tau°$ values and dilution shifts) estimated extrapolation errors; no allowance has been made for possible systematic errors of frequencies of the sidebands

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

generated by the decade oscillator, which may be as large as 0·2 c/sec for the data reported here. The isotope shifts $\Delta\tau C\underset{\sim}{H}(^{13}C\text{-}^{12}C)$, $\Delta\tau C\underset{\sim}{H}(^{29}Si\text{-}^{28}Si)$ and $\Delta\tau Si\underset{\sim}{H}(^{29}Si\text{-}^{28}Si)$ and the directly bound (C,H) and (Si,H) and the geminal (Si,H) coupling constants were measured only in concentrated solutions. Only the outer two lines of the methyl proton resonance in $(^{12}CH_3)_2\,^{29}SiHZ$ and $(^{12}CH_3)_3\,^{29}SiH$ were observed, and so the geminal (Si,H) coupling constants for each of these compounds was calculated using the mean value of the vicinal (H,H) coupling constants in the respective compound.

Long-range coupling between methyl protons was not observed in the $^{13}C\underset{\sim}{H}_3$ satellite resonances, nor was coupling observed between the $Si\underset{\sim}{H}$ protons in bis (dimethylsilyl) sulphide, ether or amine in the $^{29}Si\underset{\sim}{H}$ satellite resonances of these compounds.

The previously reported (C,H), (Si,H) and (H,H) coupling constants in dimethylsilane [5] and some trimethylsilyl compounds [4] are generally in fair agreement with the values reported here (table 2), but the proton chemical shifts of dilute solutions of these compounds [4, 5] and methyldichlorosilane [3] and dimethylchlorosilane [3] in carbon tetrachloride are between 0·0 and 0·2 p.p.m. to low field of the values reported in table 1 (obtained from cyclohexane solutions). These low-field solvent shifts from cyclohexane to carbon tetrachloride may arise from the greater polarizability of carbon tetrachloride compared to cyclohexane.

## DISCUSSION

### α-PROTON CHEMICAL SHIFTS

It has previously been shown that $\tau(Si\underset{\sim}{H}XYZ)$ increases with $\tau(C\underset{\sim}{H}XYZ)$ for many substituents.[1] The α-proton shifts of the poly-substituted methylsilanes reported here (table 1) are generally consistent with this approximate relationship,

TABLE 3.—THE EFFECT OF α-SUBSTITUTION ON α-PROTON CHEMICAL SHIFTS IN SOME DERIVATIVES OF SILANE AND METHYLSILANE[a]

| X | F | Cl | Br | I | OR | SR | $NR_2$ |
|---|---|---|---|---|---|---|---|
| $\Delta^{X}\tau[Si\overset{*}{\underset{\sim}{H}}_4]$ | −1·56 | −1·39 | −0·97 | −0·24 | −1·41 | −1·15 | −1·24 |
| $\Delta^{X}\tau[Si\overset{*}{\underset{\sim}{H}}_3X]$ | 0·05 | −0·81 | −1·00 | −0·58 | 0·07 | *b* | −0·02 |
| $\Delta^{X}\tau[Si\overset{*}{\underset{\sim}{H}}_2X_2]$ | 0·20 | −0·67 | −1·13 | −0·47 | 0·33 | *b* | 0·25 |
| $\Delta^{X}\tau[CH_3Si\overset{*}{\underset{\sim}{H}}_3]$ | −1·24 | −1·17 | −0·94 | −0·53 | −1·12 | −0·97 | −0·97 |
| $\Delta^{X}\tau[CH_3Si\overset{*}{\underset{\sim}{H}}_2X]$ | 0·03 | −0·80 | −1·12 | −0·96 | *b* | *b* | *b* |
| $\Delta^{X}\tau[(CH_3)_2Si\overset{*}{\underset{\sim}{H}}_2]$ | −1·02 | −1·05 | −0·99 | −0·91 | −0·92 | −0·89 | −0·76 |
| | | | | | | | |
| $\Delta^{CH_3}\tau[Si\overset{*}{\underset{\sim}{H}}_3X]$ | −0·03 | −0·13 | −0·32 | −0·64 | −0·06 | −0·17 | −0·08 |
| $\Delta^{CH_3}\tau[CH_3Si\overset{*}{\underset{\sim}{H}}_2X]$ | −0·04 | −0·14 | −0·31 | −0·64 | −0·06 | −0·18 | −0·05 |
| $\Delta^{CH_3}\tau[Si\overset{*}{\underset{\sim}{H}}_2X_2]$ | −0·05 | −0·12 | −0·44 | −1·02 | *b* | *b* | *b* |

$\Delta^{X}\tau[Si\overset{*}{\underset{\sim}{H}}_2YX] = \tau[Si\underset{\sim}{H}XYZ]-\tau[Si\underset{\sim}{H}_2YZ]$

[a] data taken from table 1 and ref. (1), (6), (15) and (32).

[b] not measured.

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

though significant deviations are observed for the fluorides. This relationship is clearly consistent with the changes in the α-proton chemical shifts being determined by inductive changes in local diamagnetic shielding, but it does not require this to be the only important factor.[1] It does, however, suggest that the $C\underset{\sim}{H}XYZ$ and $Si\underset{\sim}{H}XYZ$ proton chemical shifts are determined by similar factors.

Some α-proton substitution shifts in silyl and methylsilyl derivatives are listed in table 3. These shifts are generally negative but, with the exception of bromine substitution, they cannot be described by additive substituent parameters. The magnitudes of the substitution shifts for Cl or F substitution decrease with increasing number of polar groups in the molecule, though they are less dependent on the presence of non-polar groups (e.g., $CH_3$). The substitution shifts for methyl substitution (table 3) are also independent of the presence of other methyl groups in the molecule, but they are strongly dependent on the presence of polar or bulky substituents. Thus, the present results show that the most marked deviations in the additivity of α-proton substitution shifts in polysubstituted silanes are found for the more polar or bulky substituents. The α-proton substitution shifts in alkyl derivatives show a similar pattern.[14, 15]

Since substituents do not in general have an additive effect on the α-proton chemical shifts in substituted silanes and alkanes, it is unwise to attempt to relate the observed shifts to the individual properties (such as electronegativity) of the substituents.

## β-PROTON CHEMICAL SHIFTS

In contrast to the α-proton shifts, we find that the β-proton shifts in substituted methylsilanes are approximately additive properties of most α-substituents (table 4). This additivity is particularly striking in methyl substitution, for which extensive data are available (table 4). It appears that interactions between substituents are only significant for the very electronegative substituents (e.g., F and OR). The additivity of the β-proton shifts implies that these chemical shifts can be described in terms of contributions from individual substituents.

TABLE 4.—THE EFFECT OF α-SUBSTITUTION ON β-PROTON CHEMICAL SHIFTS IN SOME METHYLSILYL DERIVATIVES[a]

| X | F | Cl | Br | I | OR | SR | NR₂ |
|---|---|---|---|---|---|---|---|
| $\Delta^{X}\tau[C\underset{\sim}{H}_3Si\overset{*}{H}_3]$ | −0·25 | −0·39 | −0·56 | −0·81 | −0·14 | −0·31 | −0·13 |
| $\Delta^{X}\tau[C\underset{\sim}{H}_3Si\overset{*}{H}_2X]$ | 0·05 | −0·25 | −0·41 | −0·70 | *b* | *b* | *b* |
| $\Delta^{X}\tau[(C\underset{\sim}{H}_3)_2Si\overset{*}{H}_2]$ | −0·15 | −0·33 | −0·46 | −0·72 | −0·04 | −0·26 | −0·07 |
| $\Delta^{X}\tau[(C\underset{\sim}{H}_3)_3Si\overset{*}{H}]$ | −0·11 | −0·31 | −0·45 | −0·67 | 0·00 | −0·25 | 0·01 |
| $\Delta^{CH_3}\tau[C\underset{\sim}{H}_3Si\overset{*}{H}_2X]$ | 0·11 | 0·07 | 0·10 | 0·10 | 0·11 | 0·06 | 0·07 |
| $\Delta^{CH_3}\tau[(C\underset{\sim}{H}_3)_2Si\overset{*}{H}X]$ | 0·09 | 0·07 | 0·06 | 0·10 | 0·09 | 0·06 | 0·13 |

$$\Delta^{X}\tau[C\underset{\sim}{H}_3Si\overset{*}{H}YZ] = \tau[C\underset{\sim}{H}_3SiXYZ]-\tau[C\underset{\sim}{H}_3SiHYZ]$$

[a] data taken from table 1 and ref. (1).

[b] not measured.

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

The β-proton shifts in substituted methylsilanes and ethanes depend in a similar way on the α-substituents. The two sets of chemical shifts are approximately related by the equation $\tau(C\underset{\sim}{H}_3SiXYZ) \approx 0{\cdot}7\tau(C\underset{\sim}{H}_3CXYZ)$ (see fig. 1). This relationship suggests that it is unecessary to invoke special bonding properties of silicon (e.g., $(p \rightarrow d)\pi$ bonding) to account for the β-proton shifts in substituted methylsilanes.

The β-proton shifts in substituted methylsilanes and alkanes can be discussed in relation to changes in local shielding due to inductive,[16-19] resonance [17] and dispersion [20] interactions, and in relation to long-range shielding [18-20] and parameters called " M—C bond " shifts.[18]

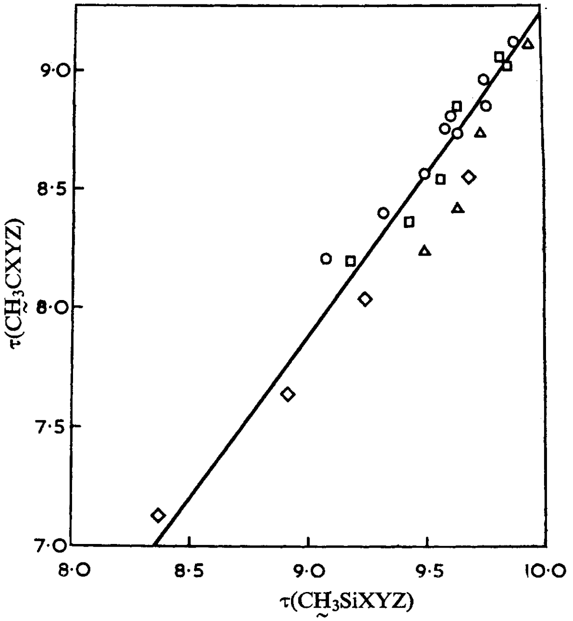


FIG. 1.—$\tau(C\underset{\sim}{H}_3CXYZ)$ against $\tau(C\underset{\sim}{H}_3SiXYZ)$. ○, $CH_3MH_2X$ ; □, $(CH_3)_2MHX$ ; △, $(CH_3)_3MX$ ; ◇, $CH_3MHX_2$. M = C or Si ; data from table 1 and ref (1), (15), (18), (19), (34), (35).

The β-proton shifts in some methylsilyl compounds containing light substituents such as F, OR, $NR_2$, and $CH_3$ can be qualitatively explained by inductive effects since the β-proton shifts decrease with increasing Huggins electronegativity [21] of the substituent. The magnitude of the β-proton substitution shift $\Delta^X\tau[M\underset{\sim}{H}_3\overset{*}{M}HYZ]$†, where M = C or Si, decreases along the series $CH_3CH_2X$,[19] $CH_3SiH_2X$,[1] $SiH_3SiH_2X$[22] for a given light substituent X, which implies that Si transmits inductive effects less efficiently than does carbon. Inductive effects, however, are unlikely to be able to account for the high field shift $\Delta^F\tau[C\underset{\sim}{H}_3Si\overset{*}{H}_2F]$ (see table 4), nor can they account for the low-field substitution shifts produced by heavier substituents, and so inductive effects are unlikely to be the only factors involved even for light substituents.

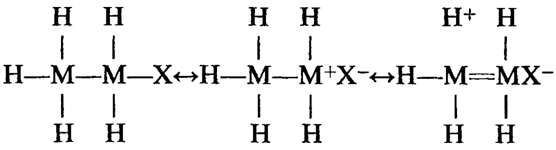
Contributions of resonance structures such as II and III can be expected to result in a decrease in the shielding of the β-protons.[17] These structures are probably more important for compounds containing heavier substituents, and so they might account

† $\Delta^X\tau[M\underset{\sim}{H}_3\overset{*}{M}HYZ] = \tau[M\underset{\sim}{H}_3XYZ] - \tau[M\underset{\sim}{H}_3MHYZ]$

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

for the low-field shift of the $\beta$-protons in $MH_3MXYZ$ ($M$ = C or Si) along the series X = F, Cl, Br, I; but the magnitude of this effect is not known.



I II III

Dispersion interaction between $\alpha$-substituents and $\beta$-protons in substituted alkanes and methylsilanes are expected to increase with the size of the substituent, and they probably result in a decrease in the proton shielding.[20] The observed decrease in the $\beta$-proton shielding with increasing substituent size could therefore be produced by dispersion interactions. Although the magnitude of this effect is not known, it is expected to decrease rapidly ($1/r^6$) with increasing group separation (r).[23] The substitution shift $\Delta^X\tau[M\underset{\sim}{H}_3M\overset{*}{H}_3]$, however, only drops from $-0{\cdot}9$ for substitution in ethane [18] to $-0{\cdot}6$ for substitution in disilane,[22] even though the shortest ($I \ldots H^{\beta}$) distance probably increases from about 2·72 Å in $CH_3CH_2I$ to about 3·68 Å in $SiH_3SiH_2I$.[24] This suggests that dispersion interactions are at least an order of magnitude too small to account for the changes in the $\beta$-proton shifts in these compounds.

The contribution of long-range shielding $\sigma^d$ from an $\alpha$-substituent X, having axial symmetry, to the $\beta$-proton shift can be related, within the limits of the dipolar approximation to the anisotropy of the magnetic susceptibility ($\Delta\chi = \chi^{\parallel} - \chi^{\perp}$) of X by the equation [25]

$$\sigma^d = \Delta\chi(1-3\cos^2\theta)/3R^3, \qquad (1)$$

where $\Delta\chi$ is the difference between the longitudinal and transverse magnetic susceptibilities of X, R is distance between the induced magnetic dipole of the substituent and the $\beta$-proton, and $\theta$ is the acute angle between this radius vector and the symmetry axis of X. It has been suggested that the values of $\Delta\chi$ for the halogen atoms in alkyl halides are negative,[19] and this is supported by a measurement of the magnetic anisotropy of $CHI_3$ which shows that the direction of maximum diamagnetic susceptibility is perpendicular to the C—H axis.[26] It is probable that $\Delta\chi$ for the halogens in methylhalosilanes are also negative. Calculations of long-range shielding of the $\beta$-protons in alkyl and methylsilyl halides, averaged over the appropriate internal rotations, using eqn. (1) with the dipole placed at the centre of X and $\Delta\chi$ taken as 10 % of the ionic susceptibility of $X^-$, predict high-field shifts which are an order of magnitude smaller than the observed low-field shifts. Thus, either the dipolar approximation is too approximate for these calculations or the long-range shielding provides only a minor contribution to the $\beta$-proton shifts in these compounds.

Finally, Cavanaugh and Dailey have proposed that changes in the proton shifts in substituted alkanes do not arise from any of the above factors but they may be related to " C—C bond " shifts which affect the $\alpha$- and $\beta$-protons equally.[18] The chemical shifts of $\alpha$- and $\beta$-protons in monomethylsilyl and dimethylsilyl compounds may be related to analogous " Si—C bond " shifts, but marked deviations from this relationship are observed for methyldihalosilanes.[15]

## COUPLING CONSTANTS

The directly bound (C,H) coupling constants in substituted methanes are an additive property of $\alpha$-substituents that are not very electronegative (e.g., $CH_3$, SR,

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

$NR_2$, I and Br but not F, OR or Cl).[27-29] Similarly in substituted silanes, the least electronegative substituents $CH_3$ and I contribute approximately additively to the directly bound (Si,H) coupling constant, but F, Cl and Br do not (see table 5). The relative changes in $\lvert J_{\mathrm{MH}} \rvert$ on substitution $\Delta_0^{\mathrm{X}} \lvert J_{\mathrm{MH}} \rvert [\mathrm{M}\overset{*}{\mathrm{H}}_4]$†, where M=C or Si, are about the same for substituted methanes and silanes (table 6), except that where first-row element is bound to silicon the change is rather less than in the analogous carbon compounds.

TABLE 5.—THE EFFECT OF α-SUBSTITUTION ON DIRECTLY BOUND (Si, H) AND β(C, H) AND VICINAL (H, H) COUPLING CONSTANTS IN SUBSTITUTED SILANES AND METHYLSILANES[a]

| X | F | Cl | Br | I | OR | SR | NR₂ |
|---|---|---|---|---|---|---|---|
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_4]$ | 26 | 36 | 38 | 38 | 19 | 21 | 9 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_3]$ | 28 | 35 | 37 | 37 | 18 | 21 | 10 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [(\mathrm{CH_3})_2\mathrm{Si}\overset{*}{\mathrm{H}}_2]$ | 27 | 34 | 36 | 36 | 16 | 19 | 5 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_3\mathrm{X}]$ | 53 | 50 | 48 | 40 | *b* | *b* | *b* |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | 51 | 52 | 50 | 41 | *b* | *b* | *b* |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_2\mathrm{X}_2]$ | 100 | 75 | 68 | 45 | *b* | *b* | *b* |
| $\Delta^{\mathrm{CH_3}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_3\mathrm{X}]$ | −7 | −9 | −9 | −9 | −9 | −9 | −8 |
| $\Delta^{\mathrm{CH_3}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | −6 | −6 | −6 | −6 | −7 | −7 | −11 |
| $\Delta^{\mathrm{CH_3}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_2\mathrm{X}_2]$ | −9 | −7 | −8 | −9 | *b* | *b* | *b* |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_3]$ | −1·4 | 0·7 | 1·6 | 2·3 | −2·1 | 0·7 | −1·6 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{CH}} \rvert [(\mathrm{CH_3})_2\mathrm{Si}\overset{*}{\mathrm{H}}_2]$ | −0·7 | 1·1 | 1·7 | 2·4 | −1·9 | 0·7 | −1·4 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{CH}} \rvert [(\mathrm{CH_3})_3\mathrm{Si}\overset{*}{\mathrm{H}}]$ | −0·3 | 1·3 | 2·0 | 2·6 | −1·3 | 1·0 | −1·2 |
| $\Delta^{\mathrm{X}} \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | 0·6 | 1·4 | 1·4 | 2·0 | *b* | *b* | *b* |
| $\Delta^{\mathrm{CH_3}} \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | −0·7 | −1·0 | −1·3 | −1·3 | −1·2 | −1·4 | −1·2 |
| $\Delta^{\mathrm{CH_3}} \lvert J_{\mathrm{CH}} \rvert [(\mathrm{CH_3})_2\mathrm{Si}\overset{*}{\mathrm{H}}\mathrm{X}]$ | −1·1 | −1·3 | −1·2 | −1·3 | −1·1 | −1·2 | −1·5 |
| $\Delta^{\mathrm{X}} \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_3]$ | −1·4 | −1·1 | −1·0 | −0·8 | −1·4 | −0·8 | −1·1 |
| $\Delta^{\mathrm{X}} \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [(\mathrm{CH_3})_2\mathrm{Si}\overset{*}{\mathrm{H}}_2]$ | −1·5 | −1·1 | −1·0 | −0·8 | −1·4 | −0·8 | −0·9 |
| $\Delta^{\mathrm{X}} \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | −2·0 | −1·3 | −1·2 | −0·9 | *b* | *b* | *b* |
| $\Delta^{\mathrm{CH_3}} \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{X}]$ | −0·5 | −0·5 | −0·5 | −0·5 | −0·5 | −0·5 | −0·3 |

$$\Delta^{\mathrm{X}} \lvert J_{\mathrm{SiH}} \rvert [\mathrm{Si}\overset{*}{\mathrm{H}}_2\mathrm{YZ}] = \lvert J_{\mathrm{SiH}} \rvert [\mathrm{SiHXYZ}] - \lvert J_{\mathrm{SiH}} \rvert [\mathrm{SiH_2YZ}]$$

$$\Delta^{\mathrm{X}} \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}\mathrm{YZ}] = \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3SiXYZ}] - \lvert J_{\mathrm{CH}} \rvert [\mathrm{CH_3SiHYZ}]$$

$$\Delta^{\mathrm{X}} \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [\mathrm{CH_3Si}\overset{*}{\mathrm{H}}_2\mathrm{Y}] = \lvert J^{\mathrm{HH}}_{\mathrm{vic}} \rvert [\mathrm{CH_3SiHXY}] - \lvert J^{\mathrm{HH}}_{\mathrm{v\ ic}} \rvert [\mathrm{CH_3SiH_2Y}]$$

[a] data taken from table 2 and ref. (1), (32), and (33).

[b] not measured.

---

† $\Delta_0^{\mathrm{X}} \lvert J_{\mathrm{MH}} \rvert [\mathrm{M}\overset{*}{\mathrm{H}}_4]$ is defined in table 6.

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

The directly bound (C,H) coupling constants in substituted methylsilanes are an additive property of the less electronegative substituents ($CH_3$, I, Br, Cl) but again significant deviations are observed for highly electronegative substituents (F, OR) (see table 5). There is little correlation between $|J_{CH}|$ and $|J_{SiH}|$ in $CH_3SiHXY$ (table 2), such as might be expected if changes in both coupling constants were determined by changes in $\sigma$-bond spin polarization. $|J_{CH}|$ $[CH_3SiXYZ]$ generally increases with $|J_{CH}|$ $[CH_3CXYZ]$,[15] but the negative values of $\Delta^X |J_{CH}| [CH_3Si\overset{*}{H}YZ]$‡, where X is $NR_2$, OR or F are unexpected since $\Delta^X |J_{\underset{\sim}{C}H}| (CH_3\overset{*}{C}H_3)$ is positive for $X = OCH_2OCH_3$[29, 31] and X = F.[15, 31] This decrease in $|J_{CH}|$ for compounds containing a first-row element bound to silicon might be associated with the smaller values of $\Delta_0^X |J_{MH}| [M\overset{*}{H}_4]$ (where M = C or Si) for substituted silanes than substituted methanes when the substituent has a first-row element bound to M (table 6).

‡ $\Delta^X |J_{MH}| [\ldots MH \ldots \overset{*}{H} \ldots] = |J_{MH}|[\ldots MH \ldots X \ldots] - |J_{MH}| [\ldots MH \ldots H \ldots]$ c/sec.

TABLE 6.—EFFECT OF $\alpha$-SUBSTITUTION ON DIRECTLY BOUND (Si, H) AND (C, H) COUPLING CONSTANTS IN SILANE AND METHANE, RESPECTIVELY[a]

| X | F | Cl | Br | I | OR | SR | $NR_2$ |
|---|---|---|---|---|---|---|---|
| $\Delta_0^X |J_{SiH}| [Si\overset{*}{H}_4]$ | 0·13 | 0·18 | 0·19 | 0·19 | 0·09 | 0·10 | 0·03 |
| $\Delta_0^X |J_{CH}| [C\overset{*}{H}_4]$ | 0·19 | 0·20 | 0·22 | 0·21 | 0·12 | 0·10 | 0·05 |

$|J_{SiH}| [MH_3X] = |J_{MH}| [1+\Delta_0^X |J_{MH}| (M\overset{*}{H}_4)]$, where M = C or Si.

[a] data taken from ref. (30) and (33).

The vicinal (H,H) coupling constants in substituted methylsilanes are also an additive property of the substituents $CH_3$, I, Br and Cl but not F and OR (see table 5). The vicinal (H,H) coupling constant in $CH_3SiHXY$ varies approximately linearly with the Huggins electronegativity of the substituents according to the equation:

$$|J^{HH}_{vic}| [CH_3SiHXY] = 4{\cdot}44(1-0{\cdot}23[\Delta E_X + \Delta E_Y]) \text{ c/sec}, \qquad (2)$$

where $\Delta E_X = E_X - E_H$, and $E_X$ is the Huggins electronegativity of X.[21] The deviations from this equation are as large as 0·7 c/sec. The geminal (Si,H) coupling constants in $CH_3SiHXY$ are rather insensitive to change of substituents X and Y (see table 2).

One of us (S.G.F.) is grateful to I.C.I. for the award of a research fellowship, and he also thanks the D.S.I.R. for a maintenance grant (during the tenure of which part of this work was done).

[1] E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, 1963, **59,** 1518.

[2] This paper is to be considered as part 5 of this series; for part 4 see E.A.V. Ebsworth and J. J. Turner, *Trans. Faraday Soc.*, 1964, **60,** 256.

[3] D. E. Webster, *J. Chem. Soc.*, 1960, 5132.

[4] H. Schmidbaur, *J. Amer. Chem. Soc.*, 1963, **85,** 2336.

[5] H. Schmidbaur, *Ber.*, 1964, **97,** 1639.

[6] E. A. V. Ebsworth and J. J. Turner, *J. Physic. Chem.*, 1963, **67,** 805.

[7] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69,** 2692.

[8] H. J. Emeléus and L. E. Smythe, *J. Chem. Soc.*, 1958, 609.

[9] H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 1958, 604.

View Article Online

Published on 01 January 1967. Downloaded by Colorado State University on 04/12/2015 18:56:37.

[10] M. G. Voronkov and Y. I. Khudobin, *Izvest. Akad. Nauk S.S.S.R. Otdel, Khim. Nauk* 1956, 713; *Chem. Abstr.*, 1957, **51,** 1819.

[11] C. Eaborn, *J. Chem. Soc.*, 1950, 3077.

[12] H. S. Booth and J. F. Suttle, *J. Amer. Chem. Soc.*, 1946, **68,** 2658.

[13] H. J. Emeléus, M. Onyszchuk and W. Kuchen, *Z. anorg. Chem.*, 1956, **283,** 74.

[14] A. A. Bothner-By, *Disc. Faraday Soc.*, 1962, **34,** 69.

[15] S. G. Frankiss, *Ph.D. Thesis* (Cambridge University, 1963).

[16] B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, 1955, **77,** 3977.

[17] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1958, **80,** 1728.

[18] J. R. Cavanaugh and B. P. Dailey, *J. Chem. Physics*, 1961, **34,** 1099.

[19] H. Spiesecke and W. G. Schneider, *J. Chem. Physics*, 1961, **35,** 722.

[20] T. Schaefer, W. F. Reynolds and T. Yonemoto, *Can. J. Chem.*, 1963, **41,** 2969.

[21] M. L. Huggins, *J. Amer. Chem. Soc.*, 1953, **75,** 4123.

[22] C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, 1964, **3,** 1071.

[23] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley and Sons, Inc., New York, 1954).

[24] *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Chem. Soc. Spec. Publ. no. 11, 1958, and no. 18, 1965.

[25] H. M. McConnell, *J. Chem. Physics.*, 1957, **27,** 226.

[26] S. Bhagavantam, *Indian J. Physics.*, 1929, **4,** 1.

[27] E. R. Malinowski, *J. Amer. Chem. Soc.*, 1961, **83,** 4479.

[28] N. Muller and P. I. Rose, *J. Amer. Chem. Soc.*, 1962, **84,** 3973.

[29] S. G. Frankiss, *J. Physic. Chem.*, 1963, **67,** 752.

[30] C. Juan and H. S. Gutowsky, *J. Chem. Physics*, 1962, **37,** 2198.

[31] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. A*, 1962, **269,** 385.

[32] H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. MacDiarmid and T. Yoshioka, unpublished observations.

[33] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Physics.*, 1962, **36,** 2628.

[34] E. A. V. Ebsworth and S. G. Frankiss, *J. Chem. Soc.*, 1963, 661.

[35] G. V. D. Tiers, *Tables of $\tau$-values for a Variety of Compounds*, 1958.