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THE PROTON MAGNETIC RESONANCE SPECTRA OF THE ETHYLHALOSILANES

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SUMMARY

The proton magnetic resonance spectra of compounds $(CH_3CH_2)_{4-n}SiX_n$, $n=1$–3, $X=Cl$, Br and I, have been measured and the variation of $\Delta[=\tau(CH_3)-\tau(CH_2)]$, $\tau(CH_3)$ and $\tau(CH_2)$ with n are discussed in terms of diamagnetic anisotropy effects. Other factors such as inductive effects, and Van der Waals dispersion forces may make minor contributions to the chemical shifts. The observed coupling constants are discussed.

INTRODUCTION

We recently reported[1] the proton magnetic resonance (PMR) spectra of the ethylgermanium compounds $(C_2H_5)_{4-n}GeX_n$ ($n=0$–3; $X=Cl$, Br, I, $\frac{1}{2}O$, and H) and discussed the variation with n and X of $\Delta[=\tau(CH_3)-\tau(CH_2)]$, and of the individual chemical shifts of the CH_2 and CH_3 groups. Van der Kelen[2] has reported similar studies on the ethylhalostannanes. In both these studies it was suggested that the results could be best rationalised in terms of diamagnetic anisotropy effects arising at the substituent X.

For ethylhalosilanes, spectra have been reported for $(C_2H_5)_3SiCl$[3,4], $(C_2H_5)_3SiBr$[3,4], $(C_2H_5)_3SiI$[4], $(C_2H_5)_2SiCl_2$[5], $C_2H_5SiCl_3$[5] and also for $(C_2H_5)_4Si$[3,5], although some of these studies[4,5] give only Δ values for neat liquids. The Δ values for the chlorosilanes, $(C_2H_5)_{4-n}SiCl_n$ ($n=0,2,3$) were shown[5] to vary linearly with n, and this was attributed to the inductive effect of the chlorine atoms. However, the chemical shifts of the triethylhalosilanes, $(C_2H_5)_3SiX$ ($X=F$, Cl, Br, I) were found to be in the opposite order to that required by the inductive effect of X and were explained in terms of diamagnetic anisotropy contributions[4,5].

As anisotropy effects in the ethylgermanes were most striking in molecules containing two or three iodine or bromine atoms we have investigated the spectra of the corresponding ethylhalosilanes. We have also redetermined the spectra of the triethyl species and of all the ethylchlorosilanes to complete the set of measurements on the compounds, $(C_2H_5)_{4-n}SiX_n$ ($X=Cl$, Br, I; $n=1, 2, 3$) under the same conditions. We have analysed all the spectra to derive $\tau(CH_3)$ and $\tau(CH_2)$ as well as Δ values.

EXPERIMENTAL

The samples of the three chlorosilanes used were redistilled commercial products and the tribromide[6] and triiodide[7] were made by standard methods. Triethyliodosilane was made by the action of iodine on the hydride and was converted to the bromide using AgBr. Diethyldibromo- and -diiodosilanes were made by halogen cleavage of diethyldiphenylsilane catalysed by aluminium. Purity was checked by vapour phase chromatography and all compounds boiled within 2° of the reported values. None of the PMR spectra showed any significant impurity except for $(C_2H_5)_3$-SiBr which contained a small amount of the corresponding oxide.

The PMR spectra were recorded at 60 Mc on a Perkin–Elmer R10 spectrometer on $10 \pm 2\%$ v/v solutions in CCl_4 using TMS as internal standard. The values tabulated are the average of at least five spectra which varied by less than 0.2 cps.

When $|\Delta|$ was less than 0.15 ppm the spectra were analysed by the graphical method previously described[1]. For $|\Delta|$ values greater than 0.15 ppm, it was possible to calculate Δ and J by the method of Narasimhan and Rogers[5]. These calculated values were then used, with the J/Δ values for A_3B_2 spectra given by Corio[8], to construct theoretical spectra. These were compared with the experimental spectra and the J and Δ values were modified till the best fit was obtained. As the intensities and, particularly, the positions of bands on the wings of the spectra are very sensitive to variations in J and Δ, this method gives Δ values within ± 0.003 ppm and J values within ± 0.1 cps.

The spectrum of diethyldichlorosilane was also recorded at 100 Mc on a Varian HA100 spectrometer.

DISCUSSION

Chemical shifts

The chemical shifts and coupling constants of the ethylhalosilanes are given in Table 1. The results for the triethylhalosilanes, $(C_2H_5)_3$ SiX, and for $C_2H_5SiCl_3$

TABLE 1

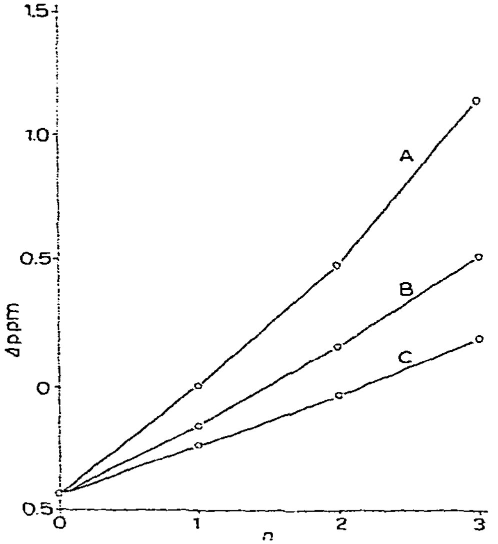
PROTON MAGNETIC RESONANCE DATA FOR ETHYLHALOSILANES[a]

Compound	Chemical shifts (ppm)			J(AB)
	CH_3	CH_2	Δ	(cps)
$(C_2H_5)_4Si$[3]	9.067	9.500	−0.433	~8.0
$(C_2H_5)_3SiCl$	8.983	9.215	−0.232	7.8
$(C_2H_5)_3SiBr$	8.978	9.136	−0.160	7.8
$(C_2H_5)_3SiI$	8.998	8.998	0	7.7
$(C_2H_5)_2SiCl_2$	8.893	8.932	−0.039	~7.8
$(C_2H_5)_2SiBr_2$	8.913	8.758	0.155	7.8
$(C_2H_5)_2SiI_2$	8.945	8.473	0.472	8.0
$C_2H_5SiCl_3$	8.785	8.602	0.183	7.8
$C_2H_5SiBr_3$	8.840	8.333	0.507	7.8
$C_2H_5SiI_3$	9.000	7.872	1.128	7.7

[a] Values measured at 60 Mc on 10% solutions in CCl_4.
$\Delta = \tau(CH_3) - \tau(CH_2)$.

agree within experimental error with previously reported values[3,4,5] when allowance is made (in some cases) for dilution shifts from the neat liquid to our 10% solutions. In the case of $(C_2H_5)_2\ SiCl_2$ where the absolute value of Δ is very small, Narasimhan and Rogers reported $\Delta = +0.015$ ppm. However, the spectrum is very similar to that of $(C_2H_5)_3GeCl$ where $\Delta = -0.025$ ppm[1] and this leads us to believe that, for $(C_2H_5)_2$-$SiCl_2$, Δ is negative (with the CH_3 resonance to *low* field of CH_2). This was confirmed by running this spectrum at 100 Mc when Δ was shown to be -0.039 ppm.

Figs. 1, 2 and 3 show, respectively, plots of Δ, $\tau(CH_2)$ and $\tau(CH_3)$ versus *n*.



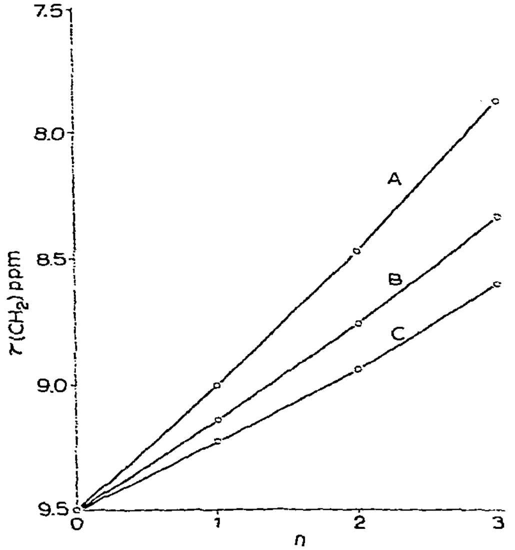


Fig. 1. The variation of $\Delta = \tau(CH_3) - \tau(CH_2)$ with *n* for ethylhalosilanes, $(C_2H_5)_{4-n}SiX_n$. Curve A, X = I; curve B, X = Br; curve C, X = Cl.

Fig. 2. The variation of $\tau(CH_2)$ with *n* for the ethylhalosilanes. A, B, C as Fig. 1.

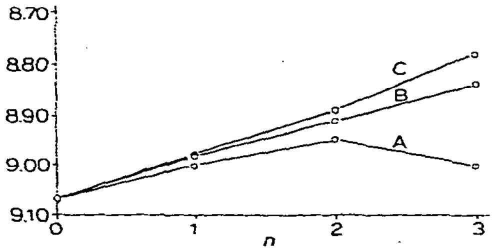


Fig. 3. The variation of $\tau(CH_3)$ with *n* for the ethylhalosilanes. A, B, C as Fig. 1. Note increased ordinate scale compared with Figs. 1, 2.

The diagrams are very similar to those for the ethylhalogermanes[1]. The plot of Δ against *n* is approximately linear for X = Cl, but curves towards low field for X = Br and I, especially for *n* = 3. The major contribution to the changes in Δ comes from the variations in $\tau(CH_2)$, which follow very similar curves (Fig. 2). In addition, the curvature of the Δ plots for X = Br, I is enhanced by small changes in $\tau(CH_3)$, (note the change of scale in Fig. 3). While the CH_3 shifts for the chlorides vary linearly with *n*. those for the bromide and iodides show a *high field* shift, especially noticeable for $C_2H_5SiI_3$ (compare $C_2H_5GeI_3$[1]). While the linear relation between Δ and *n* observed for the chlorides could be explained in terms of an inductive effect[5], or of variations in Taft σ^* coefficients of X[9], these mechanisms cannot account for the shift to low field in the order I > Br > Cl for each value of *n*, nor for the direction of curvature of the plots. As in the case of the germanes[1] and stannanes[2], these variations in the methylene and methyl chemical shifts can be rationalised in terms of the diamagnetic anisotropy arising in the Si–X bond. As the size of X increases, the induced diamagnetism increases hence the shift to low field in the order I > Br > Cl[3,4] and also for $n = 3 > 2 > 1$. The curvature in the plots of the CH_2 chemical shifts may be explained as a second order effect: when, for example in $(C_2H_5)_3SiI$, a second ethyl group is replaced by iodine, the effect is more than doubled as the induced field in each Si–I bond enhances the other. This mutual effect is least for the smaller Cl atoms, hence the approximately linear plot of Δ or $\tau(CH_2)$ *versus n* in this case.

Although the diamagnetic anisotropy phenomena provide a qualitative rationalisation of these chemical shifts, attempts to derive quantitative correlations have not been successful[10]. However, no other explanation appears to lead to the observed pattern. Inductive effects can only be responsible for minor contributions to the CH_2 shifts and are unlikely to affect the CH_3 ones. The other possible explanation is in terms of intramolecular dispersion forces but these are probably too small and may be in the wrong sense. This effect depends inversely on r^6 (the anisotropy effect is inversely proportional to r^3) and hence should be prominent in the methyl shift of $CH_3CH_2SiI_3$ where the CH_3 group is in a highly hindered position close to the iodines. However, the changes observed in CH_3 shifts are only small so that even if they reflect the effect of dispersion forces this is too small to account for the larger variations in the shifts of the more distant methylene protons.

Coupling constants

The variation in *J* (AB), the coupling between the CH_3 and CH_2 protons, ranges only over 0.3 cps and is too small to show significant trends. It has been possible to measure $^{29}Si{-}C{-}^1H$ couplings only in the case of $(C_2H_5)_3SiI$ when Δ was 0. It is assumed that the peaks observed were due to $^{29}Si{-}C{-}^1H$ and not $^{29}Si{-}C{-}C{-}^1H$ as stated by Schmidbaur[3] by comparison with the respective tin compounds[2]. In the tin compounds $^{119\text{ or }117}Sn{-}C{-}^1H$ was always greater than $^{119\text{ or }117}Sn{-}C{-}C{-}^1H$, so, as only one coupling constant was observed here, it is attributed to the two-bond coupling. As this coupling constant is small, only 9.0 cps, it is unlikely that other $^{29}Si{-}C{-}^1H$ couplings will be observed in the complex A_3B_2 spectra when $\Delta \neq 0$, and these have not been detected.

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