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A ^{29}Si AND ^{1}H NMR STUDY OF $(CH_3)_{4-n}$ SiX_n COMPOUNDS WITH $X = N(CH_3)_2$, OCH_3 AND SCH_3

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Summary

The ^{1}H and ^{29}Si NMR spectra of $(CH_3)_{4-n}$ SiX_n compounds ($X = N(CH_3)_2$, OCH_3 and SCH_3) have been studied. The ^{29}Si resonance shows an upfield shift with $X = N(CH_3)_2$, OCH_3, and $n = 2, 3, 4$. This can be accounted for by increasing Si—O and Si—N back donation. Van der Waals interactions are proposed to explain certain NMR parameters.

A linear correlation has been found between the ^{13}C—H coupling constants and the product of the electronegativity and Van der Waals radius in the $(CH_3)_3$ SiX compounds. This provides an explanation of the lower ^{13}C—H coupling constants of $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiN(CH_3)_2$ compared with those in $Si(CH_3)_4$

Introduction

In extending our NMR study of $(CH_3)_{4-n}M_{(IVB)}X_n$ compounds [1—5] we report a ^{1}H and ^{29}Si NMR investigation of $(CH_3)_{4-n}$ SiX_n compounds ($X = OCH_3$, $N(CH_3)_2$ and SCH_3). ^{1}H and ^{29}Si NMR parameters of $(CH_3)_{4-n}Si(OCH_3)_n$ have been reported by several authors [6,7] but we redetermined these in order to obtain results under identical conditions. For the other two series of compounds only ^{1}H chemical shifts have been reported [8,9].

Experimental

The NMR spectra were recorded in frequency-sweep mode on a HFX-90 MHz Bruker Physik NMR spectrometer using 25% (v/v) benzene solutions of the compounds in 5 mm NMR tubes. The benzene signal served as the lock.

The ^{29}Si chemical shifts were obtained from the ^{29}Si NMR INDOR spectra. Only broadened signals could be observed for these compounds. The error in the

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TABLE 1

CHEMICAL SHIFTS (PPM) AND COUPLING CONSTANTS IN $(CH_3)_{4-n}SiX_n$ COMPOUNDS WITH X = OMe, NMe_2 AND SMe

	Chemical shifts (ppm)			Coupling constants			
	$\delta(^1H)$ Si—Me	$\delta(^1H)$ Si—X—Me	$\delta(^{29}Si)$	^2J ^{29}Si—C—H	^3J ^{29}Si—X—C—H	$J(^{13}C$—H) Si—Me	$J(^{13}C$—H) Si—X—Me
Me_4Si	0	—	0	6.5	—	118.9	—
Me_3SiOMe	+0.04	+3.27	+17.75	6.7	4.1	118.0	141.0
$Me_2Si(OMe)_2$	+0.01	+3.34	− 1.62	7.2	3.9	118.5	141.8
$MeSi(OMe)_3$	−0.02	+3.38	−39.8	8.3	3.8	119.4	142.7
$Si(OMe)_3$	—	+3.42	−79.15	—	3.6	—	143.4
Me_3SiNMe_2	+0.04	+2.40	+ 6.52	6.5	3.5	117.7	132.8
$Me_2Si(NMe_2)_2$	+0.06	+2.44	− 1.85	6.6	3.3	118.0	133.0
$MeSi(NMe_2)_2$	+0.09	+2.46	−16.80	6.9	3.2	118.3	133.5
$Si(NMe_2)_4$	—	+2.50	−28.60	—	3.0	—	134.0
Me_3SiSMe	+0.18	+1.77	+16.46	6.7	4.2	120.0	139.5
$Me_2Si(SMe)_2$	+0.35	+1.84	+28.14	7.0	4.8	122.3	140.2
$MeSi(SMe)_3$	+0.51	+1.87	+34.00	7.3	5.5	122.8	141.0
$Si(SMe)_4$	—	+1.94	+38.59	—	6.4	—	142.4

^{29}Si chemical shifts in these circumstances is estimated to be about 0.1 to 0.2 ppm.

The ^{13}C chemical shifts of some t-butyl compounds: $C(CH_3)_4$, $(CH_3)_3COCH_3$ and $(CH_3)_3CN(CH_3)_2$ were measured with F.T. NMR .

Results and discussion

The NMR data are listed in Table 1: ^{1}H and ^{29}Si chemical shifts δ in ppm vs. the ^{1}H and ^{29}Si resonance of $Si(CH_3)_4$; positive values stand for high frequency shifts i.e. to lower field. The ^{13}C values of $(CH_3)_3COCH_3$ and $(CH_3)_3CN(CH_3)_2$, viz. 25 and 42 ppm, respectively are given relative to $C(CH_3)_4$.

1. ^{29}Si and ^{1}H chemical shifts

The ^{29}Si chemical shifts for $(CH_3)_{4-n}Si(OCH_3)_n$ and $(CH_3)_{4-n}Si(N(CH_3)_2)_{n'}$ are downfield for $n = 1$ and then more progressively high field for $n = 2, 3, 4$. This trend has been also observed for other $(CH_3)_{4-n}SiX_n$ systems and analoguous Sn compounds [3] and has been discussed in terms of several factors which along with electrical and magnetic shielding effects, mainly tend to decrease the contribution of the paramagnetic term to the shielding. One of these, increasing $Si \leftarrow X$ back-donation, has been strongly criticized as an explanation for such behaviour [3].

For the $(CH_3)_{4-n}Si(OCH_3)_n$ series this effect was proposed to explain the upfield ^{29}Si chemical shifts on increased OCH_3 substitution [7]. The ^{29}Si—O—C—H and ^{29}Si—N—C—H coupling constants discussed in section 2.2. also yield strong evidence for a substantial $Si \leftarrow OCH_3$ and $Si \leftarrow N(CH_3)_2$ back-donation. On the other hand the $(CH_3)_{4-n}Si(SCH_3)_n$ derivatives show a continuous ^{29}Si shift to lower field on increased SCH_3 substitution. This was also observed for the analoguous tin [2] and carbon compounds [10].

We believe that the contribution of two factors should be taken into consideration. First increasing Van der Waals (V.D.W.) interaction or dispersion forces may shift the ^{29}Si, ^{119}Sn, ^{13}C and ^{1}H resonances to lower field. Second, the diamagnetic anisotropy effect of the C—S bond was estimated by Spiesecke and Schneider [11] to be of similar magnitude to that of the C—I bond, and so could also contribute to the downfield shifts. The same arguments can account for the great downfield shift of the (Si—CH_3) ^{1}H resonances of these compounds vs those of the series $(CH_3)_{4-n}Si(OCH_3)_n$ and $(CH_3)_{4-n}SiN(CH_3)_n$. In Fig. 1 the ^{29}Si chemical shifts of $(CH_3)_3SiN(CH_3)_3$, $(CH_3)_3SiOCH_3$ and of $Si(CH_3)_4$ (zero point) show a linear correlation with the N and O electronegativities. Further, if the slope of this Si correlation line is compared with that for the ^{13}C chemical shift of the central carbon in the analoguous t-butyl compounds a pronounced highfield shift is observed. As was already discussed in the case of the methylsilicon halides [3] such increased shielding may originate from $Si \leftarrow N$ and $Si \leftarrow O$ $(p.d.)\pi$ back-donation.

The ^{29}Si chemical shift of $(CH_3)_3SiSCH_3$, however, was found to fit the halogen correlation line [3].

2. Coupling constants

2.1. J(^{29}SI—C—H) and J(^{13}C—H) of the Si—CH_3 moiety. The ^{29}Si—C—H

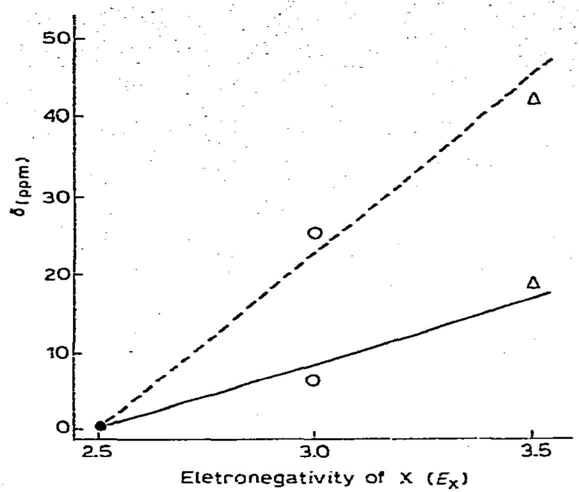

Fig. 1. Variation of ^{13}C and ^{29}Si NMR chemical shifts with the electronegativity of X for $(CH_3)_3CX$ (- - -) and $(CH_3)_3SiX$ (—), respectively; ● : X = CH_3; ○ : X = $N(CH_3)_2$ and △ : X = OCH_3.

coupling constants of the series $(CH_3)_{4-n}Si(OCH_3)_n$ are higher than those of the $(CH_3)_{4-n}Si(N(CH_3)_2)_n$ compounds. This is in accord with the electronegativity effect. Those of the $(CH_3)_{4-n}Si(SCH_3)_n$ compounds, however, are higher than those of the $(CH_3)_{4-n}Si(N(CH_3)_2)_n$ which is opposite to the electronegativity effect.

In an earlier study on methylsilicon halides [3] higher coupling constants were observed with bulkier subsituents. $J(^{29}Si—C—H)$ and $J(^{13}C—H)$ values increased in going from Cl → Br → I as substituents in mono and dihalo substituted compounds. This occurred with trimethyltin halides [3], and the explanation given there may also account for the coupling constants in the thiomethyl compounds.

It is striking that the values of the $^{13}C—H$ coupling constants of the $CH_3—Si$ moiety in the methoxy- and dimethylamino-silanes are lower than those of $Si(CH_3)_4$. This effect was not found for analogous carbon [10] and tin compounds [4,5] but was reported by Engelhardt [12] for $(CH_3)_3SiOCH_3$ and attributed by him to $(p \rightarrow d)\pi$ back-donation from oxygen to silicon. Assuming that V.D.W. interactions could also influence this behaviour we investigated the variation of the $J(^{13}C—H)$ values in monosubstituted silicon compounds as a function of the V.D.W. radii of the X atom and of its electronegativity for X = Cl, Br, I, C, N, O, S. From Table 2 the following conclusions may be drawn:

(a) The most bulky substituents such as the halogens and sulfur produce the highest coupling constants. A similar trend is observed in analoguous ^{13}C and tin compounds.

(b) With the bulky substituents the increasing trend in the coupling constant parallels the increase of the V.D.W. radii, but does not fit with the electronegativity effect.

(c) With the smaller and more electronegative substituents N and O the electronegativity effect predominates despite a decrease of the V.D.W. radii.

From this it is clear that there is no direct correlation between the $^{13}C—H$ coupling constants and either E_X or $R_{V.D.W.}$. But a plot of the $^{13}C—H$ coupling constants against $E_X.R$ (Fig. 2) yields a straight line. The N and O substituted

TABLE 2

VARIATION OF $J(^{13}C—H)$ WITH ELECTRONEGATIVITY (E_X, ALLRED) AND VAN DER WAAL'S RADII (R) OF X IN $(CH_3)_3SiX$ COMPOUNDS

X	$J(^{13}C—H)$	E_X	V.D.W. R (Å)	$E_X . R$
N	117.7	3.0	1.5	4.5
O	118.4	3.5	1.4	4.9
CH_3	118.8	2.5	2.0	5.0
S	120.0	2.8	1.85	5.2
Cl	120.9	3.2	1.80	5.7
Br	121.4	3.0	1.95	5.8
I	121.8	2.7	2.15	5.8

compounds, however, exhibit $J(^{13}C—H)$ values below that of $Si(CH_3)_4$. This suggests that the values of the $^{13}C—H$ coupling constants in these compounds are determined by competition between the electronegativity and V.D.W. effect. The higher $J(^{13}C—H)$ value in $Si(CH_3)_4$ vs. this in $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiN(CH_3)_2$ would then be due to a greater V.D.W. interaction between the four CH_3 groups. However in substituted methanes [14] or in t-butyl compounds [13] with N or O containing substituents such variation of the $^{13}C—H$ coupling constants compared to the $J(^{13}C—H)$ value in methane or neopentane is not observed. So it must be assumed that this effect does not occur in the silicon case, in which back-donation by such substituents does not much lower their electron withdrawing capacity.

2.2. $J(^{29}Si—X—C—H)$ and $J(^{13}C—H)$ of the $Si—X—CH_3$ moiety ($X = O,N,S$). The $^{29}Si—O—C—H$ and $^{29}Si—N—C—H$ coupling constants decrease on increased substitution. This can be interpreted in terms of increased total $Si \leftarrow O$, $SI \leftarrow N$ back-

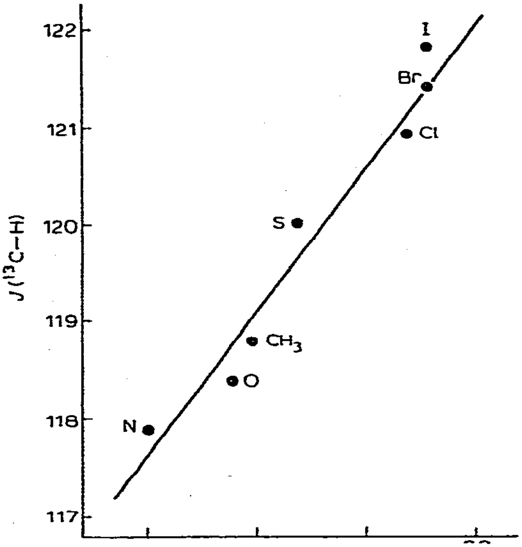

Fig. 2. Dependence of $J(^{13}C—H)$ on $E_X . R_{(V.D.W.)}$ in $(CH_3)_3SiX$ compounds. (E_X = Allred electronegativity).

donation. Starting with the $Si(OCH_3)_4$ and $Si(N(CH_3)_2)_4$ cases, one would argue that in these compounds a maximum polarization of Si occurs, yielding a maximum $(p \rightarrow d)\pi$ interaction. This would raise the bond electronegativities of O— and N= to a high level. In the less substituted compounds with $n = 3, 2$ or 1 the polarization would be lower and accordingly also the extent of $(p \rightarrow d)\pi$ participation. The bond electronegativities of the Si—O and Si—N bonds compared with those in the $Si(OR)_4$ and $Si(NR_2)_4$ species would therefore decrease and the $^3J_{(Si-H)}$ coupling constants increase, as observed. Confirmation of this interpretation can be found in a recent study of H. Noth et al. [15] of the ^{14}N resonances in silylamines, which showed that in the series $(CH_3)_{4-n}Si(N(CH_3)_2)_n$ a deshielding of the nitrogen atom paralleled increases $—N(CH_3)_2$ substitution.

The increasing values of the $^{13}C—H$ coupling constants in the $Si—X—CH_3$ moiety for both series of compounds on increased substitution may also be explained by the above hypothesis.

Contrary to the observations made for the methoxy- and dimethylaminosilanes, $J(^{29}Si—S—C—H)$ in the thiomethylsilanes increases on progressive substitution. This suggests that, taking the monothiomethyl compound as reference, the amount of *s*-character of the Si → SCH_3 orbitals increases with progressive SCH_3 substitution and the consequent rise of the orbital electronegativities may be responsible for the observed increase of the $J(^{13}C—H)$ values of the thiomethyl groups.

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