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^{29}Si and ^{13}C Chemical Shifts and Coupling Constants of Tris(phenyldimethylsilyl)methyl Silicon Compounds

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Abstract

Silicon-29 (δ ^{29}Si) NMR chemical shifts are reported for the first time for a number of tris(phenyldimethylsilyl)methyl silicon compounds (disilylated derivatives), $(PhMe_2Si^A)_3C_\alpha L$, where L = $Si^BR_1R_2R_3$, where R varies widely in electronegativity. δ $^{29}Si^B$ for these series exhibited to some extent good correlations with the electronegativities of the groups bonded to silicon (particularly, δ $^{29}Si^BMe_2X$, X = H, OH, OCH_3, $COCH_3$ and Cl). Substitution with electronegative atoms shifts the chemical shift of silicon to high field.

The ^{13}C NMR spectra of these compounds have been recorded and assigned. The chemical shifts of the α-carbon (C_α) resonances are shown to depend on the type of substituent on the silicon-B, thus $^{13}C_\alpha$ exhibit downfield shifts when X = oxygen ligand. The ^{13}C phenyl resonances have been measured and show the same order of *o, m* and *p* signals, *viz.* δ *ortho* (downfield) > δ *para* > δ *meta.*

The variation of ^{29}Si–^{1}H coupling constants with the electronegativity of X was studied.

Introduction

Over the last few years silicon has become established in the group of heteroatoms that can be studied by nuclear magnetic resonance [1, 2]. ^{29}Si NMR is presently a much exploited field within which certain groups of compounds, notably disilanes and vinylsilanes [3], have already served as the subject of chemical shift studies. In the theory of ^{29}Si NMR chemical shifts, it has been accepted that changes in the nuclear shielding constants are due to changes in the local paramagnetic term σ_p, alone [4]. The main consequence of this approximation is the existence of a U-shaped relationship between the chemical shift and the sum of the substituent electronegativity or the silicon charge values [5].

In the present paper we report the ^{29}Si together with the ^{13}C NMR chemical shifts of bulky tris(phenyldimethylsilyl)methyl compound. The investigations were mainly done in order to gain further insight into the factors governing the ^{29}Si spectra, in particular, the structural and electronic effects on the ^{29}Si resonance for this particular class of silicon compounds. In addition, because of the known sensitivity of the ^{13}C NMR signals to both electronic and steric effects, we investigated the nature of the ligand ($SiR_1R_2R_3$ group) on the resonance positions of the carbons throughout the C_6H_5 ring and the SCS effects have been calculated. The second feature of the investigation was directed at the variation of ^{29}Si–H coupling constants with the nature of the substituent groups.

Results and Discussion

The compounds examined are summarized in Scheme 1, which shows the labelling system employed.

$(PhMe_2Si^A)_3C_\alpha L^B$

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L = a; H; b, Me; c, $SiMe_2Ph$; d, SiMeEtH; e, SiMeBuH, f, SiMe(NCS)H; g, SiMeHCl; **h**, $SiMe(N_3)H$; **i**, $SiMe_2H$; **j**, $SiMe_2$-OH; **k**, $SiMe_2OCH_3$; **l**, $SiMe_2COCH_3$; **m**, $SiMe_2(NCS)$; **n**, $SiMe_2Cl$.

Scheme 1. Labelling system.

^{29}*Si Chemical Shifts (δ* ^{29}*Si)*

The ^{29}Si NMR spectrum of tris(phenyldimethylsilyl)methyl ligand (Scheme 1) was studied in detail and the results are presented in Table I. The parent tris(phenyldimethylsilyl) methyl [**Ia**, L = H] exhibits a ^{29}Si signal at δ –3.95 ppm. With L = Me (**Ib**), the ^{29}Si signal shifted to higher field, δ –2.34 ppm and with L = $SiMe_2Ph$ (**Ic**), the ^{29}Si chemical shift appears at δ ^{29}Si –2.9 ppm. Thus, the introduction of methyl group β to silicon (γ effect) seems to produce a slight deshielding effect. A more pronounced γ effect

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of the methyl group has been reported for (trimethylsilyl)cyclopropyl compounds [6]. However, the ^{29}Si chemical shift with L = H, seems to be a little displaced to low field from what might be expected for the electronegativity of hydrogen (compared with either carbon or silicon atoms). Changing L from $SiMe_2Ph$ to a different group, having a silicon atom with widely different electronic environments (Scheme 1, **Id** to **In**), led to the presence of two different silicon atoms (Scheme 1, Si^A and Si^B), disilylated derivatives.

Assignments of the $^{29}Si^B$ chemical shifts are readily identified since they are less intense and almost variant in position. The $^{29}Si^A$ chemical shifts are more intense and almost invariant in position. The results thus obtained are collected in Table I. Examination of this Table shows that in the $^{29}Si^A$ spectra the values vary from approximately –6.1 to –7.2 ppm. These results reflect the weak influence of the substituted ligand of Si^B.

The general features of the data of $^{29}Si^A$ chemical shifts can be summarized as follows. When an oxygen ligand replaces a hydrogen atom on silicon-B, there is a shift to low field *ca.* 1.0 ppm. However, similar behaviour was observed when an acetyl group replaces hydrogen on silicon-B. When a chlorine ligand replaces the alkyl group of silicon-B (**Ig**), there is a shift to high field for the $^{29}Si^A$ spectra. It is worth noting that the $^{29}Si^B$ chemical shift varies widely by changing the ligands directly bonded to it. Thus, when an oxygen ligand replaces a hydrogen atom (on silicon-B, **Ij** and **Ik**), there is a large shift to high field (*ca.* 30 ppm). This behaviour is very similar to that reported for the methoxy silicon compound [7] (*i.e.* Me_3SiOMe, δ ^{29}Si, *ca.* 17.0 ppm upfield shift). A similar behaviour was observed for the $^{29}Si^B$ spectrum when the hydrogen ligand was replaced by an acetyl ligand (*ca.* 37 ppm upfield). It is worth noting that the replacement of the hydrogen ligand by a chlorine ligand on Si-B, (**In**), leads to a large shift to high field (*ca.* 42 ppm). This result is similar to that reported for the behaviour of Me_3SiCl [7, 8] in which a high field shift was observed (*ca.* 29.9 ppm). Interestingly, the deviation of $^{29}Si^B$ chemical shifts presented here from that reported for Me_3SiOCH_3 and Me_3SiCl of *ca.* 12 ppm upfield shift, relfects the influence of the neighbour group β on the silicon-B $(PhMe_2Si)_3$ groups. The variatons are no doubt influenced by the presence of the bulky $(PhMe_3Si)_3$ groups, but electronic charge densities are probably also involved.

^{13}C Chemical Shifts (δ ^{13}C)

Because ^{13}C NMR signals are known to be sensitive to both electronic and steric effects, a meaningful interpretation of the data for the disilylated derivatives requires an understanding of the influence of the organosilyl substituent: indeed, it has recently been suggested that a study of trimethylsilyl derivatives may assist in making spectral assignments on the parent compounds [9, 10].

The ^{13}C NMR data on the compounds studied are presented in Table I. Chemical shift values obtained from proton decoupled spectra are the means of several observations. For the title compounds the ranges of ^{13}C chemical shifts of phenyl ring carbons were: *ipso* (141.90–139.03 ppm), *ortho* (136.38–133.33 ppm) and *para* (129.40–128.40 ppm). For each compound the same order of *o, m,* and *p* signals was observed, *viz.* δ_{ortho} (downfield) $> \delta_{para} > \delta_{meta}$. Moreover, for the entire set, the ranges for these three resonances did not overlap each other (Table I). The results clearly show that the nature of different groups in silicon-B has a significant and predictable effect on the ^{13}C chemical shift of the *ipso*-carbon compared with the effect on the *ortho, meta* and *para* carbons. The *ipso* resonances covered a range of over 3 ppm downfield from the other carbons. It is important to draw attention to the pronounced deshielding at *ipso* positions, which are directly bonded to the silicon-A, and might be expected to directly reflect the electronic interactions between a benzene ring and silicon substituents. These findings agree well with the established [8, 10, 11] electron-accepting properties of the SiR_3 group and with the charges calculated by Nagy *et al.* [12, 13].

Another interesting feature for the structure elucidation of disilylated derivatives was observed in the assignments of the ^{13}C chemical shifts for α-carbon (C_α), Scheme 1. The C_α signals exhibited downfield shifts relative to the analogous signal of compound **c**, and showed the largest influence from the silyl group substituents (on Si^B). When oxygen, acetyl and chlorine ligands replace the hydrogen atom on silicon-B, there is a shift to low field (*ca.* 6 ppm), compared with that observed when hydrogen is replaced by an alkyl group. The deshielding of the α-carbon reflects the influence of the substituents on silicon-B, which led to a change in the charge density on silicon-B, thus changing the electron-accepting properties of the Si^BR_3 group.

^{29}Si–^{1}H Coupling Constants

The coupling constants given in Table I are also of interest, since the coupling between directly-bonded ^{29}Si and ^{1}H[$^{1}J(^{29}Si-^{1}H)$] in Me_3SiH was found to be 184 Hz [7]. This value is typical for sp^3 silicon. The value observed for compound **d**, Table I, fits well with the reported value (**Id**, ^{1}J, 186 Hz). However, when electronegative substituents are introduced to the silicon-B atom (*i.e.* $(PhMe_2Si)_3CSiMeHCl$, $^{1}J(^{29}Si-^{1}H)$ 228 Hz) the coupling increases. Thus, the electronegativity of chlorine induces a large increase as illustrated above. A comparison was made between the carbon-13 coupling

TABLE I. ^{29}Si and ^{13}C Chemical Shifts[a] and Coupling Constants[b] for Tris(phenyldimethylsilyl)methyl Silicon Compounds

Compound	δ ^{29}Si NMR		δ $^{13}C_\alpha$	δ $^{13}C^A$ NMR					δ $^{13}C^B$ NMR		$^1J(^{29}Si-^1H)$ (Hz)	$^2J(^{29}Si-^1H)$ (Hz)
	$^{29}Si^A$	$^{29}Si^B$		*ipso*	*ortho*	*meta*	*para*	$(CH_3)_2$	CH_3	Others		
Ia $(PhMe_2Si)_3CH$	−3.95		0.29	141.90	133.33	127.64	128.40	1.76				
				(−13.40)[c]	(−4.83)	(0.85)	(0.10)					
Ib $(PhMe_2Si)_3CMe$	−2.34		2.11	140.73	134.86	127.58	128.75	−0.94	13.97			
				(−12.23)	(−6.36)	(0.92)	(−0.25)					
Ic $(PhMe_2Si)_4C$	−2.79		1.70	139.20	135.15	127.64	129.40	−1.00				
				(−10.70)	(−6.65)	(0.86)	(−0.90)					
Id $(PhMe_2Si)_3CSiMeEtH$	−6.39	−7.97	1.42	140.84	136.09	127.28	128.69	4.34	9.98	Et, 9.69, −0.88	186	6.84
				(−12.34)	(−7.59)	(1.22)	(−0.19)					
Ie $(PhMe_2Si)_3CSiMeBuH$	−6.32	−10.66	0.23	140.84	136.09	127.28	128.69	4.34	0.76	Bu, 28.36, 26.54, 17.79, 14.03		
				(−12.34)	(−7.59)	(1.22)	(0.19)					
If $(PhMe_2Si)_3CSiMe(NCS)H$	−6.34	−18.69	2.88	139.03	135.91	127.58	129.22	3.64	2.64		224	6.34
				(−10.53)	(−7.41)	(0.92)	(−0.71)					
Ig $(PhMe_2Si)_3CSiMeHCl$	−6.14	6.49	1.76	139.5	136.15	127.40	129.05	4.29	4.05		228	6.84
				(−11.0)	(−7.65)	(1.1)	(−0.55)					
Ih $(PhMe_2Si)_3CSiMe(N_3)H$	−6.44	−5.28	0.41	139.44	135.97	127.40	129.05	3.76	3.52		218	7.32
				(−10.94)	(−7.47)	(1.1)	(−0.55)					
Ii $(PhMe_2Si)_3CSiMe_2H$	−6.34	−16.63	d	140.73	136.09	127.28	128.69	4.17	2.64		188	6.83
				(−12.23)	(−7.59)	(1.22)	(−0.19)					
Ij $(PhMe_2Si)_3CSiMe_2OH$	−7.18	13.18	5.58	140.79	136.21	127.40	128.81	5.17	7.69			
				(−12.29)	(−7.71)	(1.1)	(−0.31)					
Ik $(PhMe_2Si)_3CSiMe_2OCH_3$	−6.93	14.51	6.75	141.26	136.38	127.17	128.52	5.05	3.82	$-OCH_3$, 48.79		
				(−12.76)	(−7.88)	(1.33)	(−0.02)					
Il $(PhMe_2Si)_3CSiMe_2COCH_3$	−7.03	19.49	6.40	140.37	136.21	127.40	128.81	5.23	5.69	$COCH_3$, 23.78; CO, 170.61		
				(−11.87)	(−7.71)	(−0.31)	(1.1)					
Im $(PhMe_2Si)_3CSiMe_2(NCS)$	−6.71	−6.71	d	139.55	136.21	127.58	129.05	4.87	6.87			
				(−11.05)	(−7.71)	(0.92)	(−0.55)					
In $(PhMe_2Si)_3CSiMe_2Cl$	−6.76	26.28	d	139.87	136.44	127.46	128.87	5.40	10.45			
				(−11.47)	(−7.94)	(1.04)	(−0.37)					

[a] δ in ppm relative to TMS (δSi) and to $CDCl_3$ (^{13}C), positive shifts (for ^{29}Si) representing deshielding. [b] J In Hz. [c] Values in parentheses are deviations, δΔ, relative to benzene shift at 128.50 ppm from TMS (a negative value means deshielding). [d] Signal overlaps.

constants ${}^1J({}^{13}C{-}{}^1H)$, CH_4 (125 Hz), CH_3Cl (150 Hz), CH_2Cl_2 (178 Hz) and $CHCl_3$ (209 Hz) and related compounds [14] with the ${}^1J({}^{29}Si{-}{}^1H)$ reported here. The results demonstrate a similar effect for both carbon and silicon compounds. The ratio of difference in ${}^1J$ values/${}^1J$ value of the parent compound is equal to 0.2 (*i.e.* 150 – 125/125 = 0.20 (for CH_3Cl) and 228 – 186/186 = 0.22 (for **Ig**)). Undoubtedly, the hybridization state of the silicon is not the same, but changes in the effective nuclear charge on silicon or in the average excitation energy are more likely to be the main source of these variations, similar to that reported for ${}^1J({}^{13}C{-}{}^1H)$ coupling constants [15, 16]. On the other hand, this could be due to another effect, possibly including environment and electronegativity.

Interestingly, the magnitude of the coupling constant between Si^B and methyl, the magnitude of the coupling constant between Si^B and methyl protons (${}^2J({}^{29}Si{-}{}^1H)$) remains constant within this entire series, ${}^2J$, 6.34–7.32 Hz. The same phenomenon is observed in mono-, disilylated bicyclo[n.l.o]alkanes and in disilylated cyclopropyl compounds [6, 17] for which the values found were identical (6.3 Hz).

Experimental

The organosilicon compounds were prepared by known methods [18–20]*.

Natural abundance ${}^{13}C$ NMR spectra were recorded at 25 MHz using a JEOL JNM FX-100 instrument system operating in the Fourier transformer mode with a 10 mm tunable probe. All the spectra were recorded at ambient temperature, 26 °C; the compounds were studied as 0.1 M solutions in $CDCl_3$. Chemical shift data of the ${}^{13}C$ NMR spectra were determined relative to $\delta^c = 77.145$ ppm for $CDCl_3$.

The ${}^{29}Si$ NMR spectra with proton decoupling were obtained at 19.73 MHz on a JEOL-FX 100 spectrometer with a spectral width of 2000 Hz, pulse 10 μs (45°); pulse delay 10 s; employing 8K data points. The chemical shifts are reported relative to the silicon resonance of Me_4Si, used as an external reference. The measurements of the ${}^{29}Si{-}{}^1H$ coupling constant were carried out using IRMOD: NOE.

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*Ref. 20 compounds **d**–**f** and **h**.