

NMR SPECTRA AND BASICITIES OF HALOALKYLSILYL AMINES

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Summary

N-Methyl ^{13}C — ^1H coupling constants, ^1H , ^{13}C , and ^{29}Si chemical shifts and the change in C—D stretching frequency of CDCl_3 in mixtures were determined for the series of haloalkylsilyl dimethylamines $\text{XSi}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$, where $\text{X} = \text{CH}_3, \text{ClCH}_2, \text{BrCH}_2, \text{Cl}(\text{CH}_2)_3, \text{Cl}_2\text{CH}$, and $(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)\text{N}(\text{CH}_3)_2$. The coupling constants, basicities and ^{13}C chemical shifts of the SiCH_3 carbons correlated well with σ^* and σ_I , indicating that these electron-attracting groups remove electron density from the amino group and that there is no evidence for the intramolecular α effect.

N-Methyl ^{13}C — ^1H coupling constants and basicities (toward chloroform) of simple dialkylamino derivatives of organosilanes have previously been reported [1]. Calorimetric studies [2], gas phase basicities [3], and normal mode analysis [4] for dialkylamino derivatives have also appeared. In all of these studies the decreased basicity of nitrogen attached to silicon (relative to the carbon congeners) has been attributed to (*p*—*d*) π interactions or HOMO—LUMO interactions [3]. The presence of halomethyl groups attached to silicon, e.g., $\text{XCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$, might be expected to decrease the basicity of such amines by the inductive and electrostatic field effects and to increase the value of the NCH_3 ^{13}C — ^1H coupling constant by increasing the effective nuclear charge at carbon [5] and/or increasing the amount of *s* character in the C—H bonds (through Bent's isovalent hybridization model [6]). On the other hand, evidence has accumulated that atoms bearing lone pairs in the α position frequently confer anomalous properties on silanes. An increase in electron density at silicon beyond that expected from electronegativity considerations has been postulated for halomethylsilanes on the basis of NMR [7,8], IR [9], dipole moment [10], ^{35}Cl -NQR data [10], and basicities of halomethylalkoxy silanes [11,12]. The basicities of the compounds $\text{H}_3\text{Si}(\text{CH}_2)_n\text{OCH}_3$ [13] and $\text{R}_3\text{Si}(\text{CH}_2)_n\text{NH}_2$ [14] were also found to be anomalously low when the basic site was α to the silicon. Several theoretical analyses of the effect have also

appeared [15,16]. Generally, the magnitude of the effect in compounds containing halomethyl groups decreases from chlorine to iodine and decreases as electron-withdrawing groups are added to the silicon [10].

Because of the greater basicity of silyl amines, relative to alkoxides, and the previously demonstrated dependence of *N*-methyl ^{13}C - ^1H coupling constants on the effective electronegativity of the group attached to the nitrogen [17], the amines should provide an excellent system for the study of the effects of haloalkyl groups on silyl compounds. Consequently, the compounds $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$, $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$, $\text{Cl}_2\text{CHSi}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$, $(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)\text{N}(\text{CH}_3)_2$, and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ were prepared and their *N*-methyl ^{13}C - ^1H coupling constants, ^1H , ^{13}C , and ^{29}Si chemical shifts and basicities toward CDCl_3 were measured.

Experimental section

All procedures were carried out under a nitrogen atmosphere with oven-dried glassware and sodium-dried solvents. Anhydrous dimethylamine was dried over molecular sieves. All fractional distillations were performed using a 12 in column packed with glass helices. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All chlorosilanes used in the syntheses of the silyldimethylamines were commercial products. Trimethylsilyldimethylamine was a commercial product, further purified by fractional distillation.

Chloromethyldimethylsilyl-, chloropropyldimethylsilyl-, bromomethyldimethylsilyl-, dichloromethyldimethylsilyl-, and di(chloromethyl)methylsilyldimethylamine, were prepared by dropwise addition of the appropriate halo-metal to dimethylamine in a 1/2 mole ratio in either hexane or petroleum ether

TABLE 1
PHYSICAL AND NMR SPECTRAL PROPERTIES

	B.p. ($^{\circ}\text{C}/\text{Torr}$)	Found (calcd.) (%)		$J(^{13}\text{C}-^1\text{H})$ (± 0.2 Hz) ^b	$\Delta\nu$ ± 5 cm ⁻¹
		C	H		
$(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$	85.5-87	^a [1]		132.1	50
$\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$	146-146.5	^a [19]		133.2	42
$\text{Cl}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$	99-100/41	46.20 (46.77)	10.22 (10.09)	132.6	45
$\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$	44.5-46.5/13	31.11 (30.61)	8.26 (7.19)	133.1	40
$\text{Cl}_2\text{CHSi}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$	172-179	32.98 (32.26)	7.14 (7.04)	133.6	25
$(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)\text{N}(\text{CH}_3)_2$	81.5-85/18	33.28 (32.26)	7.31 (7.04)	133.8	~25

^a Previously reported. ^b Neat samples. ^c Chemical shifts (+) = downfield from TSM; proton shifts for neat solutions, ^{29}Si and ^{13}C , 50% in C_6D_6 except for X = BrCH_2 (50% CH_2Cl_2).

(30–60°C). The exothermic reaction was carried out in an ice bath, with constant stirring. After the addition was complete, the precipitated dimethylamine hydrochloride was filtered, followed by removal of the solvent by simple distillation at atmospheric pressure and fractional distillation of the residue. Upon standing, all compounds slowly developed a small amount of precipitate. The bromomethyl derivative eventually solidified completely.

Physical and NMR spectral properties can be found in Table 1. Elemental analyses and chemical shifts are given for those compounds not previously reported in the literature.

Structural confirmations and *N*-methyl carbon-13–proton coupling constants were obtained on a Perkin–Elmer R-32 (90 MHz) spectrometer on neat samples. The coupling constants were measured with a frequency counter, using a 100 Hz sweep range. The average of at least five measurements was taken as the chemical shift for each satellite.

The *N*-methyl coupling constants for several samples were also measured in CH₂Cl₂ at a variety of concentrations but were found to be in agreement with those of the neat samples within experimental error (± 0.2 Hz).

Carbon–deuterium infrared stretching frequencies were determined with a Perkin–Elmer 621 grating infrared spectrophotometer over a 10-fold expansion of the C–D stretching region (2400–2100 cm⁻¹). The CDCl₃/base mixtures, whose molar ratios were no greater than 1/10, were analyzed in a sodium chloride solution cell and the frequencies were measured relative to that of unassociated liquid CDCl₃ (2254 cm⁻¹). The CDCl₃ was shaken twice with alumina and used immediately. Carbon-13 and silicon-29 spectra were obtained as 50% solution in C₆D₆ (except for the BrCH₂ derivative which was 50% in CH₂Cl₂) on a Bruker WM-250 with proton-noise decoupling.

$\delta(^1\text{H})$ (ppm) ^c			$\delta(^{29}\text{Si})$ (ppm) ^c	$\delta(^{13}\text{C})$ (ppm) ^c	
Si(CH ₃) ₂	N(CH ₃) ₂	Other		Si(CH ₃) ₂	N(CH ₃) ₂
	^a [1]		5.76	-1.25	37.88
	^a [19]		2.54	-4.26	37.94
0.02	2.44	0.63 1.73 3.40	—	—	—
0.18	2.47	2.36	2.71	-4.24	37.74
0.28	2.54	5.22	2.33	-5.79	38.28
0.27	2.48	2.82	-1.87	-7.07	38.06

Results and discussion

The compound resulting from the addition of the potentially ambidentate substrate chloromethyldimethylchlorosilane to dimethylamine has been previously shown to contain the dimethylamino group attached to silicon [18]. The similarity in spectral characteristics of the other haloalkyl derivatives listed in Table 1 strongly suggests that these, too, contain an Si—N bond. All compounds were sensitive to hydrolysis and in an inert atmosphere slowly developed a precipitate which has been previously ascribed to the formation of quaternary amine species [19]. The bromomethyl derivative eventually completely solidified although the freshly distilled liquid appears to be relatively stable in CH_2Cl_2 solution. Analytical data for the solid were in good agreement with carbon and hydrogen values calculated for the compound $\text{BrCH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_3)_2$ and must therefore be the compound itself or a structural isomer. Because the ^{29}Si and ^{13}C NMR spectra of the solid (in CH_2Cl_2) were appreciably different from ($\delta(^{29}\text{Si})$ 6.3, $\delta(^{13}\text{C}(\text{Si}(\text{CH}_3)_2))$ 1.39, $\delta(^{13}\text{C}(\text{N}(\text{CH}_3)_2))$ 34.4 ppm) that of the liquid (in CH_2Cl_2), the solid is apparently a structural isomer, perhaps a quaternary derivative.

The *N*-methyl ^{13}C — ^1H coupling constants presented in Table 1 can be correlated qualitatively with the electron-withdrawing character of substituent on silicon: the bis(chloromethyl) derivative has the highest coupling constant (133.8 Hz) and the parent compound, $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, has the lowest (132.1 Hz). Because of the dependence of $J(^{13}\text{C}$ — $^1\text{H})$ on effective nuclear charge and hybridization [5] and its linear relationship with Hammett σ constants [17] it can be assumed that $J(^{13}\text{C}$ — $^1\text{H})$ is a function of the effective electronegativity of the nitrogen in these compounds. Thus, the bis(chloromethyl) derivative contains the most electron deficient nitrogen either as a direct result of the inductive effect of the two chloromethyl groups or increased $(p-d)\pi$ overlap induced by the increase in effective nuclear charge at silicon, which in turn should contract the *d*-orbitals and increase the overlap with the adjacent *p*-orbitals on nitrogen.

The same qualitative relationship between the electronic effect of the silyl substituent and $\Delta\nu$, the shift in the C—D stretching frequency of CDCl_3 in mixtures with the amines, is obvious from Table 1. Assuming that the relationship [20] between change in stretching frequency and hydrogen-bond strength is valid for this series of compounds, the low $\Delta\nu$ for the bis(chloromethyl) derivative, for example, reflects its relatively electron deficient nitrogen and consequently low basicity.

The ^{29}Si and $\text{Si}(\text{CH}_3)_2$ ^{13}C chemical shifts also show a monotonic dependence on substituent electron-withdrawing effects. Both parameters, however, move to higher fields as the substituents become more electron-withdrawing. This diamagnetic shift with electron-withdrawing substituents has been previously noted in a variety of systems [21] and has, as yet, no satisfactory explanation. The *N*-methyl ^{13}C shifts show a vague downfield shift with electron-withdrawing substituents.

All of the above observations can be put on a more quantitative basis with least squares correlations between these parameters ($J(^{13}\text{C}$ — $^1\text{H})$, $\Delta\nu$, $\delta^{29}\text{Si}$, $\delta^{13}\text{C}(\text{Si}(\text{CH}_3)_2)$) and the inductive substituent constants σ^* and σ_I [22]. For

$J(^{13}\text{C}-^1\text{H})$, $\Delta\nu$, and $\delta^{13}\text{C}(\text{Si}(\text{CH}_3)_2)$ these correlations are excellent ($r > 0.97$) when using either σ_I or σ^* . The correlations of $\delta^{29}\text{Si}$ with σ_I and σ^* were only moderately good ($r = 0.84$). For 5 substituents the parameters of the equation $Y = a + b\sigma$ are: $J(^{13}\text{C}-^1\text{H}) = 132.4 + 4.5\sigma_I$; $J(^{13}\text{C}-^1\text{H}) = 132.3 + 0.73\sigma^*$; $\Delta\nu = 49.0 - 75.7\sigma_I$; $\Delta\nu = 51.8 - 12.4\sigma^*$; $\delta(^{13}\text{C}) = -2.05 - 14.9\sigma_I$; $\delta(^{13}\text{C}) = -1.53 - 2.40\sigma^*$; $\delta(^{29}\text{Si}) = 4.95 - 16.0\sigma_I$; $\delta(^{29}\text{Si}) = 5.49 - 2.57\sigma^*$.

The excellent linear relationship between essentially all variables and the inductive effect of the substituents at silicon strongly suggests that these substituents are behaving in the expected (vide supra) manner and that there is no indication of the electron releasing effect of the α -halo group observed in other systems.

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