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SILICON-29 NMR. SOLVENT EFFECTS ON CHEMICAL SHIFTS OF SILANOLS AND SILYLAMINES*

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Summary

The ^{29}Si NMR spectra of six silanols and four silylamines were examined in several solvents of varying electron pair donor ability. A linear correlation was found between the silanol silicon-29 chemical shift and solvent donor ability. The silylamines were considerably less sensitive to solvent. The effect is attributed to hydrogen bonding between the hydroxyl proton of the silanol and an electron pair of the solvent.

Although numerous studies of solvent effects on proton chemical shifts have been reported [1, 2], much less has been done on some of the less common nuclei. In particular, very little is known about the solvent dependence of silicon-29 chemical shifts [3]. Since the total chemical shift range is greater than 150 ppm, it might be anticipated that solvent effects in general would be small (< 1 ppm) compared to effects arising from structural perturbations. In cases in which strong solute—solvent interactions are possible, however, large solvent shifts might be anticipated, similar to those observed in ^{13}C spectra [4]. We wish to report substantial solvent shifts for a series of silanols and silylamines in a variety of solvents.

Six silanols and four silylamines were examined by ^{29}Si NMR in solvents of varying basicity from chloroform or nitromethane to dimethylformamide (DMF), dimethylsulfoxide (DMSO) or hexamethylphosphoramide (HMPA). All of the silanol chemical shifts were strongly solvent dependent (ranges > 5 ppm) and exhibited an upfield shift of the ^{29}Si resonance with increasing solvent basicity. Larger changes were observed for triphenylsilanol in very basic solvents such as triethylamine and sodium ethoxide—ethanol; the ^{29}Si NMR chemical shift of triphenylsilanol is -12.6 ppm in chloroform and shifts more than 13 ppm upfield to -25.4 ppm in 25% sodium ethoxide—ethanol solution. The amines showed

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much smaller shifts (0.7—3.4 ppm). Data for the ten compounds examined in various solvents are presented in Table 1. All ^{29}Si spectra were obtained on a Varian XL-100-15 NMR spectrometer operating in the Fourier transform (FT) mode at 19.9 MHz for ^{29}Si.

The chemical shifts of compounds I-VI gave an excellent linear correlation ($r > 0.98$) with Gutmann's donor number [6]. This is shown for several compounds in Fig. 1. Of the four amines examined, only IX was sufficiently sensitive to solvent donicity to provide a good linear correlation ($r = 0.99$) presumably for VII, VIII and X the changes are so small that other solvent effects are competitive and cause severe deviations from the line. Compounds without acidic protons available for hydrogen bonding, such as XI and XII, showed solvent shifts of < 0.5 ppm.

$(Ph)_3SiCl$ (XI)

$(CH_3O)_3SiH$ (XII)

All of the above information is consistent with an interaction of the type —Si—O—H···:B effecting the observed upfield shifts, in agreement with previous ^1H NMR work showing strong hydrogen bonding between silanols and DMSO [7]. In the case of the very basic sodium ethoxide—ethanol solvent system in the

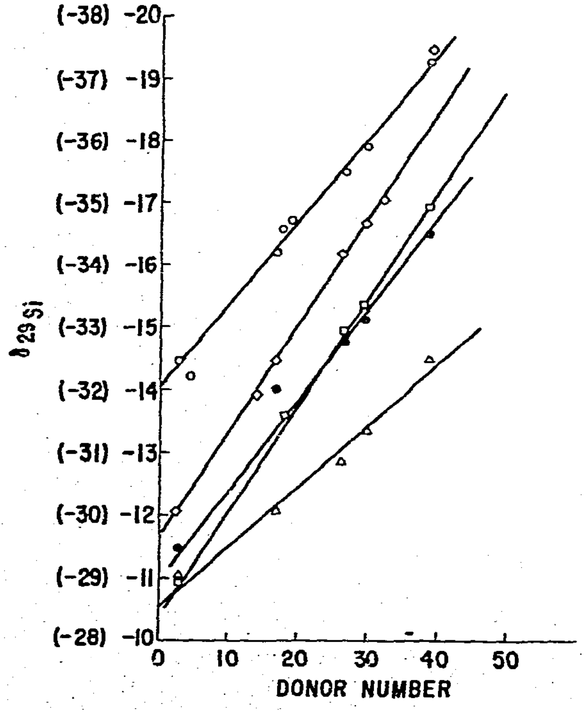
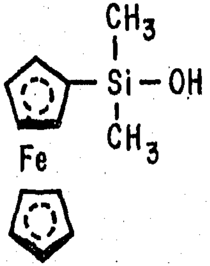


Fig. 1. Silicon-29 chemical shifts vs. Gutmann's donor number for I (○), II (◇), V (□), IV (●) and IX (△). Solvents and donor numbers are: chloroform, < 0.1; nitromethane, 2.7; nitrobenzene, 4.4; acetonitrile, 14.1; acetone, 17.0; diethyl ether, 19.2; tetrahydrofuran, 20.0; dimethylformamide, 26.6; dimethylsulfoxide, 29.8 and hexamethylphosphoramide, 38.8. The scale in parentheses corresponds to II.

TABLE 1

INFLUENCE OF SOLVENT ON SILICON-29 CHEMICAL SHIFTS[a], SOLVENT[b] AND DONOR NUMBER (in parentheses)

Compound		$CHCl_3$[c]	CH_3NO_2 (2.7)	Acetone (17.0)	DMF (26.6)	DMSO (29.8)	HMPA (38.8)	Other
$(Ph)_3SiOH$	(I)	−12.6	−14.5	−16.2	−17.51	−17.9	−19.2	−25.4 25% NaOEt/ETOH[c]
$(Ph)_2Si(OH)_2$	(II)	−30.7	−30.2 (50°C)	−32.4	−34.2	−34.6	−37.5	
$HO(Me_2SiO)_{20}H$	(III)	−10.9	−11.5	−14.0	−14.8	−15.1	−16.5	−11.5 (25% HOAc)[c]
$HO(Me_2SiO)_6H$	(IV)	−10.8	−11.5	−13.9	−14.7	−15.1	−16.1	
$(HOSiMe_2)_2O$	(V)	−10.5	−11.0	−13.6	−14.9	−15.3	−16.9	−14.8 trimethylphosphate (23.0)
	(VI)	+9.8	+8.8	+5.7	+3.6	+3.8	+1.3	
$(Me_2CHNHSiMe_2)_2O$	(VII)	−15.2	*d*	−16.1	*d*	−16.4	−16.7	
$(Me_2HSi)_2NH$	(VIII)	−11.1	*d*	*d*	*d*	*d*	−13.5	
$(PhNH)_2SiMe_2$	(IX)	*d*	−11.1	−12.1	−12.8	−13.3	−14.4	
$(EtNH)_2SiMe_2$	(X)	*d*	−4.8	−5.5	*d*	−5.0	−5.6	
$(Ph)_3SiCl$	(XI)	+1.2	*d*	*d*	+1.5	*d*	*d*	
$(MeO)_3SiH$	(XII)	−55.2	*d*	*d*	*d*	*d*	−55.6	

[a] All shifts are given in ppm relative to internal tetramethylsilane (TMS). Negative values are upfield. In order to insure that the TMS was not subject to large shifts in the solvents used in this study, we obtained its spectrum in a series of these solvents relative to external TMS. TMS in the appropriate solvent was contained in a 10 mm tube with TMS in acetone-d_6 in a 12 mm coaxial tube acting as a reference and providing the deuterium resonance for field-frequency control (lock). In all the solvents examined (acetone, DMSO, HMPA, $CHCl_3$, CH_3NO_2, Et_3N) the total range of the TMS chemical shift was < 0.9 ppm. [b] Solutions were 10—30% by weight with a small amount of $Cr(acac)_3$ added to most samples to shorten the ^{29}Si spin lattice relaxation time and eliminate the negative nuclear Overhauser enhancement arising from proton decoupling [5]. No shifts were observed upon further dilution of the samples, or in the absence of $Cr(acac)_3$. All spectra were run at 38°C except where noted. [c] No donor number is available. [d] Initially we used $CHCl_3$ and DMF, DMSO and HMPA to test the sensitivity of a sample to solvent effects. When we *realized a correlation with donor number existed*, we switched to CH_3NO_2 at the low end of the donicity scale because a value was available for this solvent. When it was apparent that a compound was not very sensitive to solvent, we did not obtain spectra in a wide variety of solvents (VII—XII).

presence of a tenfold excess of base, the triphenylsilanol exists predominantly as the anion and a very large upfield shift is observed.

$$(Ph)_3SiOH + EtO^- \rightleftharpoons (Ph)_3SiO^- + EtOH$$

The shielding effect is transmitted down the chain in IV; the internal silicon atoms also exhibit diamagnetic shifts in a linear fashion ($r > 0.99$) with increasing solvent donor ability (Fig. 2), although to a much smaller degree than the terminal silicon atoms as would be expected for an interaction at the ends of the chain. The crossover in chemical shift between D_2 and D_3 was confirmed by the synthesis of $HO(SiMe_2O)_6H$ for which D_3 is half the intensity of D_2 in the ^{29}Si spectrum, and therefore, easily discernible.

Addition of DMSO to a neat solution of IV produces the titration curves shown in Fig. 3. The chemical shift for D_1 increases and then levels off when a mole ratio of 2 : 1 (DMSO/IV) has been reached. The non-ideal behavior of the titration curve is indicative of preferential hydrogen bonding to DMSO rather than self-association. A similar effect appears in the binary solvent system acetone/hexamethylphosphoramide (HMPA), in which preferential association with the stronger donor (HMPA) is observed.

Although the magnitude of the ^{29}Si chemical shift changes are clearly dependent upon the electron pair donor ability of the solvent, the explanation for the direction of these changes requires more caution. Satisfactory theoretical interpretations of ^{29}Si chemical shift data are hampered by uncertainties regarding the relative importance for ^{29}Si nuclei of the various terms contributing to the nuclear shielding [8-10]. Furthermore, it is unclear if d-orbital terms must be included in the calculations. If it is assumed that the ^{29}Si chemical shift can be

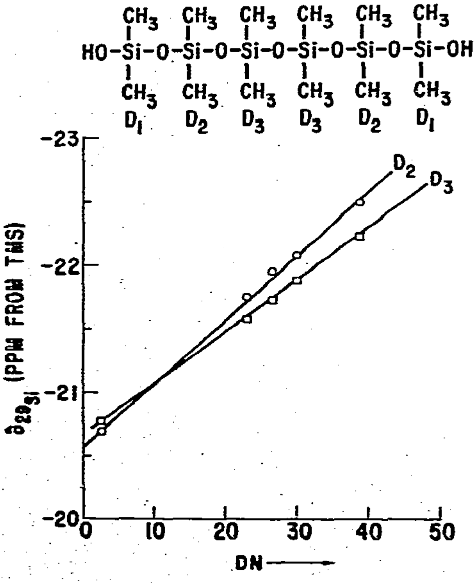


Fig. 2. Silicon-29 chemical shift vs. donor number for the internal silicon atoms in IV.

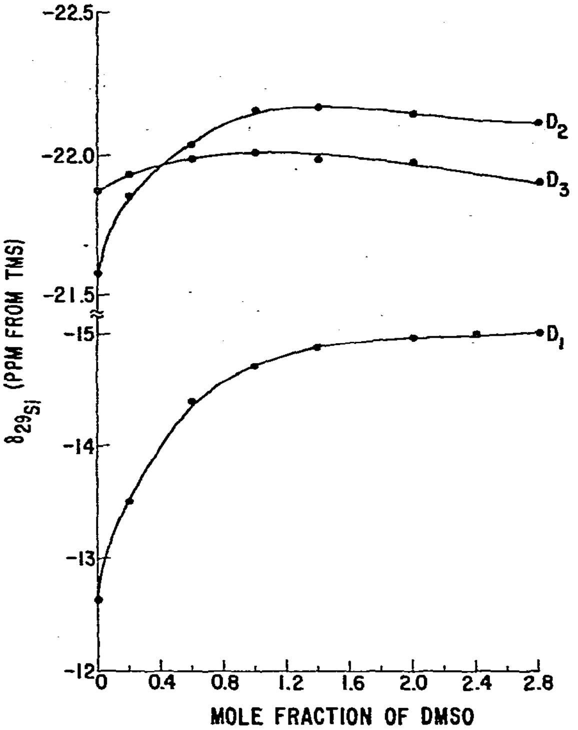


Fig. 3. Silicon-29 chemical shift vs. mole fraction of DMSO for the three different silicon atoms of IV.

satisfactorily explained without invoking the participation of *d*-orbitals the paramagnetic term (σ_p) is proportional to $\frac{1}{\Delta E}$, $<r^{-3}>p$ and Q_p, where $\frac{1}{\Delta E}$ represents the inverse of the average excitation energy, $<r^{-3}>p$ is the mean inverse cube of the distance of the valance shell *p*-electrons from the nucleus and Q_p represents the *p*-electron imbalance [8]. Qualitatively, holding other factors constant, an increase in the electron density around silicon will effect a decrease in the $<r^{-3}>p$ term and thus a decrease in σ_p, resulting in an increased shielding of the ^{29}Si nucleus. A net flow of electron density through the σ bonding framework towards silicon in the silanols would be predicted from repulsion of the O—H bonding electrons by the solvent electron pair. Unfortunately, the relationship between electronic structure and ^{29}Si chemical shifts has not been firmly established, and the direction of ^{29}Si chemical shift changes with increasing calculated electron density at silicon can vary depending upon the substitution at silicon [11, 12]. Nonetheless, it is clear that the ^{29}Si chemical shift is reflecting the hydrogen bonding between the silanol and the solvent and the effect is being felt for a distance of six bonds in IV. Further studies of these interactions are in progress.

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