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Preliminary communication

Silicon-29 NMR: unusual chemical shift trends in the substituted phenyltrifluorosilane system

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SUMMARY

The response of the silicon-29 NMR resonance to substitution on phenyl in a series of phenyltrifluorosilanes was opposite to that reported for the corresponding phenyltrimethylsilanes.

In view of the great potential of silicon NMR to the elucidation of structural, bonding and electronic problems in organosilicon chemistry and the increasing activity in this area[1], it appears desirable to communicate promptly certain results found in our laboratory and to indicate dangers in making interpretations from analogy and extrapolation of fragmentary data.

The silicon resonance of a number of *meta-* and *para*-substituted phenyltrifluorosilanes, $XC_6H_4SiF_3$ (I), have been investigated using pulsed Fourier transform and a relaxation/Overhauser-suppression reagent [chromium(III) acetylacetonate][2]. The silicon chemical shifts of the silanes have been measured under comparable conditions and are summarized in Table I. The silicon resonance of the parent phenyltrifluorosilane (X = H) appeared 5.77 ppm downfield from tetramethoxysilane (TMOS). The position of this silicon resonance proved to be quite sensitive to substitution on the phenyl ring, with electron-withdrawing groups producing unexpected shifts to higher fields, the direction usually associated with increased electron density. Electron-donating groups on the subject compounds, correspondingly, afforded silicon resonances appearing at lower fields. This shielding trend within I is directly opposed to that observed for the structurally related series of phenyltrimethylsilanes[3], $XC_6H_4SiMe_3$ (II). A comparison of the plots of silicon chemical shifts of I and II with Hammett σ_m and σ_p is shown in Fig. 1. Although the Hammett correlations are of opposite sign, both series exhibited high degrees of linearity, having correlation coefficients of 0.974 (I) and 0.991 (II).

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TABLE I

^{29}Si CHEMICAL SHIFTS OF ARYLTRIFLUOROSILANES $XC_6H_4SiF_3$, FROM TETRAMETHOXYSILANE [a,b]

X	^{29}*Si-meta (ppm)*	^{29}*Si-para (ppm)*
$-CF_3$	−4.17	−4.16
−Cl	−4.29	−5.51
−F	−4.40	−5.61
$-OCH_3$	−5.45	−6.99
−H	−5.77	−5.77
$-CH_3$	−5.91	−6.46

[a] Proton-decoupled spectra obtained on Varian XL-100 spectrometer for solution containing 0.5 *M* aryltrifluorosilane, 0.1 *M* tetramethylsilane, (TMS), and 0.1 *M* chromium(III) acetylacetonate in $CDCl_3$ using FT mode. Chemical shift of tetramethoxysilane (TMOS) under these conditions was observed to be +78.48 ppm from TMS. TMOS was not used directly because of evidence of reaction.

[b] Negative chemical shift values indicate low field side of reference; estimated accuracy: ± 0.10 ppm.

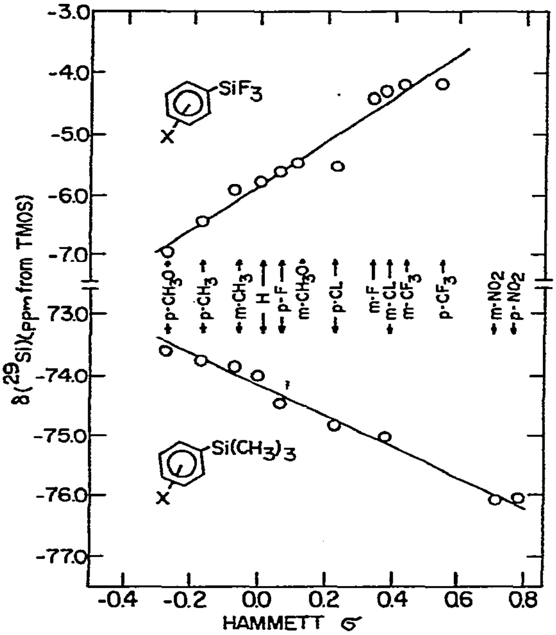

Fig. 1. Plots of ^{29}Si chemical shifts of phenyltrifluorosilanes and phenyltrimethylsilanes[3] *vs*. Hammett σ.

Since the contribution of the diamagnetic term of the Ramsey expression of shielding has been shown to be small for nuclei other than hydrogen, changes in silicon chemical shifts can be represented by changes in parameters of the paramagnetic term which largely involve electron-nuclear distances and elements of the charge-bond order matrix[4]. Although changes in these NMR-sensitive parameters with substitution are complex and difficult to predict, it is reasonable to expect them to be at least partially reflected in altered electron density at silicon. In view of this, CNDO/2 calculations[*] of total, σ and π electron density were performed for the series of phenyltrifluorosilanes. Of the various calculations, total density exhibited the best correlation ($r = 0.938$) with the silicon chemical shifts. This correlation demonstrates that the response of the silicon resonance in I to an increase in electron density is indeed a shift to lower field. The relatively poor correlation of the CNDO-computed π densities with chemical shifts ($r = 0.777$) suggests that back-bonding of fluorine p-electrons into the d-orbitals of silicon is not the dominant mechanism for the upfield shift produced by electron -attracting groups in the phenyltrifluorosilanes.

The differing signs of the silicon chemical shift dependence on Hammett σ for silanes I and II demonstrate that large changes in electron density at silicon need not necessarily consist of unidirectional changes in the silicon chemical shift. This conclusion is in agreement with the results found in several series of $(CH_3)_{4-n}SiX_n$ silanes where X = Cl, F, OCH_3, OEt, OAc[5]. These silanes exhibited shifts to lower field with the introduction of the first electronegative group on tetramethylsilane while subsequent substitution thereafter produced shifts to higher field.

Thus, the response of silicon chemical shifts to changes in electron density at silicon is not always a shift to either higher or lower fields but varies depending on the nature of the substituents bonded to silicon. This deviation in the relationship between chemical shifts and electron density indicates the caution one should exercise before using silicon chemical shift data for structural and bonding probes even for apparently closely related compounds. Normally, nuclei containing the more electronegative elements are expected to possess resonances appearing at lower fields. The application of such rationale to silicon NMR could lead to error in chemical shift assignments and thus chemical interpretations.

There appears to be a parallelism between this chemical shift behavior of silicon and reported theoretical and experimental ^{31}P chemical shifts[6]. Both positive and negative correlations were predicted for ^{31}P chemical shifts with changes in electronegativity of the attached groups. We are presently attempting to apply the theoretical considerations of Letcher and Van Wazer[6] to the silicon data. An extension of this investigation to other silanes of the general formula $XC_6H_4SiY_3$ for Y's of varying electronegativity is currently in progress. A complete report of this work will be forthcoming.

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