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Preliminary communication

SUBSTITUENT EFFECTS IN ^{29}Si NMR OF RING-SUBSTITUTED PHENOXY- AND PHENYL-SILANES. ENHANCEMENT BY THE OXYGEN LINK

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Summary

^{29}Si NMR chemical shifts in a series of *para*- and *meta*-substituted phenoxytrimethylsilanes are twice as sensitive to benzene ring substitution as the shifts in corresponding phenyltrimethylsilanes in which the silicon atom is one bond closer to the substituent.

A recent observation [1] that an oxygen link increases the sensitivity of the silicon shielding to the nature of the substituent was based on a rough comparison of two incomplete series of compounds, namely of the types $(\text{CH}_3)_3\text{SiOR}$ and $(\text{CH}_3)_3\text{SiR}$. Since such an enhancement cannot be readily accounted for by current theories [2–5] it seemed desirable to evaluate the enhancement quantitatively so that new, more refined, theories could be tested. A comparison of the Hammett dependence of silicon-29 chemical shifts in $(\text{CH}_3)_3\text{Si}-\text{C}_6\text{H}_4-\text{X}$ series of compounds (which were studied by Spialter's group [3, 6]) with that in $(\text{CH}_3)_3\text{Si}-\text{O}-\text{C}_6\text{H}_4-\text{X}$ offers a possibility of such a quantitative evaluation. The preliminary results of such an investigation are now presented, the full account of the work which includes also *ortho* derivatives and ^{13}C NMR studies will be published later.

The silicon chemical shifts in substituted phenoxytrimethylsilanes (Table 1) show a linear correlation with Hammett σ constants of the substituents X (values taken from ref. 7). The data fit the correlation line (Fig. 1) less satisfactorily than in the case of substituted phenyltrimethylsilanes [3, 6], but this can be understood since solvent effects must be more important in the compounds containing the Si—O bond. The points corresponding to *para*- and *meta*-amino derivatives (crossed circles in Fig. 1) were not included in the correlation since in these

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TABLE 1

²⁹Si CHEMICAL SHIFTS OF SUBSTITUTED PHENOXYTRIMETHYLSILANES XC₆H₄OSi(CH₃)₃^a

Substituent X	<i>meta</i>	<i>para</i>
H	17.72 ^b	17.72 ^b
F	—	18.88
Cl	20.00	19.73
Br	19.76	19.49
I	—	19.08
CH ₃	17.30	17.29
OCH ₃	18.01	17.73
NH ₂ ^c	17.90	17.40
NO ₂	21.61	22.11

^aChemical shifts in δ -scale (ppm), measured relative to internal hexamethyldisiloxane the shift of which was taken as $\delta = 6.66$ ppm. Fluoro and iodo derivatives were measured in 50% CCl₄ solutions, all others as neat liquids. The spectra were measured using gated proton decoupling in FT mode on a JEOL-PS-100/PFT-100 at 19.9 MHz, estimated accuracy ± 0.10 ppm. ^bValue in ref. 1 in error. ^cThe data excluded from the correlation in Fig. 1.

compounds some intermolecular interactions are occurring as shown by the IR spectra [8]. Despite this, it is readily apparent from Fig. 1 that the slope of the Hammett dependence is about twice as large in phenoxy than in phenyl compounds (though in the latter series of compounds the silicon atom is one bond closer to the substituent). The observed trends in the two series of silanes are in accord with theories [2–5] of the silicon shielding, but the twofold enhancement of substituent effects by the oxygen link cannot be explained by the electronegativity of the substituent, and so a refinement of the existing theories, which would also explain the observed enhancement, must be sought.

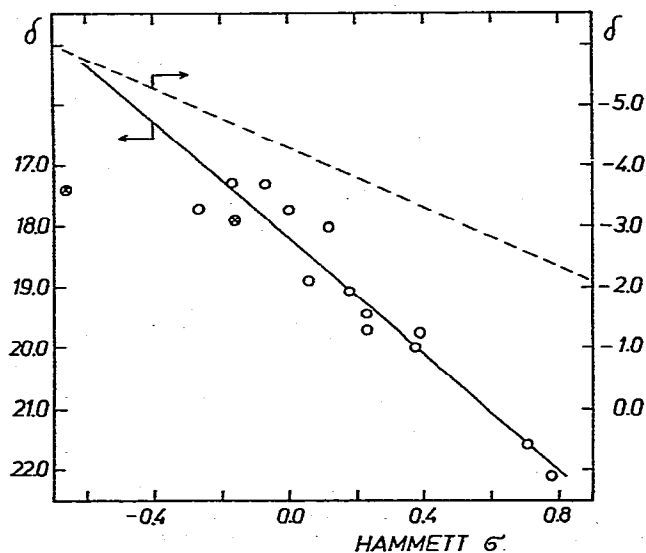


Fig. 1. Plots of ²⁹Si chemical shifts of substituted phenyltrimethylsilanes [3, 6] (dashed line, correlation coefficient $r = 0.991$) and phenoxytrimethylsilanes (solid line, $r = 0.958$, crossed circles excluded) vs. Hammett σ [7].

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