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NMR STUDY OF ORGANOSILICON COMPOUNDS

X *. THE TRANSMISSION OF SUBSTITUENT EFFECTS IN PHENOXYSILANES AS STUDIED BY ^{29}Si AND ^{13}C NMR **

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Summary

^{29}Si and ^{13}C NMR chemical shifts for a series of *meta* and *para* substituted phenoxytrimethylsilanes are given and compared with those in phenyltrimethylsilanes using the formal single and dual substituent parameter analysis of substituent effects.

The silicon chemical shift is found to be about twice as sensitive to substituent effects in phenoxytrimethylsilanes as in phenyltrimethylsilanes. The chemical shift sensitivity to substituent effects, ρ, is considered to be a product of two factors, ρ^{el} and ρ^{shield}, which describe the sensitivity of the electron density to substituent effects and the sensitivity of the shielding to the electron density, respectively.

Using ^{13}C chemical shifts and CNDO/2 net atomic charges, it is shown that the substituent effects propagate within the X—C_6H_4 fragment of phenoxysilanes no better than in phenylsilanes. The ^{13}C chemical shifts of the terminal methyl groups are affected by the substituents in the former series of com-

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* For part IX see ref. 1.

** Dedicated to Professor Eugene G. Rochow on the occasion of his 70th birthday on October 4, 1979.

pounds much less than in the latter. An increase in the relative basicity of oxygen is accompanied by an increase in silicon shielding in phenoxytrimethylsilanes.

According to CNDO/2 calculations, the substituents cause larger changes in net atomic charges on the silicon atom if it is bonded directly to the benzene ring rather than via the oxygen bridge. In spite of the fact that the possibility of a dative O → Si interaction, not reflected by the CNDO/2 calculations, cannot be completely excluded, the results indicate that the increased silicon shift sensitivity to substituent effects in phenoxysilanes is due to higher sensitivity of silicon shielding (ρ^{shield}) to electron density in these compounds rather than to a better transmission of electronic effects (ρ^{el}). The existing theory of silicon shielding must be improved or refined if it has to accommodate the increased sensitivity in the phenoxysilanes.

Introduction

In their extensive work, Scholl et al. [2] briefly mentioned that the ^{29}Si resonances of phenyl-substituted phenoxytrimethylsilanes span a somewhat wider range of shifts than the corresponding phenylsilanes. This observation, being apparently hidden by the bulk of other data, has remained unnoticed and in 1976 two independent research groups undertook detailed studies of the NMR spectra of substituted phenoxytrimethylsilanes. After publishing preliminary reports of their work [3,4], the two groups have joined their efforts and the present paper gives the full account of their results on *meta* and *para* substituted phenoxysilanes; the results on the *ortho* isomers will be published shortly.

The studies of NMR spectra of phenoxytrimethylsilanes were undertaken with the aim to provide a quantitative evaluation of the reported [5] greater sensitivity of the silicon shielding to substituent effects if these are transmitted through the C—O—Si link rather than through the C—Si bond. A quantitative comparison was needed since the sensitivity enhancement could not be readily accounted for by the theories of silicon shielding [6—9]. In view of the considerable success of the theory [10] in explaining Hammett-type dependences of silicon shielding in compounds of the structure $X_3Si—C_6H_4—Y$ [2,7], we have chosen the phenoxytrimethylsilanes as model compounds for the quantitative comparison.

The experimental results can be treated by the now standard phenomenological analysis of substituent effect—property relationships, i.e., either by single or by dual substituent parameter correlations [11,12]. The analysis leads to the description of the observed effects in terms of overall enhanced transmission of substituent effects of one or another type, depending on the model employed. However, such a phenomenological description cannot explain the more fundamental question, whether the observed increase of silicon shift sensitivity is due to a better transmission of the substituent effects of the substituent X through the $X—C_6H_4—O$ chain to the silicon atom or whether it is due to an intrinsically higher sensitivity of the silicon sheilding in phenoxy- than in phenyl-silanes.

Even in the most simplifying approximations, it is necessary to consider the overall chemical shift sensitivity to substituent effect, ρ (as obtained by the regression analysis), to be a product of two factors

$$\rho = \rho^{el}\rho^{shield} \qquad (1)$$

ρ^{el} describes the sensitivity of the electronic density at a given atom to substituent effects in the given molecular system. It is this factor which the various models of substituent effect transmission mechanisms attempt to explain. ρ^{shield} describes what we might call the intrinsic sensitivity of that given atom's nucleus shielding to the electron density around it; this factor, which may be also affected by inductive and resonance effects, is the concern of the shielding theory. The theories of silicon shielding show [6—10] that ρ^{shield} is not a monotonous function of the total electron density on the silicon atom. In the usual interpretation of substituent effects in NMR it is tacitly assumed that ρ^{shield} is constant and the changes in ρ are identified with the changes in ρ^{el}. Although this assumption may be true within one series of compounds, it is not necessarily so when two series of compounds are compared. While the assumption might be safe for the series differing in places sufficiently remote from the site of the detector (e.g., in the systems $X—C_6H_4—Z—C_6H_4—F$ in which the ^{19}F nucleus is far away from the bridge Z), it is definitely not so if the variable group Z is directly connected with the detector site (D). In systems of the type $X \cdots D—Z$ the substituents Z change the local excitation energy [13] or the total charge [7,10] of the atom to which they are attached and hence the shielding of the detector D shows different sensitivity to the effects of substituents X.

The situation is more complex if the substituent effect is transmitted through the different bridge groups Z directly bonded to the detector, $X—C_6H_4—Z—D$, as in our case. Then, the bridge not only changes ρ^{shield} by changing the local excitation energy, and by other mechanisms, but it also affects the value of ρ^{el}.

We will try to separate the contributions of these two factors by examining the electron density changes as monitored by ^{13}C NMR chemical shifts and as calculated by the CNDO/2 method for model compounds. In order to gain some deeper insight into this problem we have also studied IR spectra and basicity [14,15] of phenoxytrimethylsilanes and NMR spectra of closely related compounds of the structure $(CH_3)_3SiNHC_6H_4X$ [16—18], $(CH_3)_3SiSC_6H_4X$ [17,18], and $(CH_3)_2HSiOC_6H_4X$ [17,19].

Experimental

Compounds

Preparation, IR spectra and other physical properties of the studied compounds are given in refs. 15 and 19.

Spectral measurements

^{29}Si NMR spectra (Table 1) were measured using neat samples to which a drop of hexamethyldisiloxane was added. Only the samples of bis(trimethylsiloxy)benzenes and *p*-fluoro- and *p*-iodophenoxytrimethylsilanes were measured

TABLE 1

^{29}Si CHEMICAL SHIFTS IN SUBSTITUTED PHENOXYTRIMETHYLSILANES $X—C_6H_4—OSi(CH_3)_3$ [a]

Substituent X	*meta*	*para*	Substituent X	*meta*	*para*
H	17.72	17.72	CH_3	17.30	17.29
F		18.88 [b]	OCH_3	18.01	17.73
Cl	20.00	19.73	NH_2	17.90	17.40
Br	19.76	19.49	NO_2	21.61	22.11
I		19.08 [b]	$OSi(CH_3)_3$	17.87	17.25 [b]

[a] Chemical shifts in δ-scale, direct ^{29}Si NMR measurements in neat liquids unless otherwise noted, precision ± 0.02 ppm. [b] Measured in 50% CCl_4 solution.

as 50% CCl_4 solutions, again with a drop of hexamethyldisiloxane, the line of which served as an internal reference with $\delta(^{29}Si)$ 6.66 ppm. The spectra were measured on a JEOL-PFT-100 spectrometer at 19.87 MHz using gated proton decoupling.

The individual chemical shifts determined by $^1H—\{^{29}Si\}$ INDOR measurements [20] in 30% carbon tetrachloride solutions differ slightly [4] from the results of direct measurements. Since the direct measurements were performed on a more complete series of compounds and since the differences had no effect on the discussed trends, the INDOR data [4] are not repeated here.

^{13}C NMR (proton noise decoupled) spectra (Table 2) were measured in 10% solutions in CCl_4; the line of the solvent (δ 97.00 ppm) served as internal reference. The JEOL-PFT-100 spectrometer operated at the frequency of 25.15 MHz (lock C_6D_6 in a capillary, FT mode with 8 K used for FID accumulation of 200—500 scans of 5 kHz sweep width).

Phenoxytrimethylsilane. All the lines in the proton noise decoupled spectrum were assigned on the basis of a single resonance and off-resonance double resonance spectra assuming that the $^3J(^{13}C—^1H)$ coupling constants are larger than the $^2J(^{13}C—^1H)$ constants. The following $^{13}C—^1H$ coupling constants were determined for C(2), C(3), and C(4) carbons, $^1J(C(2))$ 159.0 Hz, $^3J(C(2))$ 4.8 Hz and $^3J(C(2))$ 7.6 Hz (the two couplings with protons on C(6) and C(4) could not be assigned), $^1J(C(3))$ 158.9 Hz, $^3J(C(3))$ 8.9 Hz, $^1J(C(4))$ 161.2 Hz and $^3J(C(4))$ 7.4 Hz.

Bis(trimethylsiloxy)benzenes. Molecular symmetry and proton—carbon NOE enhancement considerations allowed unambiguous assignment of all carbon lines on their intensity grounds except for C(2) and C(5) in the *meta* isomer which could be assigned according to the additivity rule.

Substituted phenoxytrimethylsilanes. The lines of substituted and unsubstituted carbons could be differentiated according to their intensity. Since the chemical shifts calculated according to the additivity rule differed markedly for different carbon atoms, the remaining assignment on this basis was unambiguous and no other NMR experiments were necessary.

Application of the additivity rule. The aromatic carbon chemical shifts were calculated from the corresponding carbon chemical shift in phenoxytrimethylsilane to which the appropriate substituent chemical shift (SCS) value [21] was

TABLE 2

^{13}C CHEMICAL SHIFTS IN PHENOXYTRIMETHYLSILANES $(CH_3)_3SiOC_6H_4X$ [a]

Substituent X	$SiCH_3$ δ	C(1)		C(2)		C(3)		C(4)		C(5)		C(6)	
		δ	Δ	δ	Δ	δ	Δ	δ	Δ	δ	Δ	δ	Δ
H	0.26	154.81	—	119.56	—	129.03	—	121.07	—	129.03	—	119.67	—
4-CH_3 [b]	0.17	152.57	0.63	119.47	−0.10	129.52	−0.21	129.71	−0.26	129.52	−0.21	119.47	−0.10
4-NH_2	0.22	147.04	2.03	120.20	−0.37	115.67	−0.04	140.29	1.22	115.69	−0.04	120.20	−0.37
4-Br	0.12	153.88	0.67	121.46	0.13	132.14	−0.29	113.79	−1.78	132.14	−0.29	121.46	0.13
4-Cl	0.12	153.30	0.39	120.88	−0.09	129.13	−0.29	126.46	−0.81	129.13	−0.30	120.88	−0.09
4-OCH_3 [c]	0.12	148.40	1.28	120.15	−0.52	114.18	−0.45	153.98	1.51	114.18	−0.45	120.15	−0.52
4-NO_2	0.02	160.58	−0.03	119.57	−1.00	125.39	1.16	141.94	0.87	125.39	1.16	119.57	−1.00
4-$OSiMe_3$	0.11	149.31	1.33	120.48	−0.32	120.48	−0.32	149.31	1.31	120.48	−0.32	120.48	−0.32
3-CH_3 [d]	0.26	154.76	0.05	120.49	0.12	138.50	0.57	121.95	0.18	128.79	−0.14	116.70	−0.07
3-NH_2	0.26	155.73	0.02	106.56	0.19	147.43	0.40	108.26	0.49	129.52	−0.41	109.67	−0.20
3-Br	0.17	155.73	−0.78	123.21	0.14	122.43	−1.10	124.37	−0.10	130.05	−0.68	118.31	0.24
3-Cl	0.12	155.53	−0.58	120.30	0.23	134.52	−0.71	121.56	0.09	129.71	−0.62	117.87	0.10
3-OCH_3 [e]	0.17	155.92	0.11	105.98	0.71	160.44	0.01	106.71	0.04	129.23	−0.80	111.95	−0.02
3-NO_2	0.02	155.63	−0.08	114.52	−0.35	149.08	0.05	116.02	−0.20	129.47	−0.46	125.64	0.17
3-$OSiMe_3$	0.16	156.11	0.17	112.18	0.74	156.11	0.17	113.45	0.61	129.56	−0.60	113.45	0.61

[a] All the chemical shifts are in δ scale (ppm units, relative to TMS, positive values for paramagnetic shifts). Numbering of aryl carbon atoms starts on the carbon atom bearing the trimethylsiloxygroup. Δ values are defined as $\Delta = \delta_{exp} - \delta_{calc.}$, where δ_{exp} are the values given in the table and δ_{calc} are the shifts calculated according to the direct additivity rule. [b] $\delta(CH_3) = 20.46$. [c] $\delta(CH_3) = 57.77$. [d] $\delta(CH_3) = 21.28$. [e] $\delta(CH_3) = 54.38$.

TABLE 3

CARBON-13 SUBSTITUENT CHEMICAL SHIFTS (^{13}C SCS) FOR SUBSTITUTED BENZENES

^{13}C SCS	Substituent						
	$(H_3C)_3SiO-$ [a]	$(H_3C)_3CO-$ [b]	H_3CO- [c]	$HO-$ [c]	$(H_3C)_3SiNH-$ [d]	$(H_3C)_3Si-$ [e]	$(H_3C)_3C-$ [f]
ipso	26.9	27.4	31.5	26.8	20.5	11.1	21.9
ortho	−8.2	−4.1	−14.2	−12.7	−11.3	4.4	−3.7
meta	1.1	0.6	1.2	1.6	1.6	−1.0	−0.6
para	−6.8	−5.0	−7.6	−7.1	−10.4	0.0	−3.3

[a] Present results. [b] Data from ref. 22 are within ± 0.2 ppm of the results in ref. 23, except for *ipso*-SCS for which ref. 23 gives the value of 24.7 ppm. [c] Present results in agreement with ref. 21. [d] From ref. 17. [e] From ref. 24. [f] From ref. 25.

added. The SCS values of the trimethylsiloxy group (Table 3) were calculated from the chemical shifts in phenoxytrimethylsilane and benzene ($\delta(C_6H_4)$ 127.90 ppm)

CNDO/2 calculations

In order to reduce the excessive computer time, CNDO/2 calculations were performed for a few model *meta* and *para* substituted phenylsilanes ($XC_6H_4SiH_3$) and phenoxysilanes ($XC_6H_4OSiH_3$) using the standard CNDO/2 method [26]. The overlap integrals of the π type were reduced in the sense of DelBene and Jaffé parametrization [27] using the factor $\kappa = 0.58$. The Si—O, Si—H, and S—Cl bond lengths were taken from experiments [28—30]. Calculations were performed with standard idealised geometries [26] for two conformers: conformer I had the C—O—Si plane perpendicular to the ring plane and conformer II had the silicon atom in the plane of the benzene ring. To estimate the possible role of silicon *d* orbitals, the calculations were carried out both with their neglect and with their inclusion.

Results and discussion

^{29}Si chemical shifts: substituent effect analysis

The ^{29}Si chemical shifts (Table 1) in *meta* and *para* substituted phenoxytrimethylsilanes fit the same linear correlation with Hammett σ constants. The results of regression analysis of silicon chemical shifts for a few classes of similar compounds are summarized in Table 4.

If we leave for later discussion the fact that the slopes of the correlations are related to the intercepts, the most striking result of the regression analysis is that the sensitivity of the silicon shielding to substitution of the benzene ring is increased if a bridge atom (O or S) or group (NH) is interposed between the ring and the silicon atom (for the graphs see ref. 3) and that substituent effects practically do not depend on the relative position (*meta* or *para*) of the substituent (Fig. 1). The first of these observations bears on one side a formal resemblance to the "positive bridge effect" (PBE) studied initially by chemical meth-

TABLE 4

^{29}Si CHEMICAL SHIFT LINEAR REGRESSION ANALYSIS IN $XC_6H_4ZSi(CH_3)_3$ [a]

Bridge group Z	δ_0	ρ	$\pm\Delta\rho$ [b]	s [c]	r [d]	n [e]
O [f]	18.19	4.77	0.94	0.46	0.959	13 [g]
O [h]	18.32	4.93	0.85	0.35	0.978	10
S [i]	16.47	3.64	0.88	0.29	0.922	5
NH [j]	2.26	3.37	0.49	0.54	0.981	12
— [k]	—4.30	2.72	0.32	0.14	0.991	8

[a] Parameters of the equation $\delta = \delta_0 + \rho\sigma$, values for σ from ref. 31. [b] 95% confidence limit for the slope. [c] Root-mean-square deviation. [d] Correlation coefficient. [e] Number of the data points. [f] Present data for neat liquids. [g] Amino derivatives excluded from the correlation, see ref. 3, bis(trimethylsiloxy)benzenes also excluded. [h] In CCl_4 solutions, ref. 4. [i] From refs. 17,18. [j] From ref. 16. [k] No bridge group in phenyltrimethylsilanes, data from ref. 2.

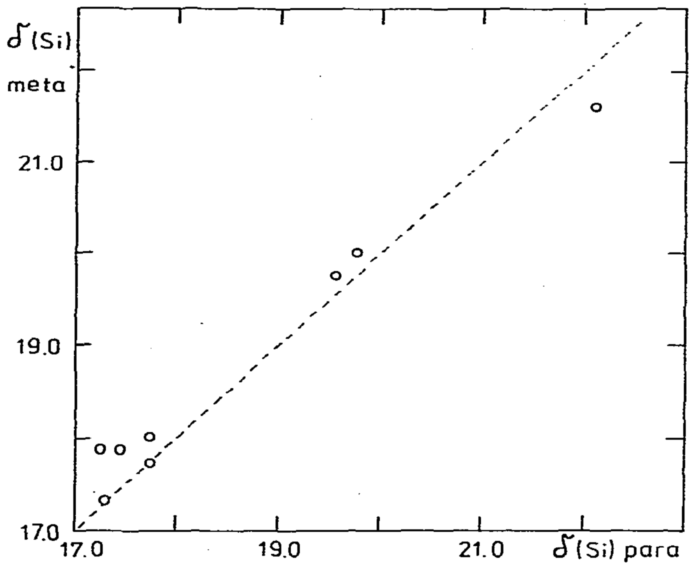


Fig. 1. Plot of ^{29}Si chemical shifts, δ(Si), in *meta* versus in *para* substituted phenoxytrimethylsilanes (the dashed line corresponds to $\delta(^{29}\mathrm{Si})_{meta} = \delta(^{29}\mathrm{Si})_{para}$).

ods by Litvinenko (for a review see ref. 32), and, on the other, it reminds one of "superconductivity" [33] and other surprising (e.g., "reversed") substituent effects in the NMR of aromatic side-chains [34—38].

It has become customary to treat these effects by the dual substituent parameter analysis (DSP) [12]. For the sake of completeness, the results of such an analysis are summarized in Table 5. (Analogous analysis in terms of Swain—Lupton [39] $\mathcal{F}$ and $\mathcal{R}$ values gives a worse fit.) The results can be

TABLE 5

DSP REGRESSION ANALYSIS OF CHEMICAL SHIFTS OF M(^{29}Si AND ^{13}C) IN COMPOUNDS OF THE TYPE 1,4-$XC_6H_2ZM(CH_3)_3$ [a]

M	Z	σ_R scale [b]	δ_0	ρ_I	ρ_R	ρ_I/ρ_R	s [c]	r [d]
Si	O	σ_R^0	18.23	5.04	4.92	1.02	0.25	0.991
		σ_R	18.16	5.17	4.15	1.25	0.31	0.986
		σ_R^-	18.10	4.38	2.88	1.52	0.18	0.995
	S [e]	σ_R^0	16.57	2.72	2.44	1.11	0.04	0.999
	NH [f]	σ_R^0	2.19	3.76	3.86	0.97	0.13	0.997
		σ_R^-	2.12	2.99	2.77	1.08	0.08	0.999
	— [g]	σ_R^0	4.45	2.52	2.40	1.05	0.06	0.998
		σ_R	4.48	2.60	1.88	1.38	0.05	0.999
		σ_R^-	4.46	3.51	2.03	1.73	0.07	0.998
C	— [g]	σ_R^0	34.4	0.67	1.76	0.38	0.09	0.989

[a] Parameters of the equation $\delta = \delta_0 + \rho_I\sigma_I + \rho_R\sigma_R$. [b] From ref. 12. [c] Root-mean-square deviation. [d] Multiple correlation coefficient. [e] From refs. 17,18. [f] From ref. 16. [g] From ref. 25, no bridge atom Z.

straightforwardly interpreted in the usual way [12], but one should keep in mind that the substituents available do not form a complete minimum substituent basis set [12] and that the intercept was taken as an adjustable parameter. The analysis shows that the relative importance of the inductive effect (ρ_I/ρ_R) depends on the σ_R scale used and that the main difference between the phenyltrimethylsilanes (siliconshift) and their carbon analogues (carbonshift) lies in the larger role of the inductive effect in the former.

The literature on substituent effects in NMR spectra of aromatic side chains has been partially reviewed (^{1}H [40], ^{13}C [34], and other nuclei [35]) without much success in finding a generally acceptable interpretation. Only the very recent interpretation of Inamoto and Masuda [36] by a combination of conjugative, homoconjugative, and hyperconjugative interactions seems to have a wider applicability. In the systems with α-heteroatoms having lone pair electrons the balance between two competing mechanisms [36] is determined by the electronegativity of the bridge atom Z [36]. Although the sensitivity of the silicon shielding seems to be related to the electronegativity of Z, the approach of Inamoto and Masuda [36] predicts a change in the sign of the slope when going from Z = O to Z = N or S which is not observed in the trimethylsilyl derivatives.

The approach of Inamoto and Masuda is very similar to the interpretation of PBE [11,32]. The PBE takes place if the bridge Z conjugates either with the substituent X or with the detector D or with both.

Conjugation of oxygen with the substituent X can be fully disregarded as a possible mechanism of sensitivity enhancement since it is incompatible with the observed independence of the silicon shielding sensitivity on temperature (described later). It has been also shown [4,5], that a similar enhanced sensitivity is observed in alkoxytrimethylsilanes, in which such a conjugation is unlikely. The shifts in these two classes of $ROSi(CH_3)_3$ compounds show the same sensitivity to σ^* constants ($\delta(^{29}Si) = \delta_0 + 4.66\ \sigma^*$), which fact demonstrates that the silicon shielding in $ROSiMe_3$ compounds is controlled by the inductive effects of the substituents R, but it does not explain the enhanced sensitivity of the silicon in these compounds. The possibility of inductively controlled bridge atom conjugation with the detector (silicon) also cannot be ruled out. The possibility of $(p{-}d)\pi$ bonding or $\sigma{-}\sigma^*$, $n{-}\sigma^*$, $\pi{-}\sigma^*$, etc., interactions have been frequently discussed in the literature [41—45], and the order of the silicon shift sensitivity in compounds with different atoms Z roughly corresponds to the order with which these atoms are supposed to be active in such interactions owing to energy and size matching. In accord with such an interpretation, no enhancement of substituent effect transmission by oxygen was noticed in ^{13}C shifts of t-butyl phenyl ethers [22] and sulphur has no insulating effect on ^{119}Sn shifts in $XC_6H_4SSn(CH_3)_3$ compounds [46].

Before attempting to disect the ρ observed into ρ^{shield} and ρ^{el} parts, let us examine what are the possible contributions to ρ^{shield}. The silicon shielding constant σ^A may be written as (for references to the original literature and definitions see ref. 47):

$$\sigma^A = \sigma_d^{AA} + \sigma_p^{AA} + \sum_{B \neq A} \sigma^{AB} + \sigma^{A,\text{ring}} \qquad (2)$$

Substituent-induced changes in the shielding contribution $\sigma^{\mathrm{A,ring}}$ from the ring current can be calculated [48] according to the formula derived by Yamada et al. [49]:

$$\sigma^{\mathrm{A,ring}} = 0.4 f(\rho, z)\sigma_{\pi} \tag{3}$$

Since the Johnson—Bovey [50] ring-current parameter $f(\rho, z)$ is 0.32 in phenylsilanes, 0.12 and 0.18 in conformers I and II of phenoxysilanes and since the Yukawa—Tsuno [51] constants σ_{π} are also less than unity, this contribution to the shielding sensitivity can be neglected.

The paramagnetic part of the neighbour anisotropy $\sigma_{\mathrm{p}}^{\mathrm{AB}}$ is constant for a series of substituted compounds [48], the diamagnetic part, $\sigma_{\mathrm{d}}^{\mathrm{AB}}$, is related to the charges on the neighbouring atoms. The diamagnetic term $\sigma_{\mathrm{d}}^{\mathrm{AA}}$ gives a linear correlation with charge density [52]. The changes in net atomic charges will be estimated in the further discussion.

The quantitative theories [6—10] of silicon shielding give specific forms for the paramagnetic contribution which has the general form

$$\sigma_{\mathrm{p}}^{\mathrm{AA}} = -\frac{K}{\Delta E_{\mathrm{av}}}\{\langle r_{\mathrm{p}}^{-3}\rangle P^{\mathrm{A}} + \langle r_{\mathrm{d}}^{3}\rangle D^{\mathrm{A}}\} \tag{4}$$

According to the silicon shielding theory [6—10], the shielding is dominated by the first term in eqn. 4 ($\langle r_{\mathrm{p}}^{-3}\rangle P^{\mathrm{A}}/\Delta E_{\mathrm{av}}$). Since the observed effects are small, the other contributions ($\sigma_{\mathrm{d}}^{\mathrm{AB}}$, $\sigma_{\mathrm{d}}^{\mathrm{AA}}$, and $\langle r_{\mathrm{d}}^{-3}\rangle D^{\mathrm{A}}/\Delta E_{\mathrm{av}}$) might be equally important causes of the difference between ρ^{shield} in phenyl- and phenoxy-silanes.

Steric interaction has not been explicitly expressed in the above equation but it could cause considerable shifts in the compounds studied. Although some authors assume free rotation around the C—O bond in substituted phenoxytrimethylsilanes [53], others [54] assume only conformer I to be present in solutions and conformational heterogeneity had to be invoked in order to explain certain features of the IR spectra [14]. We have, therefore, measured the temperature dependence of the silicon chemical shifts in three *para* substituted phenoxytrimethylsilanes (Fig. 2, lines 1, 2, and 3). Increasing temperature brings about an increasing population of conformer II in which steric 1—4 interaction with γ-CH (C(2) and C(6)) leads to upfield ^{29}Si shifts [55]. (In 2,6-substituted phenoxytrimethylsilanes (line 4), in which the steric crowding is especially accute, the interaction is of δ or ε type, which was reported to lead in some cases to downfield ^{13}C shifts [56].) The shielding increases in these compounds with increasing temperature; the sensitivity of silicon shielding to substitution is not affected by temperature nor by steric effects.

^{13}C *NMR spectra*

Aryl carbons. Although some deviations will be discussed later, the chemical shifts in disubstituted benzenes (Table 2) confirm the validity of the derived substituent chemical shift (SCS) values as well as the general applicability of the additivity rule.

A comparison with the SCS values of other groups (Table 3) reveals that all the OR substitutents have essentially the same effect on the shielding of *para* and *meta* carbons; the *ortho* effects of all these groups are different, and, surprisingly, the effects of $OSi(CH_3)_3$ and OH groups on the shielding of the sub-

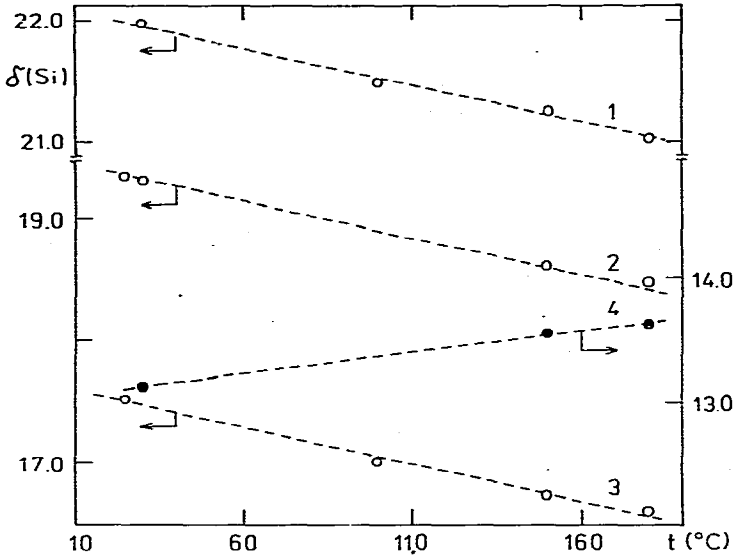


Fig. 2. Temperature dependence of ^{29}Si chemical shifts, δ(Si), in *p*-nitrophenoxytrimethylsilane (line 1), *p*-chlorophenoxytrimethylsilane (line 2), *p*-methylphenoxytrimethylsilane (line 3), and 2,6-di-t-butylphenoxytrimethylsilane (line 4).

stituted carbon (C(1)) are the same. The similarity of the substituent effects of these two groups on steroid [57] and adamantane [58] skeleton carbons has been recognized before. The presence of benzene π electrons or/and larger carbon *s* character in the C—O bond makes the SCS of the two groups closer than are their α effects in saturated fragments [58]. In contrast, the shifts sensitive to steric effects differ more in benzene derivatives (*ortho* SCS) than in saturated skeletons (γ effects).

The shifts in monosubstituted benzenes have been related to various physical quantities [21,52,59]. Since Smith and Deavenport [60,61] have shown that the "*Q*" parameter [62] does not affect the shift of the *para* carbon and that the effect on the *meta* carbon is only very small, the SCS values indicate that all the oxygeneous groups of Table 3 have approximately the same values of $\mathcal{F}$ and $\mathcal{R}$ constants (or of any other pair; e.g., correlations of ref. 63 give for all these groups $\sigma_I = 0.05 \pm 0.07$ and $\sigma_R = -0.55 \pm 0.06$). The quality of chemical shift versus reactivity parameter correlations is, however, not such as to allow detailed discussions of small differences in the SCS values.

Para-substituted phenoxytrimethylsilanes. The chemical shifts of C(2) and C(3) aryl carbons follow the additivity rule quite well (except in the nitro derivative), they correlate linearly with the corresponding chemical shifts in substituted phenyltrimethylsilanes [25], the correlations have unit slopes (0.95 and 1.04 and correlation coefficients 0.848 and 1.000, respectively), indicating identical transmission of substitutent effects to C(2) and C(3) in both series of compounds. The slope in an analogous correlation for C(1) (0.71) suggests less effective transmission to this carbon in phenoxysilanes (!). This observation, which seemingly contradicts the results of ^{29}Si NMR, deserves detailed discussion.

Approximate linear correlations of the chemical shifts with σ^+ constants of the substituent X in the *para* position (on C(4)) were noted [64—66] for the C(1) ring carbons bearing the substituent Y. The present results for the C(1) carbon shifts exhibit a similar approximate linear dependence on the σ^+ constants (Fig. 3). The fit can usually be improved if the DSP treatment (with inclusion of an adjustable intercept) is used (use of $\mathcal{F}$ and $\mathcal{R}$ constants does not improve the correlation, $r = 0.926$), but the improvement is hardly sufficient to justify the introduction of one more parameter. Nevertheless, for the purpose of comparison of substituent effect transmission, Table 6 summarizes also the results of the DSP analysis for some closely related systems [37,38,65—67].

As the data in Table 6 indicate (irrespective of the ρ values compared), the overall sensitivity of the C(1) carbon chemical shift to the *para* substituent in phenoxytrimethylsilanes is slightly larger than it is in substituted anisoles, but it is lower than in monosubstituted benzenes, ethylbenzenes and phenyltrimethylsilanes.

Following the reasoning of Bromilow et al. [67], the σ-donating ability of the $Si(CH_3)_3$ group enhances π-inductive effects of the *para* substituents and, in contrast, the $OSi(CH_3)_3$ group with its σ-accepting properties reduces the π-inductive effects (though not as much as does the OCH_3 group). In agreement with this interpretation we observe larger deviations from additivity in C(4) than in C(1) carbon shifts but the large deviations in the cases of X = $OSi(CH_3)_3$ and NH_2 cannot be explained in this way. Obviously, this interpretation suffers from the mentioned inadequacy of assuming the same ρ^{shield} for the carbons bearing different substituents.

The deviations are, however, consistent with the interpretation of non-additive behaviour offered by Lynch [13]. According to the proportionality rela-

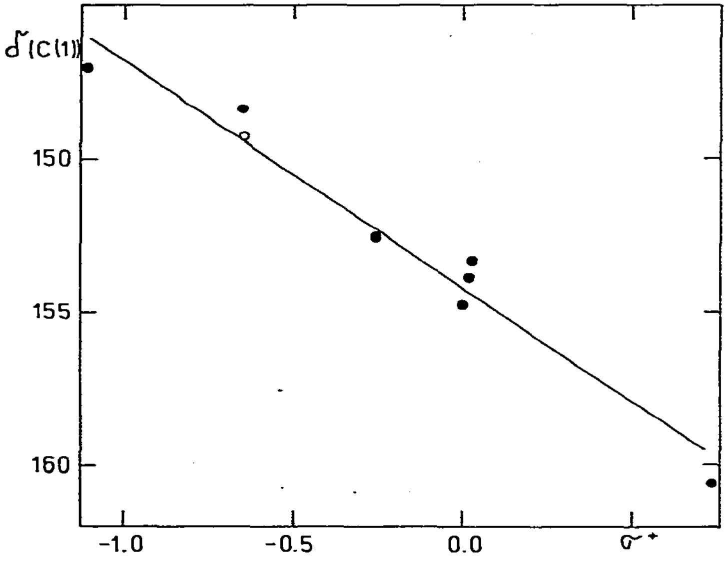
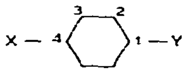


Fig. 3. Plot of ^{13}C chemical shift of C(1) aryl carbon in *para* substituted phenoxytrimethylsilanes versus σ^+ constant of the *para* substituent X [39] (the solid line is a least-square fit of the full points, for parameters see Table 6; the open point corresponds to X = $OSi(CH_3)_3$).

TABLE 6

REGRESSION COEFFICIENTS IN C(1) CARBON CHEMICAL SHIFTS CORRELATIONS $\delta(C(1)) = \delta_0 + \rho_+\sigma^+$ AND $\delta(C(1)) = \delta_0 + \rho_I\sigma_I + \rho_R\sigma_R^0$ IN SOME SERIES OF COMPOUNDS OF THE TYPE 1,4-XC_6H_4Y [a]

Fixed substituent Y	Source [b]	ρ_+	r [c]	ρ_I	ρ_R	r [c] (f) [d]
OCH_3	67	6.40	0.975	3.56 [e]	15.00 [e]	(0.10) [e]
$OSi(CH_3)_3$	[f]	7.42	0.978	5.24	17.13	0.998
NH_2	67	7.45	0.975	4.70 [e]	16.94 [e]	(0.08) [e]
$NHSi(CH_3)_3$	17	10.23	0.987	7.33	19.40	0.988
H	64	8.51	0.979	4.73 [e]	20.98	(0.10) [e,g]
C_2H_5	37	10.25	0.985	6.95 [e]	22.50 [e]	(0.17) [e]
$Si(CH_3)_3$	25	11.81	0.901	9.58	28.05	0.991
$C(CH_3)_3$	25	10.97	0.988	7.58	22.04	0.999

[a] Chemical shift $\delta(C(1))$ of C(1) in  values of σ^+ taken from ref. 39, σ_I and σ_R^{U} from ref. 12. [b] The source of the data used in the correlation and the source of the DSP parameters. [c] Correlation coefficient. [d] f = SD/RMS, see ref. 12. [e] DSP analysis with $\delta_0 = 0.00$ and $\delta(C(1))$ relative to the derivative with X = H. [f] Present work. [g] Data of this source used in the DSP analysis, carried out here.

tionship [13], the chemical shift of the ith carbon, $\delta(C(i))$, observed in a disubstituted benzene with the substituent X on the xth carbon can be expressed as

$$\delta(C(i)) = a_0(i) + b \cdot SCS(1 + |x - i|) \tag{5}$$

where $a_0(i)$ is the calculated shift for the ith carbon in the parent species (X = H) and SCS(1 + $|x - i|$) is the substituent chemical shift of X for the carbon in the (1 + $|x - i|$)th position in monosubstituent benzene (Y = H).

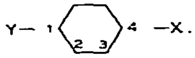
As is evident from Table 7, the proportionality relationship describes the chemical shifts in *para*-substituted phenoxytrimethylsilanes with a very good precision. If we use eq. 5 for predicting the shifts in *p*-bis(trimethylsiloxy)benzene (which were not used in deriving the parameters) the following values are obtained for C(1), C(3), and C(4) carbon shifts: 149.35, 120.70, and 149.54, respectively, which are within ±0.2 ppm from the experimental values. Similarly, the C(4) chemical shifts in substituted phenoxytrimethylsilanes can be calculated from a and b values given by Lynch [13] for the substituents X as the fixed substituent using the SCS parameters of the $OSi(CH_3)_3$ group. Chemical shifts thus calculated are also in an excellent agreement with experiment.

It is generally believed [52,68] that changes in ^{13}C chemical shifts reflect the changes in the total electron density on the relevant carbon atom. Therefore, one is tempted to interpret the fact that C(1) carbon chemical shift changes in phenylsilanes are larger than in phenoxysilanes as an indication of a larger electron density variation at C(1) in the former series of compounds. However, the published correlations of chemical shifts with electron densities do not allow such a straightforward interpretation (e.g., in fluorobenzenes [69], halogen derivatives fit a line which has a slope of different sign compared with the line for all the derivatives pooled together). This is especially true for the C(1) carbons for which correction factors had to be introduced [64,70] to fit the cor-

TABLE 7

PROPORTIONALITY RELATIONSHIPS IN *PARA*-DISUBSTITUTED BENZENES YC_6H_4X [a]

Fixed substituent Y	Carbon	a_0 [b]	b [b]	r [c]	n [d]
$Si(CH_3)_3$	1	140.00	1.25 ± 0.10	0.997	8 [e]
	4	128.86	1.01 ± 0.05	0.997	8 [f]
OCH_3	1	160.15	0.71 ± 0.06	0.995	6 [e]
$OSi(CH_3)_3$	1	155.20	0.85 ± 0.02	0.998	6 [g]
	3	128.92	1.01 ± 0.04	0.996	6 [g]
	4	120.22	1.09 ± 0.02	0.999	6 [g]
NH_2	1	146.97	0.83 ± 0.09	0.993	6 [e]
$NHSi(CH_3)_3$	1	148.53	1.09 ± 0.05	0.995	6 [h]

[a] 

[b] Defined in eq. 5. [c] Correlation coefficient. [d] No. of data points. [e] Parameters taken from ref. 13. [f] Data from ref. 25 used in the calculations. [g] Data from Table 2 (except $X = OSi(CH_3)_3$) and from ref. 21 used in the calculations. [h] Data from refs. 17 and 21 used in the calculations.

relation. Recent ab initio calculations [68,71] and more approximate CNDO/2 calculations [13] for monosubstituted and *para*-disubstituted benzenes show parallel trends in electron densities and hence the different slopes b or ρ_+ (Table 6) are not a consequence of differing variations in the electron density [13] (different ρ^{el}).

Lynch [13] has suggested that the trends in the slopes b are due to changes in the localized excitation energy and proposed that the slope is a linear function of the reciprocal of the ionization potential of the key atom of Y or of the valence-state ionization potential. This suggestion is confirmed by the present results. The ratio of the slopes b in compounds with $Y = OSi(CH_3)_3$ and $Si(CH_3)_3$ is 0.69, in good agreement with the ratio of the reciprocals of ionization potentials, 0.60 [72], or with the ratio of the reciprocals of valence-state ionization potentials, 0.68 [73]. In view of this agreement, the larger sensitivity of the C(1) carbon chemical shift to *para* substituent effects in phenylsilanes than in phenoxysilanes can be fully accounted for by the changes in the excitation energy and it is not necessary to invoke enhanced π-inductive effects under the influence of σ-donating ability of the $Si(CH_3)_3$ group in the former compounds, which would also explain the reduced silicon sensitivity in these compounds.

Meta-substituted phenoxytrimethylsilanes. All aryl carbon chemical shifts in the *meta* derivatives follow satisfactorily the additivity rule ($b = 1.00 \pm 0.05$), although in a few instances the deviations are as large as 1.1 ppm. It is pertinent for the present discussion to note the very small range of the C(1) carbon chemical shift (1.3 ppm only) which is, of course, due to the small magnitude of the *meta* SCS of the substituents [21]. Data on the corresponding *meta* substituted phenyltrimethylsilanes are not available. One would expect the values of ρ^{shield} of the C(1) carbons to be the same in the *meta* and *para* isomers and, hence, would tend to interpret the small range of the C(1) carbon chemical shifts as an indication of small variations in electron density on this carbon due to a small ρ^{el} value. Ab initio calculations have shown [68], however, that in monosubstituted benzenes the slope in carbon chemical shift versus total charge density (which both vary only little) is for the *meta* carbon about only one third of that for the *para* carbon. Obviously, not only the directly attached substituents affect the value of ρ^{shield}. Since the range of C(1) carbon chemical shifts in the *meta* substituted phenoxytrimethylsilanes is about nine times smaller than that in their *para* isomers, it seems that even with a three times larger slope in electron density versus chemical shift the experimental facts suggest a smaller variation in the total electron density on the C(1) carbon in the *meta* than in the *para* derivatives.

Methyl groups. The carbon chemical shifts of $OSiCH_3$ groups in the *para* derivatives do not show a simple correlation with substituent constants. With regard to the limited number of compounds and to the small range of observed δ values (0.02—0.26), attempts for a multiple regression analysis would be unjustified. In the *meta* derivatives the correlation with Hammett constants is quite good ($r = 0.954$, 7 data points) but "reversed".

In the *para*-substituted phenyltrimethylsilanes [25] the CH_3 carbons are more shielded; the substituent effects are larger (range —0.72 to —1.25) and show a good ("reversed") linear correlation with Hammett constants ($r = 0.952$, 8 data points).

According to these comparisons, the substituent effect (which was shown above to be about the same at C(1)) is transmitted much less through the O—Si linkage to the methyl group carbon than through the Si atom alone. Since in both series of compounds the methyl carbon is bonded to a silicon atom, the local excitation energy is constant and the smaller substituent effect can be interpreted as indicating at least the same, if not smaller, changes in electron density around the carbon atom in phenoxy- than in phenyl-trimethylsilanes. This finding appears to be contrasted by ^1H NMR data. The reported [74] equal sensitivity to substituent effects in the two series of compounds was based on an erroneous plot. However, our measurements [17] show a linear correlation ($r = 0.894$, 10 data points) between ^1H chemical shifts and Hammett constants [31] having a slope somewhat higher than the slopes determined for phenyltrimethylsilanes [75—78]. But since the slope in phenyltrimethylsilanes is strongly concentration- and solvent-dependent and since this effect may be even stronger in phenoxysilanes, which are good proton acceptors [14,15], comparison of the slopes in the two series of compounds is not conclusive. Also interpretation of these slopes in terms of electronic effects propagation would be complicated by the other factors contributing to the proton shifts.

Oxygen basicity

Using ^{13}C NMR chemical shifts as electron density monitors, we have so far shown that the substituent effects on the electron densities of C(1) and methyl carbons are not sufficiently different in phenyl- and phenoxy-silanes so as to explain the twofold increase in silicon chemical shift sensitivity in the latter. In other words, if the increased ρ values of the silicon shift have to be attributed to an increase in ρ^{el}, the increase must take place and be localized in the O—Si moiety.

Pignataro and Lunazzi [79] have shown that in $C_6H_5SM(CH_3)_3$ compounds the effects of the $M(CH_3)_3$ substituents on the electron density on the sulphur

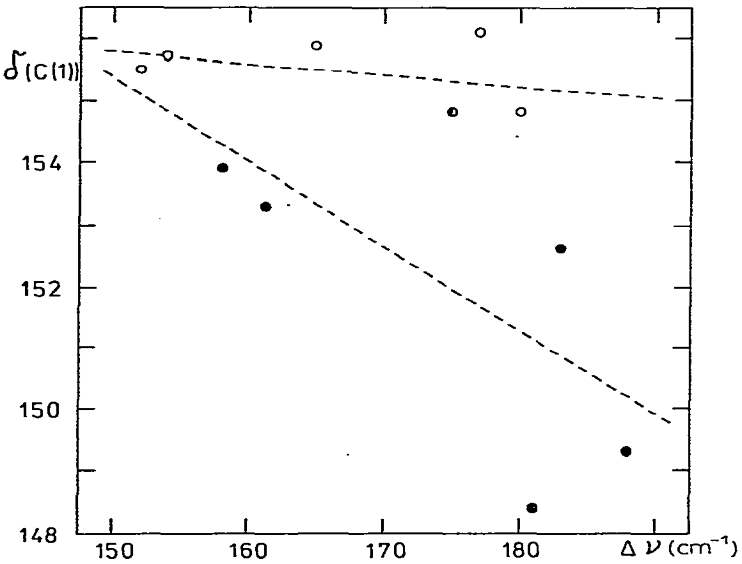


Fig. 4. Plot of ^{13}C chemical shift of C(1) aryl carbon in phenoxytrimethylsilanes versus their relative basicity $\Delta\nu$ [15]. ((●) *para*-derivatives, (○) *meta*-derivatives).

atom (as manifested by $S_{2p3/2}$ ESCA ionization energy) are paralleled by those on the C(1) aryl carbon (as manifested by the carbon chemical shifts). For the compounds studied here, the ESCA or ^{17}O NMR shifts are not available, but the relative basicities of the oxygen atoms in these compounds have been determined from the IR association shift of a proton donor (phenol) [14,15]. An analoguous correlation between the relative basicity of oxygen and C(1) carbon chemical shifts does not hold. As is clear from Fig. 4, the *meta* derivatives show a large variation of the relative basicity at virtually constant C(1) chemical shift; for the *para* isomers some trend is apparent, but the correlation is poor. On the other hand, silicon chemical shifts (in *meta* and *para* derivatives together) show a good linear correlation with the relative basicity (Fig. 5). The silicon shielding increases with increasing oxygen basicity. If the increased basicity indicates higher total electron density, then the molecules with a more shielded silicon atom have also a higher electron density on the oxygen atom (and this density is not related to the electron density on C(1)).

If we are seeking an interpretation in terms of the electronic effect transmission (ρ^{el}), this observation, together with those mentioned above, leads us to postulate some dative O → Si interaction by which the electron density on the silicon atom is increased at the expense of the oxygen. It is not possible to specify further this interaction except that it must be of such a type that our CNDO/2 calculations (although with idealized and not optimalized molecular geometry, but both with and without inclussion of *d* orbitals) failed to reflect it. Naturally, if we accept ρ^{shield} to be larger in phenoxytrimethylsilanes than in phenyltrimethylsilanes, then there is no need to assume any special interaction *.

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* Note added in proof; A referee pointed out that the greater sensitivity of ^{13}C—^{1}H coupling, constants to substitution effects in anisoles than in toluenes [81] makes the explanation of ρ^{shield} terms less feasible. In phenoxydimethylsilanes, however, the ^{29}Si—^{1}H coupling constants are less sensitive than in phenyldimethylsilanes [17].

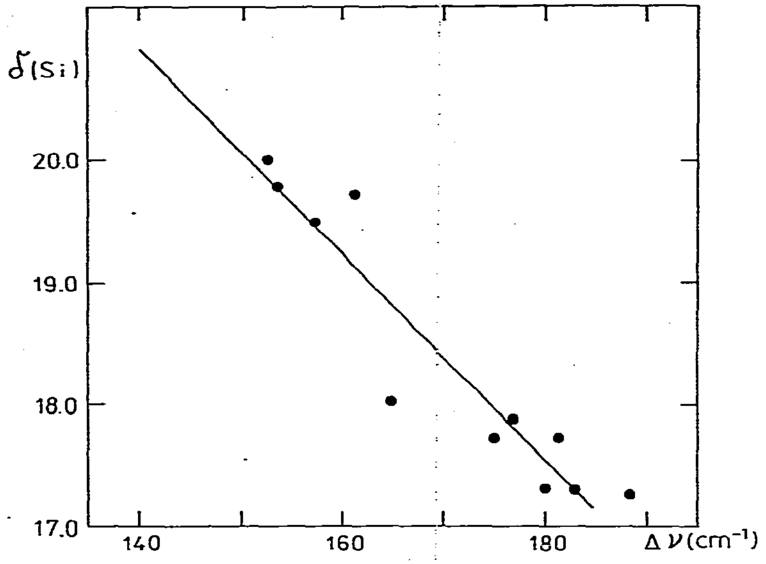

Fig. 5. Plot of ^{29}Si chemical shifts in phenoxytrimethylsilanes, δ(Si), versus their relative basicity Δν [15] (*meta* and *para* derivatives together).

CNDO/2 atomic net charges

The CNDO/2 calculations on model *para* and *meta* substituted phenoxysilanes ($XC_6H_5OSiH_3$) have shown that the conformers I with the C—O—Si plane perpendicular to the benzene ring are energetically more favoured than the conformers II with the silicon atom in the ring plane (the difference between the total energies of the two conformers varied around 65 and 113 kJ mol^{-1} with and without *d* orbitals, respectively). The calculations thus confirm the assumption of preferential population of the former conformer [14,54] but no indication of conformational heterogeneity for phenoxysilanes was found (the difference in the total energies varied with *para* substitution by less than 5%). It has been shown above that the aryl carbon shifts deviations from additivity, which were earlier quoted [14] as a secondary evidence for the conformational heterogeneity, have a different origin. With the difference in conformer energy found, the assumption of free rotation of the $OSi(CH_3)_3$ group around the O—C bond [53] seems unsound.

The calculated net atomic charges on aryl carbon atoms confirm the above interpretation of their chemical shifts. The *para* substituents cause almost parallel changes in net charges on C(1) and C(2) in phenoxy- and phenylsilanes. In the *meta* substituted phenylsilanes, where the range of the charges is smaller, the charges on C(1) vary somewhat more than in the corresponding phenoxysilanes. According to those observations, which are independent of the use of *d* orbitals and conformers, the diamagnetic part of the neighbour anisotropy, σ_d^{AB}, does not contribute to the difference in the silicon shielding sensitivity.

The net atomic charges (*q*) on the silicon atoms in substituted phenoxy- and phenyl-silanes show the expected linear correlations with both the Hammett

σ constant of the substituent

$$q = q_0 + \rho^{\mathrm{el}}\sigma \tag{6}$$

and with the silicon chemical shift

$$\delta = \delta^0 + \rho^{\mathrm{shield}} q \tag{7}$$

which, after substitution, gives

$$\delta = \delta_0 + \rho^{\mathrm{el}}\rho^{\mathrm{shield}}\sigma$$

confirming eqn. 1.

The actual values of regression coefficients in eqs. 6 and 7 depend strongly on the geometry of the molecules assumed in the calculations and are also sensitive to the inclusion of the *d* orbitals. Precise evaluation of ρ^{el} and ρ^{shield} contributions would require much more elaborate quantum chemical calculations with geometry optimalization. Our calculations allow only qualitative conclusions, which is readily apparent from Fig. 6: (I) ρ^{el} in phenoxysilanes is not larger than in phenylsilanes, and (II) larger silicon shielding sensitivity (ρ) in the former series of compounds is due to a larger ρ^{shield}.

The ratio of the silicon shielding sensitivity substitution in phenoxy-, phenylthio-, and phenylaminosilanes to that in phenylsilanes (1.75, 1.34, and 1.24, respectively, if given by the ratio of the corresponding ρ value in Table 4) does not seem to be related to the inverse ionization potentials (or valence-state potentials) of the bridge atom or group as is the C(1) carbon shift sensitivity [13]. Comparison of the silicon chemical shift with the first ionization potential

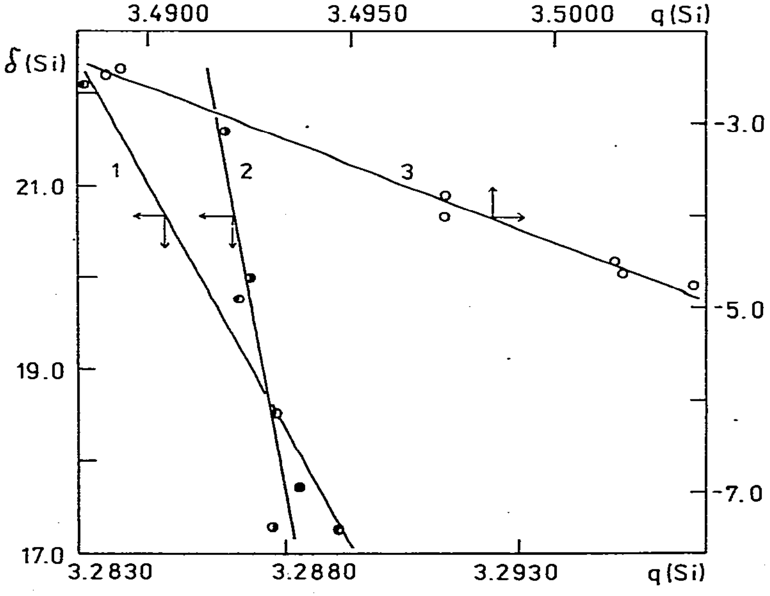

Fig. 6. Plot of ^{29}Si chemical shifts, δ(Si), versus net atomic charge on silicon, *q*(Si), in *para* substituted (line 1) and *meta* substituted (line 2) phenoxytrimethylsilanes and phenyltrimethylsilanes (line 3) [7] (the solid lines are the least-squares fits of the data points).

[80] of the substituted phenoxytrimethylsilanes indicates, however, that the excitation energy also plays some role here.

The present form of silicon shielding theory [6—10] must be improved in order to accommodate the larger ρ^{shield} in the phenoxysilanes.

Conclusions

The effects of substituents X propagate within X—C_6H_4— fragments of phenoxysilanes no better than in those fragments of phenylsilanes. The effects on the carbon atom of the terminal methyl groups are much smaller in the former than in the latter series of compounds.

The substituents cause larger changes in net atomic charges on the silicon atom if it is bonded directly to the benzene ring rather than if it is bonded via the oxygen bridge. In spite of the fact that the possibility of a dative O → Si interaction, not reflected by the CNDO/2 calculations, cannot be completely excluded, the results indicate that the increased silicon shifts sensitivity to substituent effects in phenoxysilanes is due to a higher sensitivity of silicon shielding (ρ^{shield}) to electron density in these compounds rather than to a better transmission of electronic effects (ρ^{el}). The existing theory of silicon shielding must be improved or refined if it has to accommodate the increased sensitivity in the phenoxysilanes.

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