THE ROLE OF ELECTRONIC AND STERIC EFFECTS IN ^{29}Si-NMR SPECTRA OF COMPOUNDS WITH Si—O—C GROUP*

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^{29}Si-NMR chemical shifts are presented for several classes of compounds of general formula $(CH_3)_{4-n-m}Cl_nSi(OR)_m$ (for $n = 0$ $m = 1$—4 and for $n = 1$—3, $m = 1$). In most of the classes the shifts correlate linearly with polar constants of the substituents R or with Del Re net atomic charges on the silicon. The slopes in these correlations are all positive (*i.e.* the shielding decreases with electron withdrawal) and decrease with increasing n or m (*i.e.* the sensitivity of silicon shielding to substituent effects decreases with increasing number of electronegative substituents bonded to the silicon). This finding contradicts the available quantitative theories but can be accounted for by the qualitative model which considers back-bonding to silicon. Each methyl group in the γ position causes a diamagnetic shift of 2 to 3 ppm, depending on the values of m and n, the effects are additive. Compounds with some heteroatoms in the γ position ($R = CH_2Cl$, $CH_2Si(CH_3)_3$, but not $R = CH_2Ge(CH_3)_3$) behave anomalously, the origin of the anomalous shifts could not be ascertained.

The available quantitative[1,2] as well as qualitative[3] theories of ^{29}Si chemical shifts predict, in accord with the experimental evidence (see[3] for a review), a "sagging" pattern for the gross dependence of the silicon chemical shift on some measure of the electron density around this nucleus (be it either the number of electronegative substituents[1,4], n, or a net atomic charge[1,5], Q or a sum of substituent electronegativities[2], $\sum E_X$, or substituent constants, $\sum \sigma_X$, Fig. 1). Naturally, the actual parameters of the dependence (especially the position of the minimum) vary according to the theory or according to the experimental points used in the plot construction. The sagging pattern of the dependence is, however, general; the first electron-withdrawing substituent causes a decrease in the shielding (A-branch) and after some leveling off additional electron withdrawals (B-branch) have an opposite effect (which is attributed to a back bonding by the qualitative model[3]).

In some cases, this gross general dependence gives also correct predictions for the slopes (ϱ) of detailed correlations observed in some narrow ranges where the de-

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pendence appears as linear. The best illustration comes from the Hammett-type correlations of the silicon chemical shifts in substituted phenylsilanes $Y-C_6H_4-$ $-SiX_3$. While in the phenylsilanes with $X = H$ or CH_3 the shielding increases with the substituent constant of Y (A-branch of the dependence, ϱ positive) in those with $X = F$, Cl or OC_2H_5, which are on the B-branch, decreases (ϱ negative).

On the other hand, a few examples can be found in which the observed effects are not in harmony with the general trend. The examples include different signs of chlorine substituent effects on different silicon chemical shifts in cyclic methyl-siloxanes[6] and the same sign of the slopes in chemical shift *versus* $pK_a(AH)$ dependences observed[7] for $n = 1, 2$, and 3 in $(CH_3)_{4-n}SiA_n$.

Our first cursory investigation[8] of substituent effects in compounds containing the fragment $X-Si-O-(CH_2)_m-Y$ has also revealed effects not consistent with the interpretation of the general dependence as provided by the quantitative theories[1,2] and suggested a similarity to the effects observed on atoms which are multiple bonded, *e.g.* $^{13}C=N-R$.

Since the last mentioned observation might have an important bearing upon the theory of the silicon chemical shifts, we have extended the measurements[8] to include more classes of compounds containing such fragment. In the course of this work we have noticed the enhanced sentivity of the silicon shielding to the substituents connected to the silicon atom *via* an oxygen link. While the possibility of analytical utilization of this sensitivity has been treated elsewhere[9] the experimental results and their theoretical implications are discussed in this paper.

The studied compounds are divided into classes $I-VII$, the substituents R are listed in Table I.

Class	$(CH_3)_{4-n}Si(OR)_n$	Class	$(CH_3)_{3-n}Cl_nSiOR$
I	$n = 1$	*V*	$n = 1$
II	$n = 2$	*VI*	$n = 2$
III	$n = 3$	*VII*	$n = 3$
IV	$n = 4$		

Each type of the studied compounds can be taken as representing a selected point on the gross dependence. Its position being given by the substituents directly attached to the silicon atom. The vicinity of the points can be probed by varying the substituents R and the slopes of the dependence at the selected points can thus be estimated. To serve this purpose we have chosen to correlate the observed chemical shifts with the net atomic charges on silicon, Q, and with the polar substituent constants, σ^*. The choice was distated by practical considerations and should not be taken as indicating that the shifts correlate with these parameters best or interpreted in the terms of substituent effects transmission mechanism. The atomic charges on the silicon atom are readily estimated by the Del Re method (for the procedure

and parameters used see[15]) for the compounds *I—IV*. Polar substituent constant σ^*, besides that they have already been shown by Pola and coworkers[16] to correlate with some of the silicon chemical shifts determined here for compounds *I*, are available or can be estimated for the most of the substituents employed (Table I). Statistical tests have proved that the points for which the σ^* values could be only calculated from other substituent constants (values in parenthesis in Table I) can be treated jointly with the other data in all the series of studied compounds.

RESULTS

^{29}Si *Chemical Shifts*

In general, the ^{29}Si chemical shifts collected here in Tables II—IV fit the gross dependence of Fig. 1; in detail, however, some discrepancies between the expected and found trends are apparent.

Series of $(CH_3)_3SiOR$ *compounds (class I).* Since the point corresponding to R = $= CH_2Cl$ (No 21) falls clearly off the correlations of the chemical shifts with both polar substituent constant (Fig. 2) and net atomic charge (Fig. 3) it has not been included into the calculations. Possible origins of anomalous behaviour of this compound have been discussed by Pola and coworkers[16].

The least-squares linear fit of the data in Fig. 2 (33 points) gives $\delta = 14 \cdot 53 \, (\pm 0 \cdot 56)$ $+ \, 7 \cdot 516 \, (\pm 1 \cdot 14) \, \sigma^*$ which correlation is significant at 5% significance level ($r = 0 \cdot 895$). The regression coefficients are within the indicated confidence limits the same as those found by Pola and coworkers[16] in less than a half of our data. Inspection

FIG. 1

General Dependence of ^{29}Si Chemical Shifts on Electron Density

The density is approximated by the number of electronegative substituents n or by the summ of their electronegativities or substituent constants or by the Del Re net charge on the silicon atom. Two selected points with positive (A-branch) and negative (B-branch) slopes (ϱ) are shown.
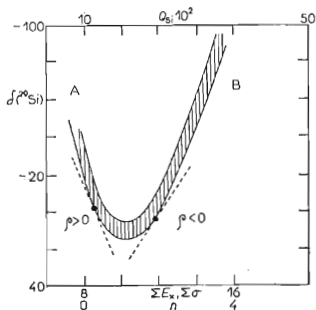
TABLE I

Substituents R Employed in this Study, their Serial Number No, Polar Substituent Constants σ^{*} and Del Re Net Atomic Charges on Silicon Atom Q in Compounds of the Classes I–IV

No[a]	1	2	3	4	5	6	7
R	CH_3	CH_2CH_3	$CH_2Si(CH_3)_3$	$(CH_2)_2Cl$	$Si(CH_3)_3$	$(CH_2)_2NH_2$	$(CH_2)_2N(CH_3)_2$
σ^{*}[b]	0·000	−0·100	−0·26	0·385	(−0·81)[c,d]	(0·17)[e]	0·13[f]
Q^g I[h]	229·39	229·12	229·88	229·46	228·76	229·20	229·17
Q^g II[c]	440·16	439·55	441·26	440·32	438·76	439·74	439·68
Q^g III[h]	549·13	648·14	650·90	649·39	646·85	648·44	648·36
Q^g IV[h]	869·96	855·53	859·40	857·28	853·71	i	i

No[a]	8	9	10	11	12	13	14
R	$(CH_2)_2CH_3$	$(CH_2)_3CH_3$	$CH(CH_3)_2$	$C(CH_3)_3$	$CH_2C(CH_3)_3$	$(CH_2)_2C(CH_3)_3$	$(CH_2)_3C(CH_3)_3$
σ^{*}[b]	−0·115	−0·130	−0·190	−0·300	−0·165	(−0·059)[e]	(−0·021)[e]
Q^g I[h]	229·10	229·10	228·91	228·75	229·08	229·10	229·10
Q^g II[h]	439·51	i	439·09	438·73	439·47	439·51	i

No[a]	15	16	17	18	19	20	21
R	$CH(CH_3)CH_2CH_3$	C_6H_5	$CH_2C_6H_5$	$(CH_2)_3Si(CH_3)_3$	$(CH_2)_4Si(CH_3)_3$	$(CH_2)_2Si(CH_3)_3$	CH_2Cl
σ^{*}[b]	−0·210	0·600	0·215	(−0·093)[e]	(0·033)[e]	(−0·012)[e]	1·050
Q^g I[h]	i	i	i	229·18	229·11[i]	229·10	231·90
Q^g II[h]	439·06	j	j	439·70	439·54[i]	i	i

No[a]	22	23	24	25	26	27	28
R	$(CH_2)_3Cl$	$(CH_2)_4Cl$	$(CH_2)_5Cl$	$(CH_2)_6Cl$	CH_2CHCl_2	CH_2CCl_3	$(CH_2)_2Br$
σ*[b]	0·14[f]	0·050[f]	(0·018)[e]	(0·006)[e]	(0·693)[e]	(0·946)[e]	0·36[f]
Q[g] I	229·15	229·10	229·10	229·10	229·77	230·04	229·50

No[a]	29	30	31	32	33	34	35
R	$(CH_2)_2OCH_3$	$(CH_2)_3OCH_3$	$C(O)CH_3$	$CH_2CH{=}CH_2$	$cy\text{-}C_6H_{11}$	$CH_2Ge(CH_3)_3$	$(CH_2)_2Ge(CH_3)_3$
σ*[b]	0·24[f]	0·02[f]	1·65[j]	0·17[f]	−0·15[j]	k	k
Q[g] I[h]	229·25	229·12				229·44	229·12

No[a]	36	37	38	39	40
R	$(CH_2)_3Ge(CH_3)_3$	$(CH_2)_4Ge(CH_3)_3$	$(CH_2)_2OSi(CH_3)_3$	$(CH_2)_3OSi(CH_3)_3$	$(CH_2)_2Si(CH_3)_2OC_2H_5$
Q[g] I[h]	229·10		229·25	229·12	229·11
σ*[b]	k	k	k	k	k

No[a]	41	42	43	44
R	$(CH_2)_4Si(OC_2H_5)_3$	$Si(CH_3)_2OSi(CH_3)_3$	$Si(CH_3)(OSi(CH_3)_3)_2$	$Si(OSi(CH_3)_3)_3$
σ*[b]	k	(−0·810)[c]	(0·81)[l]	(−0·81)[l]
Q[g] I[h]	229·10	228·55	228·39	228·27

[a] Serial number of the substituent R; by this number the compounds of the classes *I—VII* are denoted. [b] Unless indicated otherwise, original Taft[10] values were used; the values shown were used in calculations though the significant number of digits might be smaller. [c] Estimated[11] as $\sigma^* = 6 \cdot 23\sigma_I$. [d] Value in agreement with the estimate according to [c]; the value of ref.[12] is not applicable. [e] Estimated[13] as $\sigma^*(XCH_2) = \sigma^*(X)/2 \cdot 8$ the values of $\sigma(X)$ being taken either from ref.[10] or ref.[14]. [f] Value taken from ref.[14] or ref.[15]. [g] DelRe net atomic charge on the silicon atom, $Q \cdot 10^3$, for the details of the calculation see ref.[15]. [h] The class of the compound. [i] Compound not available. [j] Cannot be calculated. [k] No estimate available. [l] Estimate based on a comparison of σ^* of substituents Nos B and 42.

of Fig. 2 reveals, however, that the points 1, 2, 10 and 11 (full points) form another line with a somewhat larger slope. These points correspond to varying number of γ-methyl groups[20]. The largest steric γ-effect is expected to occur in compounds with three γ-methyl groups, *i.e.* in compounds Nos 11 and 5. According to an earlier made estimate[20] the steric effect can amount in these compounds up to 9 ppm. Despite that the polar σ^* constant of alkyl groups probably contain a small steric component[14], the quality of the fit is improved is these two compounds are omitted from the correlations: Compounds with $R = CH_2Si(CH_3)_3$ show here also some deviations from correlations discussed farther and were therefore omitted from the calculations. With this reduction of the data base we get

$$\delta = 14{\cdot}70\,(\pm0{\cdot}45) + 7{\cdot}148\,(\pm0{\cdot}920b)\,\sigma^* \qquad (1)$$

for 30 data points with $r = 0{\cdot}928$.

Correlation of the chemical shifts with net atomic charges which do not reflect any steric influences or back-bonding, exhibits the same notable features the slope of a separate line through the points Nos 1, 2, 10, and 11 is not different on 90%
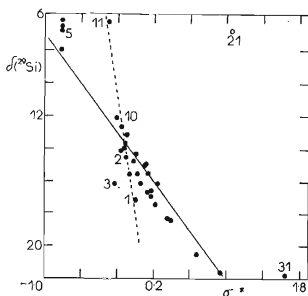

FIG. 2

^{29}Si Chemical Shift Dependence on Polar Substituent Constant in Class *I* Compounds

The line is a least-squares fit of all full points ($n = 33$, $r = 0{\cdot}895$), the open point not included. The broken line is a fit of points Nos 1, 2, 10, and 11 only ($r = 0{\cdot}981$). For substituent serial number see Table I.
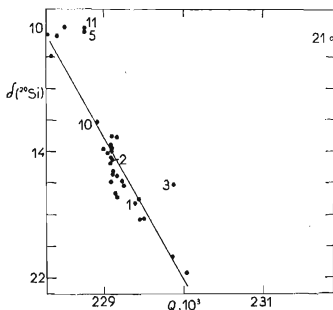
FIG. 3

^{29}Si Chemical Shift Dependence on the Net Atomic Charge in Class *I* Compounds

The solid line is a least-squares fit of all full points ($n = 34$, $r = 0{\cdot}871$). For substituent serial number see Table I.

confidence level according to the t-test from that of the common line. The correlation is also improved if points Nos 3, 5, and 11 are omitted. For 31 data points we get

$$\delta = -2004 \cdot 13 \left(\pm 8 \cdot 62 \right) + 8811 \cdot 024 \left(\pm 94 \cdot 038 \right) Q \qquad (2)$$

with $r = 0 \cdot 947$.

Series of $(CH_3)_2 Si(OR)_2$ *compounds (class II)*. Despite that the increased complexity of the molecules with possible interactions between the substituents R brings about a larger spread around the regression lines the same deviations as in series *I* are apparent in this considerably smaller series of compounds. Again the points Nos 3, 5, and 11 fall off both correlations (Figs 4 and 5), in agreement with the doubled number of γ-methyl groups the deviations from the regression lines are also doubled for points No 5 and 11 as compared with series I. In the correlation with substituent σ^* constant again the points 1, 2, 10, and 11 form another line. With points 3, 5, and 11 omitted the least-squares fits yield

$$\delta = 5 \cdot 68 \left(\pm 1 \cdot 11 \right) + 5 \cdot 997 \left(\pm 2 \cdot 224 \right) \sigma^* \qquad (3)$$
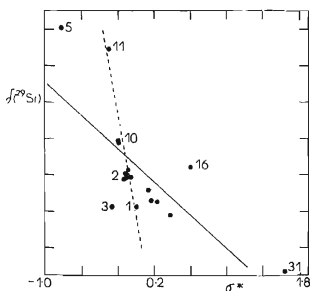

FIG. 4

^{29}Si Chemical Shift Dependence on Polar Substituent Constant in Class *II* Compounds

The solid line is a least-squares fit of all data ($n = 17$, $r = 0 \cdot 727$). The broken line is a fit of points Nos 1, 2, 10, and 11 only ($r = 0 \cdot 969$). For substituent serial number see Table I.
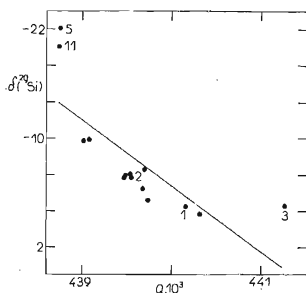
FIG. 5

^{29}Si Chemical Shift Dependence on the Net Atomic Charge in Class *II* Compounds

The solid line is a least-squares fit of all data points ($n = 14$, $r = 0 \cdot 771$). For substituent serial number see Table I.

TABLE II

^{29}Si and ^{13}C-NMR Chemical Shifts in Class I Compounds^a

R—No^b	δ(^{29}Si) SiO	δ(^{13}C)					
		CH$_3$SiO	SiOC	SiOCC	SiOCCC	SiOCCCC	CH$_3$
1^c	17·2	—1·9	48·9				
2^d	14·53	—0·47	57·84	18·69			
3	16·1^e.	—2·1^e	53·8				—4·6^f
4^g	18·36	—0·51	63·16	44·89			
5^h	6·83	2·43					
6^i	16·9	—0·6	65·2	44·6			
7^i	15·6	—0·6	61·6	61·0			45·8
8	13·8	—1·5	63·3	25·3	9·4		
9	14·0^j	—1·5	61·3	34·4	18·3	12·9	
10^g	12·12	0·15	64·69	25·91			
11	6·20^k	2·58^g	71·91^g	32·11^g			
12	14·1	—1·4	71·9	31·8	25·5		
13	15·60^g	1					
14^g	14·69	—0·48	63·37	28·14	40·12	30·01	9·42
16^g	19·62	0·16	155·06	129·37	120·05	121·41	
17^g	17·40	—0·46	64·42	140·92	128·10	126·31	
18	13·1^m	13·1^f	—1·9^f	57·7	20·3		—2·4^f
20	13·9	—1·3^f	60·8	35·7	19·4	15·6	—2·5^f
21^g	6·81	1·91	76·29				
22	16·7	—0·5	58·6	35·8	41·4		
23	16·1	—0·4	61·7	29·8^f	30·3^f	44·7	
24	14·9	1					
25	14·3	1					
26^g	20·65	—0·48	69·25	72·05			
27^g	21·75	—0·36	76·12	98·84			
28^g	18·29	—0·45	62·96	32·76			
29^g	16·25	—0·39	62·14	74·28			58·66
30^g	15·53	—0·57	69·22	33·05			58·31
31	21·8	—0·6	170·2	22·1			
32^g	16·59	—0·41	63·55	137·57	113·88		
33	12·7^n	1					
34	16·5^j	—2·0	5·5				—5·1
35	13·0^j	—1·9	58·6	20·3			—3·0
36	13·6^j	—1·4	—63·9	27·2	11·8		—3·2
37	1	—1·5	60·7	35·2	20·3	15·6	—3·3
38	16·0	—0·3	—64·3				
39	15·3	—0·3	58·9	36·1			
40	14·3°	—0·6	65·0	26·7	12·3		—2·2^p
41	14·0^q	1					
42^c	6·1	1·2					
43^c	6·7	1·6					
44^c	8·0	1·3					

$r = 0.811$, $n = 14$) and

$$\delta = -2836.32\,(\pm 13.84) + 6439.15\,(\pm 143.83)\,Q \qquad (4)$$

$r = 0.939$, $n = 11$).

Series of $CH_3Si(OR)_3$ *and* $Si(OR)_4$ *compounds (classes III and IV).* Since the number of usable data is small and since the substituents also cover a small range of substituent constants no statistically significant linear correlation of the chemical shifts with either polar substituent constants or atomic charge was found. Obviously, the increased complexity of the molecules with possible interactions among the substituents spreads the points away from any possible linear correlation.

Series of $(CH_3)_{3-n}Cl_nSiOR$ *compounds (classes V, VI and VII).* As it is apparent from Fig. 6 the chemical shifts in the compound classes V, VI, VII (and I) with substituents Nos 2, 4, 22, 26, and 27 correlate well the polar substituent constants ($r = 0.98 - 0.99$), the good fit being partially due to structural similarity of the chlorine containing substituents. Notable deviations from the regression lines are found again for substituents Nos 3 and 11. Good fit makes even the deviations of the isopropyl derivatives (No 10) significant. (The regression lines and coefficients shown in Fig. 6 were calculated with the points Nos 3, 10, and 11 excluded, points 10 and 11 are shown in Fig. 6.). The reduction of the data base has only a very little effect on the regression coefficients of the class I compounds (compare dashed and solid lines) and hence the regression coefficients obtained here from limited data for the other classes of compounds are taken for good estimates of their true values.

DISCUSSION

Electronic effects. Though the slopes of correlations holding for classes I, II, V, VI, VII with n differing by unity are not significantly different, the trend in the slopes is clearly established here. Electron-withdrawing substituents R cause paramagnetic shifts, and the sensitivity of the silicon to such effects decreases with increasing number of chlorine or oxygen atoms directly bonded to the silicon atom.

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[a] All the chemical shifts are in δ-scale (*i.e.* in ppm relative to TMS, paramagnetic shifts positive) with approximate error ± 0.3 ppm. If literature data are given then the compound was either not studied here or the literature data are more precise. [b] Substituent serial number, for the structure see Table I. [c] Taken from[6]. [d] Taken from[17]. [e] $\delta(SiCH_2)$. [f] Assignment uncertain. [g] Taken from[9]. [h] Taken from[18]. [i] Taken from[19]. [j] The value might be subject to a systematic error upto -1.2 ppm. [k] Taken from[20]. [l] Not measured. [m] $\delta(SiCH_2) = 1.3$. [n] Converted from[21]. [o] Assignment uncertain, other signal at $\delta(Si) = 14.6$. [p] $\delta(CH_3C) = 57.8$, $\delta(CH_2CH_3) = 18.6$. [q] $\delta(SiCH_2) = -49.0$.

Since the slopes in correlations holding for classes of compounds $I - VII$ are all of the same sign the corresponding selected points should lie on the same branch of the general dependence, and, since the slopes are positive, it should be the A-branch (Fig. 1). The trend in the slopes suggests that the selected points should approach (from the left) the minimum of the dependence as the number of electronegative substituents directly attached to the silicon atom is increased. And yet, according to the chemical shift values of the corresponding compounds in series $I - VII$ the dependence has a minimum either between the point corresponding to $(CH_3)_4Si$ and class I (or class V) or between class I (or class V) and class II (or class VI).

These conflicts with the theories of silicon shielding are, in our opinion, a consequence of the fact that the theories[1,2] present the silicon chemical shift in a series of closely related compounds as a function of one variable only. Then, necessarily, the determined slope must be taken for the derivative of such a function. If, however, the chemical shift is considered a function of two (at least) properties of the substi-

TABLE III

^{29}Si-NMR Chemical Shifts in Class II, III, and IV Compounds[a]

Compound class R—No[b]	II $\delta(^{29}Si)$	III $\delta(^{29}Si)$	IV $\delta(^{29}Si)$
1	— 2·5[c]	—40·8	— 79·2
2	— 5·74[d]	—44·21[d]	— 82·40[d]
3	— 2·5[e]	—40·9[f,e]	— 78·8[e]
4	— 1·6	—41·9	— 83·8
5	—22·1[f]	—65·0[g]	—105·2[h]
6	— 3·2[i]	—41·5[i]	
7	— 4·4[i]	—43·8[i]	
8	— 6·0		
10	— 9·8		
11	—19·9		
12	— 5·6		
13	— 5·9		
15	— 9·7		
16	— 6·8	—54·0[j]	—101·1[j]
17	— 3·0		
18	— 6·6		
31	4·6	—43·7	— 97·8
32		—42·9	

[a] See footnote in Table II. [b] Substituent serial number No, see Table I. [c] Taken from ref.[6]. [d] Taken from ref.[17]. [e] $\delta(SiCH_2) = -0.5$. [f] $\delta(Si) = 6.1$. [g] $\delta(Si) = 6.7$. [h] $\delta(Si) = 8.0$. [i] Taken from ref.[19]. [j] Taken from ref.[1].

tuents (as does the qualitative theory[3]), the slope would represent only a partial derivative with respect to the varied parameter at the selected point. According to the qualitative theory the position of the selected point is given by a combination of inductive and back-bonding effects of silicon substituents which affect the shielding in the opposite ways. With increasing number of e.g. oxygen atoms bonded to the silicon the second effect becomes dominant and we observe the dependence of Fig. 1. In the case of a fixed number of electronegative substituents X attached to the silicon

TABLE IV
^{29}Si Chemical Shifts in Compounds of Class V, VI, and VII[a] Compounds

Compound class R—No[b]	V	VI	VII
2	12·18[c]	—10·71[c]	—38·34[c]
3	14·0[d]	— 8·8[e]	—37·0[f]
4	15·0	— 8·8	—37·8
10	9·5	—13·5	—41·0
11	6·5		
22	14·1	— 9·3	—38·1
26	16·1	— 7·9	
27	17·22[c]	— 7·22[c]	—36·43[c]

[a] See footnote[a] in Table II. [b] Substituent serial number No, see Table I. [c] Taken from ref.[9]. [d] $\delta(SiCH_2) = -0.4$. [e] $\delta(SiCH_2) = -0.2$. [f] $\delta(SiCH_2) = 0.2$.

FIG. 6
^{23}Si Chemical Shift Dependence on Polar Substituent Constant in Class I, V, VI, and VII Compounds
The solid lines are least-squares fits of points Nos 2, 4, 22, 26, and 27 in the classes. The broken line is a line corresponding to Eq. (1). The indicated values are the slopes with their symmetrical 90% confidence limits. The correlation coeficients are class I r = 0·994, V r = 0·986, VI r = = 0·984, and VII r = 0·981.
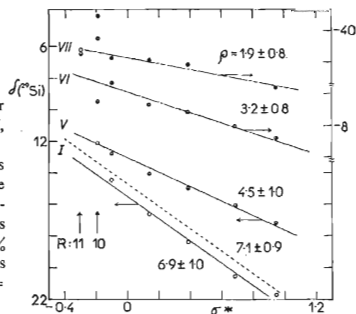
a remote electron-withdrawing substituent R connected to the silicon *via* an oxygen link enhances the inductive and diminished the back-bonding effects of the oxygen. The result is, in all classes of compounds with Si—O—R fragment, a paramagnetic shift. And, since in this fragment the change caused by the inductive effect is paralleled by a change in the back-bonding contribution, silicon exhibits in compounds with Si—O—R fragments larger sensitivity than in compounds with Si—R linkage[9]. The observed decrease in sensitivity with increasing number of chlorine or oxygen atoms bonded to silicon can be accounted for by compensating polarization of X—Si bonds.

The above finding has also a negative practical consequence. The enhanced sensitivity of silicon shielding in class I compounds to substituent effects (as compared with $(CH_2)_3SiR$ compounds)[9] renders some analytical potential to ^{29}Si-NMR. The general dependence of Fig. 1 promises even greater sensitivity to such effects in compounds of the type X_3SiOR (X being an electronegative substituent). The present results show, however, that this is not the case and that the structural sensitivity of ^{29}Si-NMR spectroscopy cannot be further increased in this way. This interpretation can be also applied to the doubled sensitivity of silicon shielding in substituted phenoxysilanes as compared with phenylsilanes[22].

γ-Effects. In all studied classes of compounds methyl groups in the γ-position relative to the silicon atom cause diamagnetic shifts of the silicon resonance. In series I and II the effects of methyl groups are additive. Depending on the class of the compounds and on the nature of the substituent R the diamagnetic shift varies between 1·0 and 3·7 ppm (Table V). After correcting for the increasing inductive effect with the degree of branching of the substituent[23] R, the net steric effect is $2-3$ ppm in classes *I, II, V, VI,* and *VII* in agreement with the earlier estimate[20]. In the series

TABLE V

Steric γ-Effects of Methyl Groups on ^{29}Si Shielding in Class *I—VII* Compounds[a]

Class R(No[b])	I[c]	II	III	IV	V	VI	VII
CH_2CH_3 (2)	2·7	1·8	1·2	1·0	—	—	—
$CH(CH_3)_2$ (10)	2·5	1·8	—	—	2·7	2·8	2·7
$C(CH_3)_3$ (11)	3·7	2·9	—	—	3·0	—	—

[a] ^{29}Si substituent chemical shifts (SCS) per one γ-methyl group SCS values relative to the methoxyderivatives in classes *I—IV* and relative to ethoxyderivatives in classes *V—VII.* [b] Substituent serial number, see Table I. [c] Taken from ref.[20].

$(CH_3)_{4-n}Si(OR)_n$ the magnitude of the effect seems to decrease with increasing n.

The anomalous shifts observed in compounds with $R = CH_2Cl$, $CH_2Si(CH_3)_3$ i.e. in compounds in which there are heteroatoms in γ position to silicon are not likely to be caused by steric effects only.

Though some hypothetical account was offered by Pola and coworkers[16] there are not sufficient data available at present which would allow some meaningfull conclusion regarding the role of heteroatoms at this position.

EXPERIMENTAL

The identity of the investigated compounds was checked by ^{13}C-NMR spectroscopy and their purity by gas–liquid chromatography. The measurements of the spectra were carried out as described earlier[24,25].

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