

PROBLEMS OF BOND UTILIZATION OF SILICON *d*-ORBITALS

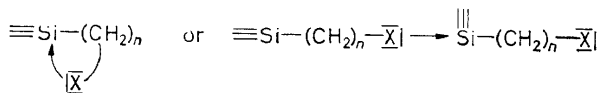
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To explain some of the properties of silicon compounds the ability of silicon to offer for utilization its unoccupied $3d$ -orbitals for bonding interactions was postulated. It is possible that silicon, which occurs in all its tetravalent compounds in the hybrid sp^3 state, can in compounds with strongly electronegative substituents undergo a contraction of its d -orbitals with resulting hybridization with the s - and p -orbitals to the sp^3d^2 state. In this way the d -orbitals can be utilized for increasing the number of σ bonds. In addition, the d -orbitals can be used for producing bonds with π -symmetry which, in the case of overlapping d_{π} orbitals of silicon with the p_{π} occupied orbitals of neighbouring atoms, are designated as $(p \rightarrow d)_{\pi}$ dative bonds. The utilized p_{π} orbital can be occupied either by a free electron pair, as in fluorine or oxygen, or by electrons of another π -bond, such as those in phenyl or vinyl groups.

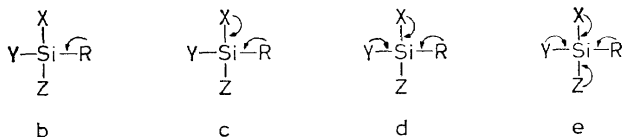
In addition to the assumption of bond utilization of the $3d$ -orbitals of silicon further views were advanced to account for some properties of silicon compounds. Thus, 20 years ago Pauling explained the reduction of the bond distance of Si-Cl by the character of the double bond without involving the role of silicon d -orbitals¹. The choice between this resonance concept and the view of a $(p \rightarrow d)_{\pi}$ bond is complicated by the polarity of the σ bond, which, in addition to exerting a direct influence on the π -orbitals, brings about changes in the hybridization of the σ -binding orbitals. The effects of these changes on observable parameters are difficult to assess since the mutual relationship between the $(p \rightarrow d)_{\pi}$ bond and rehybridization is not yet clear. Some properties of organosilicon compounds ascribed to the $(p \rightarrow d)_{\pi}$ bond can also be explained by second-order hybridization. The question thus arises which of the three phenomena, the $(p \rightarrow d)_{\pi}$ bond, second-order hybridization, and resonance of structures without the use of silicon $3d$ -orbitals, is decisive for a particular property of the molecule. The term $(p \rightarrow d)_{\pi}$ bonds is being used exclusively in this communication, only to prevent repetition of the above fundamental consideration with the individual cases discussed.

In our laboratories we study firstly the effect of structure of organosilicon compounds on the possibility of formation of intramolecular or intermolecular $(p \rightarrow d)\sigma$ bonds in systems such as



a

where silicon as the electron acceptor is isolated from the electron donor by a minimum of one atom; and secondly the formation of $(p \rightarrow d)_\pi$ bonds. The object is to obtain data on the relative trends towards the formation of $(p \rightarrow d)_\pi$ bonds in different atoms and groups attached to silicon, in particular in bonds of silicon with oxygen, chlorine, vinyl group, and phenyl group. The interesting question is that of mutual influences of a greater number of such bonds on a single silicon atom. If the silicon atom binds a group R which is capable of forming the $(p \rightarrow d)_\pi$ bond with silicon (b)



it may be expected that an electronegative atom X, capable of the same interaction will enhance the formation of the $(p \rightarrow d)_\pi$ bond of the R through its own $-I$ effect (c). If another substituent Y at the silicon atom (d) is of a similar nature as X the situation is more complex. It is well known that it has not yet been established whether more than two d -orbitals of silicon can participate in the formation of $(p \rightarrow d)_\sigma$ bonds: thus, *e.g.* silicon tetrahalides form demonstrable complexes of this type with a maximum of two molecules of monoamines². A similar curtailment of formation of $(p \rightarrow d)_\pi$ bonds on a single silicon atom has not yet been demonstrated. If it exists it might be expected that in cases when the substituent Y (d), or even the substituent Z (e) are capable of forming $(p \rightarrow d)_\pi$ bonds no further enhancement of $(p \rightarrow d)_\pi$ bond formation takes place with rising number of these electronegative substituents. If these substituents are identical one would observe a rise in their average electronegativity or basicity. If the $(p \rightarrow d)_\pi$ bond of Si-R were more slightly developed than in other bonds the R group should be displaced from its interaction in cases (d) and (e) so that in these cases one should observe a rise in basicity directly in the group R. It is understandable that in view of the complexity of the mutual relationships between the various groups where not only the induction effects and formation of $(p \rightarrow d)_\pi$ bonds must be considered but also steric effects, changes in valency angles, hindrance to free rotation, etc.; the phenomena can be estimated only qualitatively and with extreme caution. In spite of this, it might be interesting to compare some of our data on model series of compounds obtained by studying the reactivities, with others derived from physical properties of these compounds and to consider whether such data might not support the above considerations.

One of the criteria from which the existence of $(p \rightarrow d)_\pi$ bonds in an organosilicon compound can be estimated is the study of stretching vibrations of the Si-H bond of suitable silicon hydrides. It is known from the work of a number of authors³⁻⁵ that the effect of substituents attached to silicon merely by a σ bond on the frequency shift of this vibration is additive in character. *Figure 1* shows these frequencies for several model series of silicon hydrides. The linearity of the frequency shift with progressive substitution is preserved not only for the series of methylethylsilanes (from triethylsilyl hydride to trimethylsilyl hydride) and of phenylsilanes (from silane to

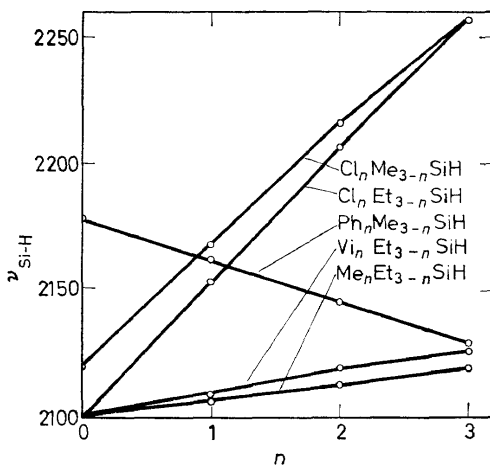
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Figure 1. Dependence of Si-H on Silicon Substitution

triphenylsilyl hydride), but approximately even for ethylvinylsilanes (from triethylsilyl hydride to trivinylsilyl hydride) and for methylchlorosilanes (from trimethylsilyl hydride to trichlorosilane) and for ethylchlorosilanes (again from triethylsilyl hydride to trichlorosilane). According to these data it appears that if these compounds contain a developed ($p \rightarrow d$) $_{\pi}$ bond between the vinyl or phenyl group and the silicon atom it is so slight that even when three such groups are present at the silicon no mutual displacement from interaction with silicon *d*-orbitals takes place. A completely different situation results with oxygen-containing substituents as is evident from Figure 2. Both in the series of (trimethylsiloxy)-methylsilanes and (*tert*-butoxy)methylsilanes and finally also in the approximately isostructural

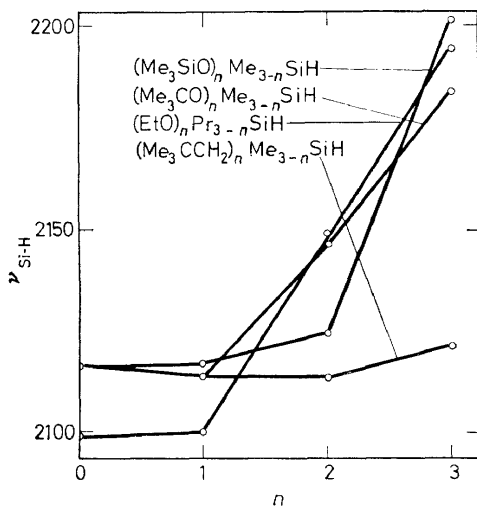


Figure 2. Dependence of Si-H on Silicon Substitution

series of (ethoxy)propylsilanes the frequency shift of the stretching vibration of the Si-H bond is clearly greater, due to the presence of the second or the third oxygen-containing substituent (not in the case when a first such group is present). The above frequencies of a series of neopentylmethylsilanes show by comparison that the deviation from linearity due to the mutual steric effect of substituents is relatively small. In isosteric alkoxysilanes (trimethylsiloxymethylsilanes and *tert*-butoxymethylsilanes) it should be even smaller on account of greater bond distance and greater bond angles. A greater shift towards higher frequencies is due to substituents with a higher $-I$ effect. For this reason the relatively small shifts observed with the first oxygen-containing substituent can be interpreted by a pronounced role of its $(p \rightarrow d)_\pi$ bond with silicon. A marked shift in the presence of a second and especially a third alkoxy group would then indicate that the second and the third alkoxy-groups do not have the same chance of forming a $(p \rightarrow d)_\pi$ dative bond with silicon and exert their influence more and more through their $-I$ effect.

Table 1. Dipole moments of $\text{Me}_{4-x}\text{Si}(\text{OEt})_x$ and $\text{Me}_{4-x}\text{Si}(\text{OSiMe}_3)_x$

Compound	$\mu [D]$	Compound	$\mu [D]$
Me_3SiOEt	1.18	$\text{Me}_3\text{Si}(\text{OSiMe}_3)$	0.80
$\text{Me}_2\text{Si}(\text{OEt})_2$	1.36	$\text{Me}_2\text{Si}(\text{OSiMe}_3)_2$	1.11
$\text{MeSi}(\text{OEt})_3$	1.70	$\text{MeSi}(\text{OSiMe}_3)_3$	1.40
Group moments (if $\text{Si} \rightarrow \text{Me} = 0.2$)			
$\text{Si}(\text{OEt})$	1.38	$\text{Si}(\text{OSiMe}_3)$	1.0
$\text{Si}(\text{OEt})_2$	1.59	$\text{Si}(\text{OSiMe}_3)_2$	1.34
$\text{Si}(\text{OEt})_3$	1.90	$\text{Si}(\text{OSiMe}_3)_3$	1.60

Considerable differences between the polarity of the first and the second and the third SiO bond can be observed also when measuring the dipole moments of methylalkoxysilanes. If the total molecular moment (Table 1) is used for calculating the first approximation average moments of the Si-OR bonds in such a way that it is assumed that the silicon-methyl moment is constant and equal to 0.2 D it may be seen from Figure 3 that

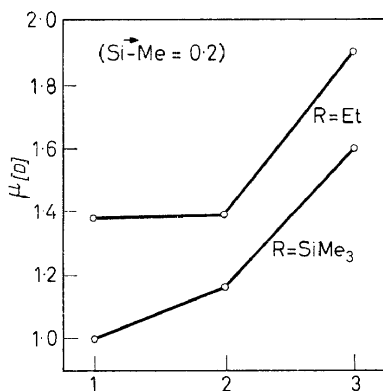


Figure 3. Calculated average bond moments $(\text{Si}-\text{OR})$ of methylethoxysilanes, $\text{Me}_{4-x}\text{Si}(\text{OR})_x$

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the values of average bond moments are extraordinarily increased particularly in the case of methylethoxysilanes, from the dialkoxy to the trialkoxy derivatives.

Let us now deal with still more complex molecules in which the silicon atom binds a group about which it is assumed on the basis of previous experience that its tendency towards ($p \rightarrow d$) π bond formation with silicon is lower than with oxygen, such as the vinyl of phenyl group, and further a different number of alkoxy groups. Table 2 shows as examples the total

Table 2. Dipole moments of $\text{ViMe}_{3-x}\text{Si}(\text{OEt})_x$, $\text{PhMe}_{3-x}\text{Si}(\text{OEt})_x$, and $\text{ViMe}_{3-x}\text{Si}(\text{OSiMe}_3)_x$

	$\mu[D]$		$\mu[D]$		$\mu[D]$
ViMe_3Si	0.3	PhMe_3Si	0.42	ViMe_3Si	0.3
$\text{ViMe}_2\text{Si}(\text{OEt})$	1.26	$\text{PhMe}_2\text{Si}(\text{OEt})$	1.34	$\text{ViMe}_2\text{Si}(\text{OSiMe}_3)$	0.95
$\text{ViMeSi}(\text{OEt})_2$	1.32	$\text{PhMeSi}(\text{OEt})_2$	1.32	$\text{ViMeSi}(\text{OSiMe}_3)_2$	0.93
$\text{ViSi}(\text{OEt})_3$	1.76	$\text{PhSi}(\text{OEt})_3$	1.65	$\text{ViSi}(\text{OSiMe}_3)_3$	1.12

dipole moments of vinylmethylethoxysilanes, phenylmethylethoxysilanes and vinylmethyl(trimethylsiloxy)silanes. In these model series one may assume a constant preservation of the dipole moment only in the silicon-methyl bond whereas the character of the silicon-vinyl or silicon-alkoxy bonds will vary more or less in the individual series. If the bond moments of the silicon-alkoxy group are computed on the assumption that the moments of silicon-vinyl or silicon-phenyl remain constant and equal to the moments of these bonds in trimethylsubstituted derivatives, values shown graphically in Figure 4 for vinylmethylethoxysilanes and vinylmethyl(trimethylsiloxy)-

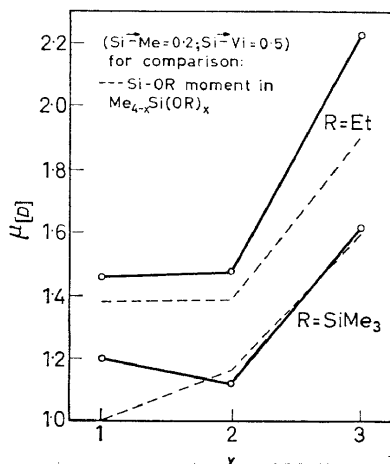


Figure 4. Calculated average bond moments (Si-OR) of vinylmethylethoxysilanes and vinylmethyl(trimethylsiloxy)silanes, $\text{ViMe}_{3-x}\text{Si}(\text{OR})_x$

silanes and in Figure 5 for phenylmethylethoxysilanes are obtained. For the sake of comparison, the broken curves in both figures indicate the moments of the bond of silicon with the corresponding alkoxy group calculated, as

mentioned before, for methylalkoxysilanes. It may be seen that in comparison with methylethoxysilanes the moments thus computed would be generally somewhat higher in vinyl- and phenyl-substituted derivatives and that, in particular, the difference between the polarity of the first two and the third bond of silicon to the alkoxy group would be greater. The assumption of a constant value for the moment of the silicon-vinyl bond under which the

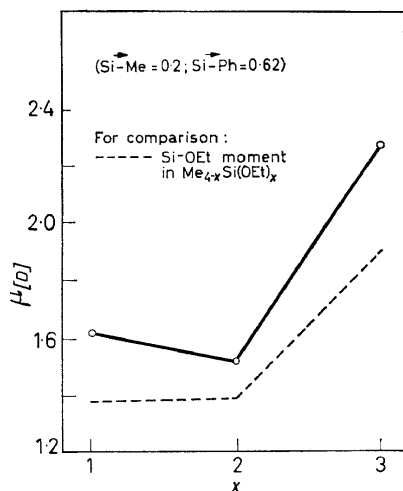


Figure 5. Calculated average bond moments (Si-OEt) of phenylmethylethoxysilanes $\text{PhMe}_{3-x}\text{Si}(\text{OEt})_x$

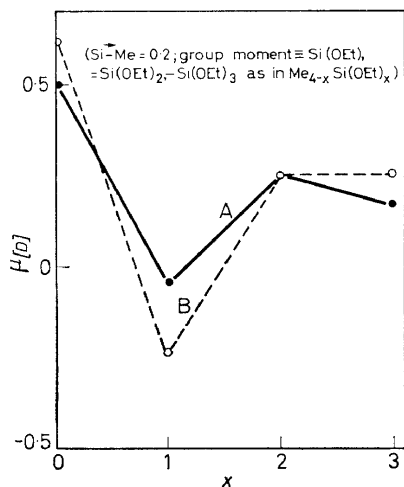


Figure 6. (A) Calculated average bond moments (Si-Vi) of vinyl substituted ethoxy derivatives, $\text{ViMe}_{3-x}\text{Si}(\text{OEt})_x$
 (B) Calculated average bond moments (Si-Ph) of phenyl substituted ethoxy derivatives, $\text{PhMe}_{3-x}\text{Si}(\text{OEt})_x$

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calculations were made is probably not justified since the effect of strongly electronegative oxygen atoms and their strongly developed ($p \rightarrow d$) $_{\pi}$ bonds on the character of the silicon–vinyl bond will be certainly important. If, on the other hand, the moments of the silicon–vinyl and silicon–phenyl bonds are computed in the above series under the assumption that the bond moments of the silicon–alkoxy group are identical with those in the corresponding methylalkoxysilanes, values are obtained which are compiled for vinyl-substituted and phenyl-substituted ethoxy derivatives in *Figure 6* and for vinylmethyl(trimethylsiloxy) derivatives in *Figure 7*. The relationships

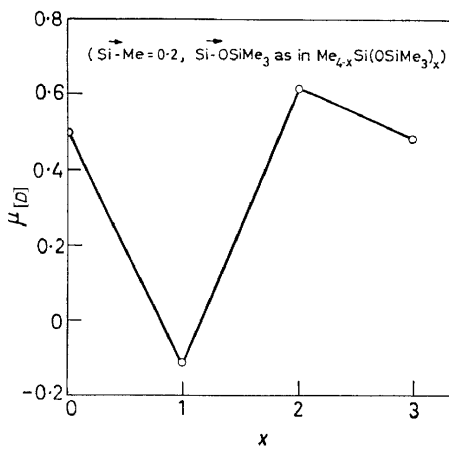
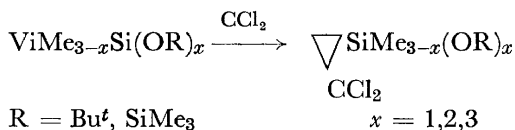


Figure 7. Calculated average bond moments (Si–Vi) for vinylmethyl(trimethylsiloxy) derivatives, $\text{ViMe}_{3-x}\text{Si}(\text{OSiMe}_3)_x$

obtained (considerable decrease in polarity of the bond between silicon and vinyl in the presence of an alkoxy group and its rise in the presence of a second and third alkoxy group) might be interpreted in such a way that the first oxygen-containing group supports through its –I effect the formation of the ($p \rightarrow d$) $_{\pi}$ bond between vinyl and silicon whereas further groups displace it from the interaction with the *d*-orbitals of silicon. In these last-named calculations, too, a considerable simplification was used. The more interesting it then appears that the relationship between the polarity of the vinyl–silicon bond and the substitution of silicon by alkoxy groups agree qualitatively with the results of our studies on the reactivity of the above vinylmethyl-alkoxysilanes during Doering–Hoffmann addition of dichlorocarbene. During this electrophilic addition the reactivity can be



related according to the existing experience to the basicity of the C=C double bond.

Figure 8 shows that the overall character of the dependence of the reactivity of the vinyl group in vinylmethyl(trimethylsiloxy) silanes⁶ is similar to the

last-named dependence of the bond moment of silicon–vinyl on the number of oxygen-containing groups of the compound in question. It thus appears that the reactivity of the vinyl group is determined only partly by steric factors; this is indicated first of all by the ratio of reactivities of mono-(trimethylsiloxy) and bis(trimethylsiloxy) derivatives which can rather be

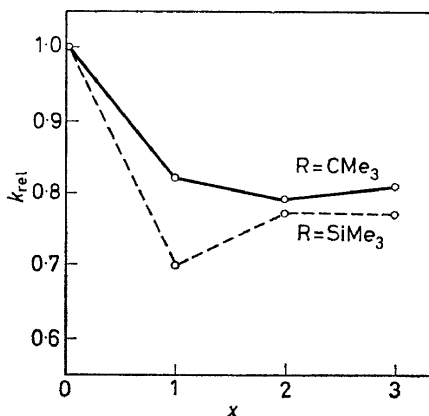


Figure 8. Relative reaction rates of dichlorocarbene addition to vinylmethyl(trimethylsiloxy)silanes, ViMe_{3-x}

explained by a displacement of the vinyl group from its relatively slight interaction with silicon *d*-orbitals by oxygen, the $(p \rightarrow d)_\pi$ bond of which is stronger. This type of competitive interaction is suggested also by our measurements of i.r. spectra of vinylsilicon compounds (Table 3). These

Table 3. Wave numbers of some fundamental vibrations of the vinyl group in the i.r. spectra of alkenylsilanes

	Asym. stretching =CH ₂ (cm ⁻¹)	Stretching C=C (cm ⁻¹)	k _{rel} (CCl ₂)
Me(CH ₂) ₄ Vi	3077	1645	1.0
Me ₃ Si(CH ₂) ₂ Vi	3079	1643	1.2
Me ₃ SiCH ₂ Vi	3081	1635	4.97
(Me ₃ SiO) ₃ SiCH ₂ Vi	3071	1636	1.95
Me ₃ SiVi	3052	1598	0.047
(EtO)Me ₂ SiVi	3051	1595	—
(EtO) ₂ MeSiVi	3055	1599	—
(EtO) ₃ SiVi	3062	1602	—
(Me ₃ SiO)Me ₂ SiVi	3054	1598	0.033
(Me ₃ SiO) ₂ MeSiVi	3057	1599	0.036
(Me ₃ SiO) ₃ SiVi	3061	1602	0.036
(Bu ^t O)Me ₂ SiVi	3050	1593	0.038
(Bu ^t O) ₂ MeSiVi	3053	1594	0.037
(Bu ^t O) ₃ SiVi	3064	1598	0.038

relationships are complicated by the possibility of a role of the mass effect of silicon, the definitely smaller steric effect of the alkoxy groups and by other factors, but in general the frequencies of asymmetric stretching vibration of

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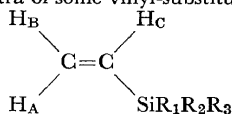
=CH_2 agree interestingly with the reactivities of the corresponding compounds. The values of these frequencies and relative rate constants increase with increasing +I effect from 1-heptene to trimethyl- γ -butenylsilane to trimethylallylsilane, relatively decrease toward tris(trimethylsiloxy)allylsilane and are substantially lower in all vinylsilanes⁷. In comparison with vinyl-trimethylsilane the values for alkoxydimethylvinylsilanes are usually still lower, but rise again for dialkoxy and trialkoxy derivatives. A less characteristic picture is obtained with the apparent molar absorption coefficients of characteristic vibrations shown in Table 4 (wagging vibrations of the vinyl group is covered in the ethoxy derivatives by the strong absorption of the alkoxy group).

Table 4. Values of the apparent molar absorption coefficients $\epsilon_{\text{max}}^{(a)}$ of characteristic vibrations of the vinyl group

	Stretching C=C [$\epsilon_{\text{max}}^{(a)}$](CCl ₄)	Wagging CH=CH ₂ [$\epsilon_{\text{max}}^{(a)}$](CS ₂)	Asym. stretching =CH ₂ [$\epsilon_{\text{max}}^{(a)}$](CS ₂)
Me(CH ₂) ₄ Vi	40	123	32
Me ₃ Si(CH ₂) ₂ Vi	43	201	37
Me ₃ SiCH ₂ Vi	78	201	43
(EtO) ₃ SiCH ₂ Vi	69	164	35
Me ₃ SiVi	8	95	42
(EtO)Me ₂ SiVi	15	—	43
(EtO) ₂ MeSiVi	22	—	34
(EtO) ₃ SiVi	27	—	35

Another method used for studying the properties of vinylsilanes was n.m.r. spectrometry. The results of analyses of the individual spectra referred to a uniform scale of frequencies based on cyclohexane, using the working frequency of 40 Mhz, are compiled in Table 5 and in Figure 9. In discussing

Table 5. N.m.r. spectra of some vinyl-substituted silanes of the type



R ₁ R ₂ R ₃	Chemical shifts								
	A	B	C	J _{AB}	J _{AC}	J _{BC}	J	CH ₃ ^{SI}	CH ₃ ^R
Me ₃	-167.3	-176.9	-186.5	3.8	20.4	14.5	38.7	55.4	—
(Bu ^t O)Me ₂	-169.3	-176.4	-187.6	3.9	20.7	14.8	39.4	52.7	9.2
(Bu ^t O) ₂ Me	-172.0	-176.0	-183.1	4.1	20.6	15.2	39.9	52.3	7.0
(Bu ^t O) ₃	-176.4	-176.4	-176.4	—	—	—	—	—	5.5
(Bu ^t O) ₂ Cl	-179.5	-179.5	-179.5	—	—	—	—	—	4.2
(Me ₃ SiO)Me ₂	-176.8	-184.0	-193.5	4.5	21.8	14.9	41.2	55.4	57.1
(Me ₃ SiO) ₂ Me	-178.7	-184.6	-188.2	4.2	21.3	15.7	41.1	55.9	55.9
(Me ₃ SiO) ₃	-175.6	-175.6	-175.6	—	—	—	—	—	53.9
(EtO)Me ₂	-171.2	-179.8	-185.7	3.8	21.0	15.4	40.3	52.9	12.7
(EtO) ₂ Me	-178.7	-178.7	-178.7	—	—	—	—	54.6	11.3

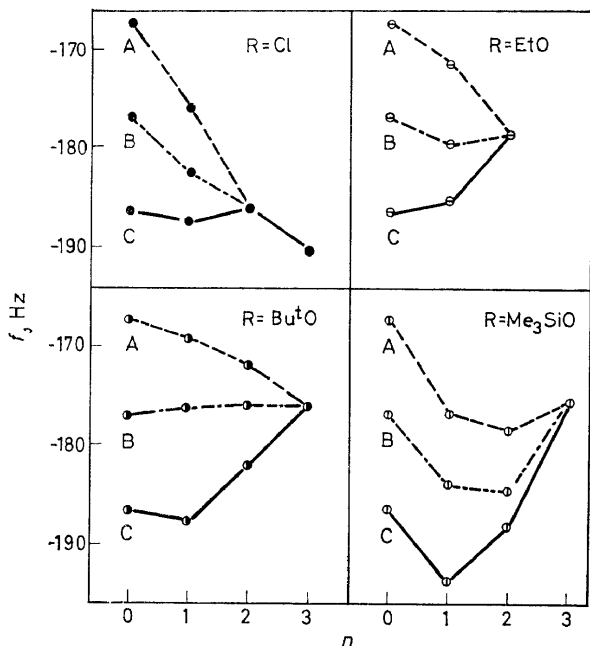


Figure 9. Dependence of vinyl proton (ABC) chemical shift on substituent number (n) in $\text{ViMe}_{3-n}\text{SiR}_n$

the results obtained we shall proceed from a comparison of the spectra of vinylsilanes with those of their closest carbon analogues. In view of the possible hyperconjugation effects of methyl groups it is better to compare trimethylvinylsilane with the isostructural *tert*-butylethylene than with the unbranched 1-olefins. The vinylsilanes studied here are characterized in particular by the following properties: (i) vinyl protons, especially on the β -carbon, are screened more in silanes than in *tert*-butylethylene; (ii) in vinylsilanes, in contrast with carbon compounds, protons A are screened more than protons B; (iii) the total span of chemical shifts of vinyl protons is smaller in silanes than in carbon compounds; (iv) all the interaction constants of vinylsilanes are greater than the corresponding constants of carbon compounds. Workers on the n.m.r. spectra of vinylsilanes so far agree in the interpretation of decreased screening of vinyl protons in vinylsilanes as being a result of the $(p \rightarrow d)_n$ bond. Differences in the changes of shifts of vinyl protons in differently substituted vinylsilanes can also be explained by a diamagnetic effect of bulky oxygen-containing substituents. At the same time, the varied differences in screening of vinyl protons A, B and C can be attributed to different values of magnetic anisotropy, particularly of the Si-C bond. Since, however, the lack of knowledge of the geometry of the molecules and magnetic anisotropies of all bonds in the shown model series precludes any calculations to be made, the results of our measurements have been compared with assumptions mentioned heretofore. If the decreased screening of vinyl protons is due to a $(p \rightarrow d)_n$ bond of vinyl-silicon the bond

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type remains preserved in the vinylsilanes studied here, with the possible exception of compounds with three electronegative substituents.

In our interpretation we proceed from the fact that the postulated ($p \rightarrow d$)_π bond of silicon–vinyl and the –I effect of electronegative substituents at the silicon atom (designated as R) decrease the screening of vinyl protons which, on the other hand, is increased by the ($p \rightarrow d$)_π bond of the R substituents and by hyperconjugation Si[–] = CH₃⁺.

The screening of methyl groups is increased by both types of ($p \rightarrow d$)_π bonds and decreased by the –I effect and by hyperconjugation. Under these assumptions it may be deduced from the analysis of spectra that in oxygen-containing derivatives the replacement of the first methyl group of vinyl-trimethylsilane brings about mostly an increase of the ($p \rightarrow d$)_π character of the silicon–vinyl bond. We are apparently dealing here with parallel effects of decrease of hyperconjugation and –I effect of the substituent which provides the effective positive charge to the silicon atom. The rise of the ($p \rightarrow d$)_π character of the silicon–vinyl bond by further replacement of methyls is partly compensated in oxygen-containing substituents by the formation of a ($p \rightarrow d$)_π silicon–oxygen bond. The above explanation accounts qualitatively not only for the changes in shifts of vinyl protons but also for methyl shifts at the silicon and for chemical shifts of substituent signals. It may be seen that it also corresponds roughly to the interpretation of reaction rates of an electrophilic addition of dichlorocarbene to trimethylsiloxyvinylsilanes and *tert*-butoxyvinylsilanes, of their i.r. spectra and dipole moments.

In view of the similarity of the character of silicon–vinyl and silicon–phenyl bonds which, as I mentioned earlier, was also observed during an investigation of the dipole moments of phenylmethylethoxysilanes (*Figure 6*), we intend to compare further also some silyl substituted benzoic acids. Of the results obtained so far mention may be made of the half-neutralization potentials of (trimethylsiloxy)methylsilylbenzoic acids as measured during their potentiometric titration with tetrabutylammonium methoxide in dimethylformamide. *Table 6* shows the Hammett σ constants of the corresponding silyl substituents. It follows from *Table 6* that the first trimethyl-

Table 6. Half-neutralization potentials of some silyl substituted benzoic acids and σ -values of the corresponding silyl groups

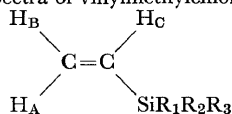
<i>Compound</i>	σ	<i>H.N.P.</i> (mV)
<i>p</i> -Me ₃ SiC ₆ H ₄ COOH	– 0.037	– 536
<i>p</i> -Me ₃ SiOMe ₂ SiC ₆ H ₄ COOH	+ 0.018	– 529
<i>p</i> -Me ₃ SiO ₂ MeSiC ₆ H ₄ COOH	– 0.040	– 537
<i>p</i> -Me ₃ SiO ₃ SiC ₆ H ₄ COOH	+ 0.039	– 527

siloxy group acts predominantly through its –I effect so that the acidity of this acid is relatively raised. The second trimethylsiloxy group appears to displace the phenyl group from its ($p \rightarrow d$)_π bond with silicon, thus reducing the acidity. The third oxygen-containing group acts probably after displacing the phenyl group again mostly through its –I effect and again raises the acidity of the corresponding derivative. The complicated competitive action of the –I effects and formation and rupture of ($p \rightarrow d$)_π bonds is suggested by the relatively very minute differences in acidity of all the four

derivatives mentioned. In spite of this the observed differences in half-neutralization potentials, amounting to as much as 10 mV, are sufficiently significant (the error being about 2 mV). Thus, the overall type of the dependence of the character of the silicon–vinyl or silicon–phenyl bond on the number of oxygen–containing substituents may be considered as established by an other independent method.

In addition to the effect of the oxygen-containing substituents I would like to say a few words about some results concerning the effect of chlorine substitution at the silicon. The linearity of the frequency shift of the stretching vibration of Si–H with gradual substitution with chlorine is clearly broken at trichlorosilane in both the methylchlorosilane and the ethylchlorosilane series (*Figure 1*). A very minute deviation from linear decrease of the Si–Cl bond moment with substitution will also be observed with methyltrichlorosilane in the methylchlorosilane series. Even if within the context of this debate it would be attractive to ascribe these deviations to the fact that the degree of electronegative substitution in trichlorosilane and methyltrichlorosilane offers substantially greater possibilities of the silicon–chlorine ($p \rightarrow d$) $_{\pi}$ bond formation the deviations from linearity are rather small and other explanations may be found. In any case, it may be said that the strength of the ($p \rightarrow d$) $_{\pi}$ bond will be considerably lower with chlorine, just just as with vinyl and phenyl, than it is with oxygen. It will thus be very interesting to follow their mutual effects. It follows from the measurement of a number of methyl chloro-substituted vinylsilanes (*Table 7*) which were

Table 7. N.m.r. spectra of vinylmethylchlorosilanes of the type



R ₁ R ₂ R ₃	Chemical shifts								
	A	B	C	J _{AB}	J _{AC}	J _{BC}	J	CH ₃ ^{SI}	CH ₃ ^R
Me ₃	–167.3	–176.9	–186.5	3.8	20.4	14.5	38.8	55.4	—
ClMe ₂	–176.0	–182.6	–187.6	2.8	21.1	15.9	39.8	40.6	—
Cl ₂ Me	–186.2	–186.2	–186.2	—	—	—	—	27.5	—
Cl ₃	–190.3	–190.3	–190.3	—	—	—	—	—	—

shown graphically in *Figure 9* for comparison with oxygen-containing derivatives, that the chemical shifts of vinyl and methyl protons in vinylchlorosilanes are of a different character than in vinylalkoxysilanes since the induction effect of chlorine predominates over its π -binding capacity. For the sake of comparison the dipole moments of vinylmethylchlorosilanes and phenylmethylchlorosilanes shown in *Table 8* were measured. In view of the approximately comparable strength of the individual ($p \rightarrow d$) $_{\pi}$ bonds in these compounds the average moments of the silicon–chlorine bond were computed on the assumption that in chlorine-substituted derivatives the moments of the silicon–vinyl and silicon–phenyl bonds remain constant just as in vinyltrimethylsilane or phenyltrimethylsilane; after that the moments of silicon–vinyl and silicon–phenyl bonds were computed on the assumption

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 Table 8. Dipole moments of $\text{Me}_{4-x}\text{SiCl}_x$, $\text{ViMe}_{3-x}\text{SiCl}_x$, and $\text{PhMe}_{3-x}\text{SiCl}_x$

Compound	μ [D]	Compound	μ [D]	Compound	μ [D]
Me_3SiCl	2.09	ViMe_3Si	0.3	PhMe_3Si	0.42
Me_2SiCl_2	2.28	ViMe_2SiCl	2.00	PhMe_2SiCl	2.21
MeSiCl_3	1.93	ViMeSiCl_2	2.27	PhMeSiCl_2	2.58
		ViSiCl_3	2.04	PhSiCl_3	2.49
Group moments (if $\text{Si} \rightleftharpoons \text{Me} = 0.2$)					
		SiCl	2.29		
		SiCl ₂	2.51		
		SiCl ₃	2.13		

that the moments of silicon–chlorine bonds remain the same as in methylchlorosilanes of the same number of chlorine atoms. The dependence of the moments of silicon–chlorine bonds on the degree of substitution are shown in *Figure 10*. However, our further studies (to be mentioned later) are much

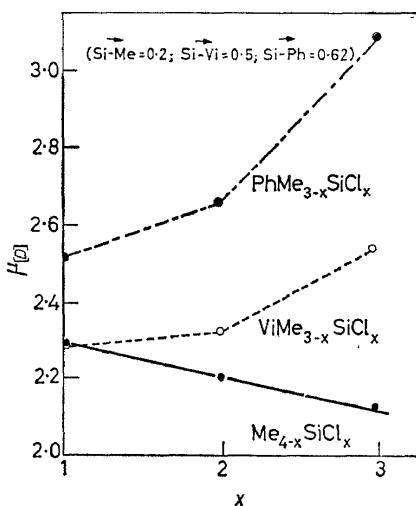


Figure 10. Dependence of average bond moments of silicon–chlorine bonds (Si–Cl) on the degree of substitution

more readily related to the dependence of the moments of silicon–vinyl and silicon–phenyl, as shown in *Figure 11*, and calculated on the basis of the second-named assumption. *Figure 11* shows that in the series of phenylmethylchlorosilanes all the three chlorines act mostly through their induction effect which enhance the $(p \rightarrow d)_\pi$ character of the silicon–phenyl bond up to a change of sign of the moment. The increment of the moment value decreases so that the third chlorine atom acts only negligibly, but not even three chlorine atoms will displace the phenyl from its π -interaction with silicon. The conclusion that the $(p \rightarrow d)_\pi$ bond is more developed between silicon and phenyl than between silicon and chlorine was reached by

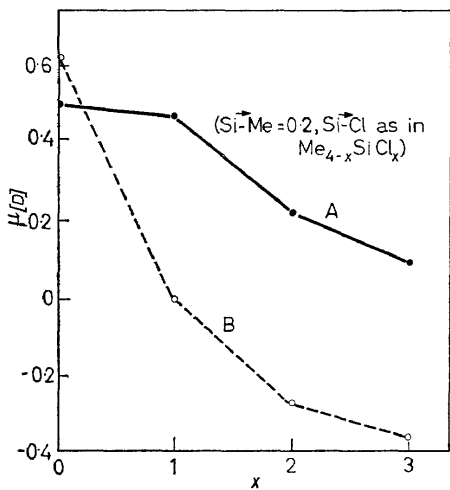


Figure 11. Dependence of the moments of: (A) Silicon-vinyl (Si-Vi), and (B) silicon-phenyl (Si-Ph) bonds on the degree of substitution in compounds of the type (Vi or Ph) $\text{Me}_{3-x}\text{SiCl}_x$

studying the effect of phenylchlorosilyl substituents on the rate of radical chlorination and bromination of silyl-substituted toluenes.

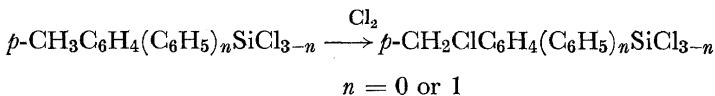


Figure 12 shows the σ values thus obtained for the *p*-trichlorosilyl group and for the *p*-phenyldichlorosilyl group, as well as those for the *p*-diphenylchlorosilyl group and *p*-triphenylsilyl group found in the literature^{8,9}. Since the phenyl group has a lower -I effect than chlorine it may be expected that

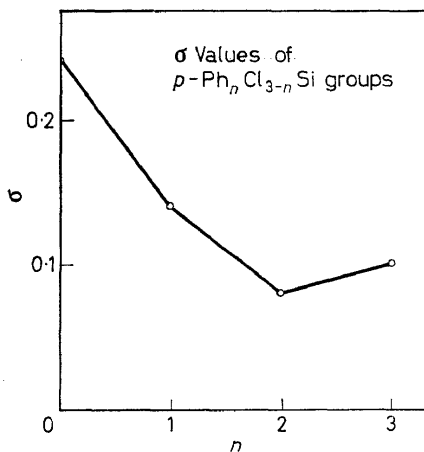


Figure 12. Values of *p*-trichlorosilyl, *p*-phenyldichlorosilyl, *p*-diphenylchlorosilyl, and *p*-triphenylsilyl groups

gradual replacement of chlorine atoms by phenyl groups will bring about gradual increase in the reactivity of the corresponding toluenes towards the electrophilic chlorine radical which will also be reflected in the lower final value of the substitution constant σ . This prerequisite is fulfilled. The replacement of the first chlorine in the trichlorosilyl group by a phenyl group brings about a marked decrease in the value of σ , the replacement of the second chlorine causes a lesser change and the replacement of the third results in practically no change at all. This fact may be explained only on the basis of the assumption that the π -electron system of the aromatic nucleus is capable of stronger interaction with silicon *d*-orbitals than free electron pairs of chlorine as long as the remaining substituents at silicon are sufficiently electronegative. Then it may be expected that the replacement of the first chlorine of trichlorosilyl by a phenyl group will result in a marked decrease of the final polar effect of the phenyl group with which the second aromatic group, tolyl, does not yet compete for the formation of the $(p \rightarrow d)_\pi$ bond with silicon. In the diphenylchlorosilyl group and even more markedly in the triphenylsilyl group the phenyl groups have a lesser possibility of π -interaction with silicon and hence apparently exert more on the induction effect.

The character of the mutual interaction of the vinyl group with chlorine atoms as it appears from *Figure 11* was verified by determining the relative reaction rates of dichlorocarbene addition to a series of vinylmethylchlorosilanes. In this case it was not possible to generate dichlorocarbene according to Doering and Hoffmann's method and we used the pyrolysis of trichloromethyl-trichlorosilane as described by Haszeldine. According to the results achieved, as with the calculated bond moments of silicon-vinyl, the chlorine substituents in this series exert predominantly their $-I$ effect.

References

- ¹ L. Pauling. *The Nature of the Chemical Bond*. Cornell University Press, Ithaca, N.Y. (1948).
- ² C. Eaborn. *Organosilicon Compounds*. Butterworths, London (1960).
- ³ H. W. Thompson. *Spectrochim. acta* **16**, 238 (1960).
- ⁴ A. L. Smith and N. C. Angelotti. *Spectrochim. acta* **14**, 412 (1959).
- ⁵ V. A. Ponomarenko and Yu. P. Egorov. *Izvest. Akad. Nauk SSSR, Otdel. khim. Nauk.* 1133 (1960).
- ⁶ J. Cudlín and V. Chvalovský. *Coll. Czech. Chem. Comm.* **28**, 3088 (1963).
- ⁷ J. Knížek, M. Horák and V. Chvalovský. *Coll. Czech. Chem. Comm.* **28**, 3079 (1963).
- ⁸ J. J. Eisch and J. T. Trainor. *J. org. Chem.* 487 (1963).
- ⁹ R. A. Benkeser, C. E. De Boer, R. E. Robinson, and D. E. Saure. *J. Am. chem. Soc.* **78**, 682 (1956).