AN INTRAMOLECULAR INTERACTION
IN SILYLMETHYL CHLORIDES AS SEEN FROM DIPOLE MOMENT
AND SPECTRAL DATA*

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The effect of silyl groups on other molecular centers of the silylmethyl chlorides $XYZSiCH_2Cl$ is discussed on the grounds of the data gathered chiefly from literature. The magnetic shielding of the CH_2 protons in X_3SiCH_2Cl is shown to be in accordance with operation of inductive effect of the X_3Si groups. The ^{35}Cl-NQR frequencies are influenced by intramolecular interaction (the α-effect) and this interaction is disclosed to diminish with increasing electron-withdrawing ability of the substituents bonded to the silicon atom. The discussion of dipole moments of X_3SiCH_2Cl is presented. The importance of the α-effect in silylmethyl chlorides is supported by the proton acceptor ability of the oxygen in $(C_2H_5O)_{3-n}(CH_3)_nSiCH_2Cl$.

There has been much recent interest in the α-carbofunctional organosilicon compounds. A great number of evidence on their anomalous reactivity explained often by a specific participation of the silicon atom[1−7] and their spectral properties[8−17] can be rationalized in terms of the control of the silyl group's polar effect in the ground state of R_3SiCH_2Y molecules by the Y group[16,18−20] or by variation of the silyl group's polar effect during reaction course[16,21]. The intramolecular interaction termed the α-effect was advanced[8,14,22] in order to explain the ground state properties of the functional group Y, and having later been subjected to theoretical treatment[23] it can be described by at least two parallel mechanisms of the electron acceptor action of the silicon atom[23]. Despite the effort to determine the dependence of the extent of the intramolecular interaction on nature of the substituents bonded to silicon no success has yet been approached due to either low sensitivity of chosen method[24] or masking effect of solvent[25].

In connection with our other papers[26,27] we compiled in this work the ^1H-NMR, ^{35}Cl-NQR and IR spectral data on the α-carbofunctional silanes $XYZSiCH_2Cl$ in order to examine the effect of the substitution on silicon on the other molecular centers. We additionally present the discussion of dipole moments of X_3SiCH_2Cl $(X = CH_3, H, Cl)$ and attempt to estimate whether the extent of intramolecular interaction is affected by nature of the substituents attached to silicon.

EXPERIMENTAL

Chloromethyltrichlorosilane, 2-chloroethyltrichlorosilane, 2-chloroethyl(methyl)diethoxysilane, (2-chloroethyl)triethoxysilane, bis(2-chloroethyl)diethoxysilane and chloromethyltriethoxysilane were from the laboratory stock. 2,2-Dichloroethyltriethoxysilane was prepared by the reaction of 2,2-dichloroethyltrichlorosilane with ethanol in the presence of pyridine in ether b.p. 110°C/12 Torr, n_D^{20} 1·4430. The purity of all the compounds was checked by gas liquid chromatography. The IR spectra of hydrogen bonds of phenol interacting with ethoxyorganosilanes were recorded as described[22]. The ^{1}H-NMR chemical shifts, δ(H), for neat liquids or CCl_4 solution (cyclohexane as internal standard) were obtained on a modified Tesla BS 477 spectrometer operating at 60 MHz.

RESULTS AND DISCUSSION

Dipole Moments

The dipole moment of polyatomic molecules can be considered as the resultant of the vectorial combination of the moments of the individual bonds. Provided the molecular geometry is known, the calculation of dipole moment is carried out by vectorial combination of the bond moments. This procedure has been successfully used to calculate the molecular moments of a number of organosilicon species[9,28]. The deviations of experimental values from calculated ones in the case of the H_3Si. .CH_2Y compounds (Y = Cl, Br, I) were attributed to nonbonded interaction between the halogen and the silicon[9]. As already mentioned, this interaction was often put forward in order to explain unusual properties of halogenomethylsilanes. However, the analysis of H_3SiCH_2X (X, O, N, F) by CNDO/2 calculation[23] favors mechanism of the α-effect as orbital interaction leading to the HOMO of the $n-\sigma + \sigma^*_{Si-C}$ or $n-\sigma + \sigma^*_{Si-X}$ form. Therefore, the α-effect might bring about some increase in μ_{X_3Si} and/or μ_{Si-C} value and the difference between the calculated and found molecular moments of X_3SiCH_2Cl might be controlled by changes of three bond moments $\Delta\mu_{C-Cl}$, $\Delta\mu_{X_3Si}$ and $\Delta\mu_{Si-C}$. These changes would be, of course, reflected in the molecular moment of X_3SiCH_2Cl unequally and importance of their effect in determining the molecular moment would depend on X.

We have chosen X_3SiCH_2Cl with isotropic silyl groups for the discussion of dipole moments of silylmethyl chlorides. Presumed all X_3SiCH_2Cl with X = H, CH_3, Cl possess undistorted tetrahedral angles (this is justified on the grounds of microwave spectra of H_3SiCH_2Cl[27] and electron diffraction study of $(CH_3)_3SiCH_2Cl$[28]), the molecular dipole moments were calculated by vector addition of these bond moments[29-31]: $\overrightarrow{Si-C}$ (0·6 D), $\overrightarrow{H-C}$ (0·3 D), $\overrightarrow{Si\text{-alkyl}}$ (0·2 D), $\overrightarrow{Si-H}$ (1·0 D) and $\overrightarrow{C-Cl}$ (1·57 D). The value of C—Cl bond moment 1·57 D was acquired by adjusting customarily used value of C—Cl bond moment in chloromethane (1·47 D) (ref.[32]) with regard to the recently reported[31] value of H—C bond moment 0·3 D. The $SiCl_3$

group moment was taken 2·07 D as obtained from the dipole moment of methyltrichlorosilane[33]. Calculated and experimental electric dipole moments of X_3SiCH_2Cl $(X = CH_3, H, Cl)$ are seen from Table I. There is a good match between calculated and experimental value for $(CH_3)_3SiCH_2Cl$, the difference $\mu^{calc.} - \mu^{exp.}$ being only 0·08 D. The difference, however, grows more significant when going to H_3Si.CH_2Cl and further to Cl_3SiCH_2Cl. One might now easily incline to recognize the extent of the intramolecular interaction to be greater when going from $(CH_3)_3$.$SiCH_2Cl$ to Cl_3SiCH_2Cl. Inadequacy of such consideration is however manifested by the dependences of the calculated molecular dipole moment (μ^{total}) of X_3SiCH_2Cl on the values of μ_{C-Cl}, μ_{X_3Si} and μ_{Si-C} (Figs 1–3). We mark the value of μ_{C-Cl}, μ_{X_3Si} and μ_{Si-C}, based on those the calculation was carried out, $\mu^{standard}$. The quantity $\Delta\mu$ designates the difference $\mu^{standard} - \mu^{changed}$, where $\mu^{changed}$ is the value of partial moment declined from its standard value. As it turns out from Fig. 1, the slope of the

TABLE I

Electric Dipole Moments, $\mu(D)$ of X_3SiCH_2Cl

X_3Si	$\mu^{exp.}$	$\mu^{calc.}$	$\lvert\mu^{exp.} - \mu^{calc.}\rvert$
$(CH_3)_3Si$	$2·01^a$	1·93	0·08
H_3Si	$1·63^b$	1·80	0·17
Cl_3Si	$1·62^a$	2·13	0·51

[a] For the sake of comparison we prefer dipole moment values obtained under the same experimental conditions (ref.[15]). The μ values reported for $(CH_3)_3SiCH_2Cl$ (2·03 D, ref.[46]) and Cl_3SiCH_2Cl (1·62 D, ref.[35]) elsewhere do not practically differ from them. [b] Ref.[9].

FIG. 1

Plot of Calculated Molecular Dipole Moments of X_3SiCH_2Cl, μ^{total}, versus the Quantity $\Delta\mu(\mu^{standard} - \mu^{changed})$

The $\mu^{standard}$ in Debye: 1·57 (C—Cl), 0·20 $((CH_3)_3Si)$, 1·0 (H_3Si) and 2·07 (Cl_3Si). The curves 1–3 relate to the $\Delta\mu_{C-Cl}$ in H_3SiCH_2.Cl, $(CH_3)_3SiCH_2Cl$ and Cl_3SiCH_2Cl respectively. The curves 4–6 relate correspondingly to the $\Delta\mu_{H_3Si}$, $\Delta\mu_{(CH_3)_3Si}$ and $\Delta\mu_{Cl_3Si}$.
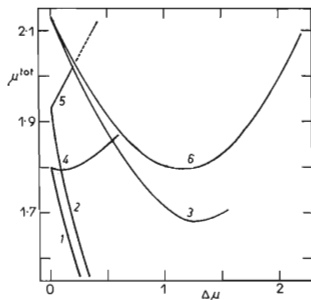
plot μ^{total} vs $\Delta\mu_{\text{C-Cl}}$ for H_3SiCH_2Cl and $(CH_3)_3SiCH_2Cl$ is much steeper than that for Cl_3SiCH_2Cl. The same decrease in $\mu_{\text{C-Cl}}$ affects thus least of all molecular moment of Cl_3SiCH_2Cl. (The decrease in μ_{x_3Si} affects the μ^{total} even in two different ways according to the X, the value of μ^{total} being decreased for X = Cl, but increased for X = CH_3 and H.) The increase of μ_{X_3Si} results in the increase in μ^{total} quantity for X = Cl and H (the latter being very slight) and the decrease in μ^{total} value for X = CH_3 (Fig. 2). Fig. 3 shows how is the μ^{total} varied if the value of $\mu_{\text{Si-C}}$ grows over its standard value. The apparent increase in the μ^{total} is observed for X = CH_3, the opposite situation is seen for X = Cl. The value of μ^{total} slightly decreases and then slightly increases for X = H.

Supposing now that the intramolecular interaction in X_3SiCH_2Cl is represented by the former of the aforementioned orbital interactions, and that it results in about the same decrease in $\mu_{\text{C-Cl}}$ in all compounds, its manifestation in the molecular dipole moment is made the most apparent for X = CH_3, slightly masked for X = H and hardly recognizable for X = Cl. Supposing the latter $(n-\sigma + \sigma^*_{\text{Si-C}})$ orbital interaction is operative, the manifestation of the α-effect is made most apparent for X = Cl, still unhidden for X = H and unrecognizable for X = CH_3. Presuming now the $\mu_{\text{C-H}}$ partial moments not to deviate from its standard value, the low experimental dipole moment for H_3SiCH_2Cl can be attributed to the α-effect (as it was done before[9]). The experimental dipole moment of $(CH_3)_3SiCH_2Cl$ does not turn out
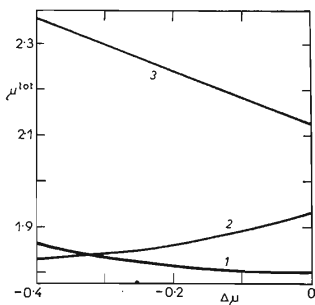

FIG. 2

Plot of Calculated Molecular Dipole Moments of X_3SiCH_2Cl, μ^{total}, *versus* the Quantity $\Delta\mu(\mu^{\text{standard}} - \mu^{\text{changed}})$

The curves *1 − 3* relate to the $\Delta\mu_{H_3Si}$, $\Delta\mu_{(CH_3)_3Si}$, and $\Delta\mu_{Cl_3Si}$ correspondingly.
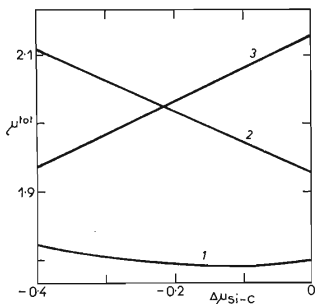
FIG. 3

Plot of Calculated Molecular Dipole Moment of X_3SiCH_2Cl, μ^{total}, *versus* the Quantity $\Delta\mu_{\text{Si-C}}$ $(\mu^{\text{standard}}_{\text{Si-C}} - \mu^{\text{changed}}_{\text{Si-C}})$

The curves *1 − 3* relate to the X = H, CH_3 and Cl respectively.

to be necessarily in harmony with suggestion of lesser importance of the α-effect in this compound only if the $n - \sigma + \sigma_{Si-X}^*$ molecular interaction is operative. In the case of Cl_3SiCH_2Cl the plot of μ^{total} vs $\Delta\mu$ (Fig. 1) provides evidence that the decrease of either μ_{SiCl_3} or μ_{C-Cl} even to zero does lead to μ^{total} still higher than experimental molecular dipole moment. In this case the variation of only one partial moment can not explain the experimental value of dipole moment and the variation of at least two partial moments has to be considered. The predicted[23] operation of the α-effect resulting in the increase of μ_{Cl_3Si} or μ_{C-Si} affects (Fig. 2 and 3) μ^{total} insignificantly. We therefore suppose that low dipole moment of Cl_3SiCH_2Cl might be consistent with mutual interaction of Si—X and C—Cl bond moments.

^{1}H-NMR *Spectra*

The magnetic shielding of the $CH_2(Si)$ protons in X_3SiCH_2Cl (X = H,CH$_3$, Cl) should be dominated by the diamagnetic term. In order to examine how the silyl groups shield the CH_2 protons in these compounds we have attracted attention to the chemical shift, $\delta(H)$, of the CH_2Cl in $X_3Si(CH_2)_nCl$ where $n = 1$ and 2 (Table II). Linear relationship between $\delta(CH_2Cl)$ in ppm and the Taft polar constants of the X_3Si groups[36] $\sigma_{X_3Si}^*$ can be established, the slope of the plot $\delta(CH_2Cl)$ vs $\sigma_{X_3Si}^*$ for the compounds with $n \doteq 1$ being 0·15. The estimation of the slope of the same dependence for $X_3SiCH_2CH_2Cl$ (0·055) is based only on two points (Table II), but both the slopes yield the ratio 2·7 in accordance with the polar effect transmission through the CH_2 group[37]. The protons of the CH_2 group in X_3SiCH_2Cl with isotropic silyl groups thus seem to be influenced as if by only inductive effect of X_3Si group. We are but aware of ^{1}H-NMR data for $F_3SiCH_2Cl^{38}$ and $(C_6H_5)_3SiCH_2Cl^{39}$, $\delta(H)$ of those do deviate from the above mentioned $\delta(CH_2)$ vs $\sigma_{X_3Si}^*$ plot.

TABLE II
^{1}H — Chemical Shift, $\delta(CH_2Cl)$ in ppm, of Some $X(CH_2)_nCl$ ($n = 1, 2$) Compounds

X	$\delta(CH_2Cl)$		σ_X^{*a}
	$n = 1$	$n = 2$	
$(C_2H_5)_3Si$	$2·70^b$	—	$-1·10$
$(CH_3)_3Si$	$2·72^c$	$3·61^d$	$-0·72$
H_3Si	$2·94^e$	—	$0·87$
Cl_3Si	$3·21^d$	$3·77^f$	$2·27$

^{a} Ref.^{36}; ^{b} ref.^{39}; ^{b} ref.^{47}; ^{d} this work; ^{e} ref.^{48}; ^{f} ref.^{49}.

NQR *Spectra*

The ^{35}Cl-NQR frequencies for XYZSiCH$_2$Cl have been recently reported[40] to depend linearly on the sum of the Taft $\sum \sigma^*_{XYZ}$ constants of X, Y, Z groups, the ν^{77} frequencies being increased with increasing $\sum \sigma^*_{XYZ}$ value. It was shown that correlation lines of the relationship $\nu^{77} = \nu_0 + \varrho \sum \sigma^*_{XYZ}$ for XYZSiCH$_2$Cl and XYZCCH$_2$Cl bisect one another at about $\sum \sigma^*_{XYZ} = 6$, the ^{35}Cl NQR frequencies for the organosilicon compounds being higher up to $\sum \sigma^*_{XYZ} = 6$ and lower for $\sum \sigma^*_{XYZ} > 6$ than the frequencies for their carbon analogues. Considerably flatter slope of the dependence ν^{77} vs $\sum \sigma^*_{XYZ}$ for the XYZSiCH$_2$Cl (0·308) with respect to that for the XYZCCH$_2$Cl (0·594) was ascribed to lesser ability of the Si—CH$_2$ group to transmit polar effect of X, Y, Z substituents to the chlorine atom. This property of the Si—CH$_2$ group may be related to some extent to the α-effect. An appraisal of a role of the α-effect in lower ability of the Si—CH$_2$ group to transfer polar effect is thus worth-doing.

The correlation between ^{35}Cl—NQR frequencies of R—CH$_2$Cl and Taft σ^* constants of R group has been reported[41]. Earlier derived[36] Taft constants of silyl groups in silylhydrides XYZSi—H allow the ν^{77} values for XYZSiCH$_2$Cl to be got from the correlation. Such obtained ν^{77} values are shown in Table III to deviate from ν^{77} values found experimentally. The deviation is greater with greater $\sum \sigma^*_{XYZ}$ value. The σ^* values of the XYZSi groups were obtained from the force constant of the Si—H bonds of the XYZSi—H compounds and they are assumed to reflect polar effect of silyl groups rather well. The fact that experimental and derived ν^{77} values of XYZSiCH$_2$Cl don't coincide has to be brought about by different polar effect of the silyl groups in XYZSiCH$_2$Cl and XYZSiH species. The α-effect in XYZSiCH$_2$Cl has been demonstrated earlier[14], and the growing difference between both types of ν^{77} has to reflect the diminishing of the extent of the α-effect in XYZSi.

TABLE III
^{35}Cl-NQR Frequenices, ν^{77} in MHz, in XYZSiCH$_2$Cl

XYZSi	ν^{77a}	ν^{77b}	$\Delta\nu^{77c}$	$\sum \sigma^*_{XYZ}{}^d$
F$_3$Si	36·886	37·50	−0·61	9·3
Cl$_3$Si	36·786	35·77	1·02	8·7
Cl$_2$CH$_3$Si	36·108	34·60	1·51	5·8
Cl(CH$_3$)$_2$Si	34·827	33·41	1·42	2·9
(C$_6$H$_5$)$_3$Si	34·715	32·37	2·35	1·8
(CH$_3$)$_3$Si	34·320	32·14	2·18	0·0

[a] Experimental values[40]; [b] derived; [c] ν^{77} derived − ν^{77} experimental; [d] from ref.[40].

.CH_2Cl with increasing electron-withdrawing ability of the substituents bonded to the silicon atom. We can thus conclude that the $ClCH_2$ group increases its electron donating ability with increasing electron donating ability of Y, X, Z groups (structures I and II).

XYZ Si—CH_2⌒Cl   XYZ Si‑ ‑CH_2⌒Cl

I   II
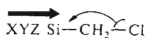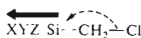
α-effect pronounced   α-effect diminished or extinguished

IR Basicity Data

The IR absorption spectra of hydrogen bonds of phenol interacting with the oxygen containing compounds R—O—Y (Y = alkyl, hydrogen) in CCl_4 have been shown to reflect proton acceptor ability of oxygen and to provide information on polar

TABLE IV

Wavenumber Shift, $\Delta\nu(OH)$ in cm^{-1}, in Phenol IR Spectra Due to Interaction with $XYSi.(OC_2H_5)_2$ and $XSi(OC_2H_5)_3$ in CCl_4

Compound	$\Delta\nu(OH)$	$\sum\sigma^*$
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	271[a]	−0·24
$n\text{-}C_4H_9(CH_3)Si(OC_2H_5)_2$	266[b]	−0·13
$C_2H_5(CH_3)Si(OC_2H_5)_2$	265[b]	−0·10
$(CH_3)_2Si(OC_2H_5)_2$	257[c]	0·0
$Cl(CH_2)_2SiCH_3(OC_2H_5)_2$	239	0·39
$(ClCH_2CH_2)_2Si(OC_2H_5)_2$	206	0·77
$ClCH_2SiCH_3(OC_2H_5)_2$	226[d]	
$n\text{-}C_4H_9Si(OC_2H_5)_3$	247[b]	−0·13
$n\text{-}C_3H_7Si(OCH_5)_3$	245[a]	−0·12
$CH_3Si(OC_2H_5)_3$	237[c]	0·0
$Cl(CH_2)_3Si(OC_2H_5)_3$	232	0·14
$ClCH_2CH_2Si(OC_2H_5)_3$	216	0·39
$Cl_2CHCH_2Si(OC_2H_5)_3$	208	0·69
$ClCH_2Si(OCaH_5)_3$	210	

Ref.[50], [b] ref.[51]; [c] ref.[52]; [d] ref.[53].

effect of the substituents bonded to the oxygen[42,43]. We decided to examine the IR basicity of the organosilicon compounds $(C_2H_5O)_nSi(CH_3)_{3-n}CH_2Cl$, the oxygen atom of those can be looked upon as the indicative center giving information on polar effect of the $ClCH_2$ group. The $\Delta\nu(OH)$ values of phenol due to its interaction with $XYZSiOC_2H_5$ compounds were reported earlier and good linear correlation $\Delta\nu(OH)$ vs $\sum\sigma^*_{XYZ}$ was described[44] for all the compounds with X, Y, or Z groups uncapable of back bonding to the silicon, except $ClCH_2Si(CH_3)_2.OC_2H_5$, the basicity of which deviates upwards from the correlation line. The higher $\Delta\nu(OH)$ of this compound can be ascribed to the decrease of $-I$ effect of the $ClCH_2$ group due to the α-effect.

Analogous correlation $\Delta\nu(OH)$ vs $\sum\sigma^*_{XY}$ or σ^*_X can be constructed also for the $XYSi(OC_2H_5)_2$ and $XSi(OC_2H_5)$ species on the grounds of the data collected in Table IV. (Care has to be taken to include into this correlation only such compounds, the oxygen of those ought to be influenced solely by I effect of the X and Y groups — if this is not so, different slope is got[45]). The slopes of $\Delta\nu(OH)$ vs $\sum\sigma^*$ plot for the ethoxysilanes were read as follows: 62 for $XYZSiOC_2H_5$ (ref.[44]), 64 for XYSi. $.(OC_2H_5)_2$, and 48 for $XSi(OC_2H_5)_3$. The values of σ^* polar constant for the $ClCH_2$ group in $ClCH_2Si(CH_3)_n(OC_2H_5)_{3-n}$ were developed from the corresponding correlations to be 0.57 ± 0.05 ($n = 0$), 0.54 ± 0.05 ($n = 1$) and 0.57 ± 0.05 for $n = 2$. The Taft constant for the $ClCH_2$ group in all $(C_2H_5O)_{3-n}(CH_3)_nSiCH_2Cl$ with $n = 0-2$ was thus estimated to be very similar and always lower than is generally considered (1.05). The α-effect resulting in the decrease of $-I$ effect of $ClCH_2$ group in $(C_2H_5O)_{3-n}(CH_3)_nSiCH_2Cl$ can thus be advanced as possible explanation of the decreased electronwithdrawing ability of the $ClCH_2$ group and it may be assumed to be in all $(C_2H_5O)_{3-n}(CH_3)_nSiCH_2Cl$ of significant importance.

CONCLUSION

Following the theoretical prediction of the mechanism of the α-effect, the manifestation of this interaction in dipole moments of X_3SiCH_2Cl (X = H, CH_3, Cl) by lower value of μ experimental compared to μ calculated is shown to be masked by the increase of μ_{X_3Si} for X = Cl and μ_{Si-C} for X = H. The magnetic shielding of the CH_2 protons in X_3SiCH_2Cl appears to be affected by I effect of the silyl groups.

The ^{35}Cl-NQR frequencies in $XYZSiCH_2Cl$ and proton acceptor ability of the oxygen in $(C_2H_5O)_{3-n}(CH_3)_nSiCH_2Cl$ reflect the operation of the α-effect that results in the increase of the electron density in neighbourhood of the chlorine. The extent of the α-effect decreases with increasing electron withdrawing ability of the substituents bonded to the silicon.

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