

AN INTRAMOLECULAR INTERACTION BETWEEN HALOGEN AND SILICON DISPLAYED IN SOME PHYSICAL PROPERTIES OF SILYLMETHYL HALIDES*

Josef POLA and Václav CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát 2*

Received February 13th, 1978

A discussion of dipole moment and NMR and IR spectral data for silylmethyl halides gathered from literature and obtained in this work is presented. The dipole moments for $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ having $\text{Y} = \text{F}, \text{Cl}, \text{Br},$ and I and NMR spectral data for $\text{X}_3\text{SiCH}_2\text{Y}$ having $\text{X} = \text{CH}_3, \text{H}, \text{C}_2\text{H}_5\text{O}$ and halogen appear to be consonant with the assumption of an intramolecular interaction between the halogen and the silicon. Confirmatory evidence for this interaction in $\text{X}_3\text{SiCH}_2\text{Y}$ is gained by the oxygen basicity in $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{3-n}\text{SiCH}_2\text{Y}$ obtained from the IR spectra of hydrogen bonds of phenol interacting with $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{3-n}\text{SiCH}_2\text{Y}$ in CCl_4 .

Many experimental data reported on silylmethyl chlorides suggest operation of an intramolecular interaction between chlorine and silicon termed the α -effect¹⁻⁵. To date, no detailed study on other silylmethyl halides have been carried out except the work of Bellama³ and MacDiarmid, who suggested that intramolecular interaction between the silicon and the halogen diminishes when going from $\text{H}_3\text{SiCH}_2\text{Cl}$ via $\text{H}_3\text{SiCH}_2\text{Br}$ to $\text{H}_3\text{SiCH}_2\text{I}$. As a continuation of our study of α -carbofunctional organosilicon compounds we discuss in this note dipole moment, NMR, and IR spectral data for $\text{X}_3\text{SiCH}_2\text{Y}$ having $\text{Y} = \text{F}, \text{Cl}, \text{Br}$ and I with the aim to assess a role of the α -effect in these compounds.

EXPERIMENTAL

All the compounds studied of the types $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ and $(\text{C}_2\text{H}_5\text{O})_n(\text{CH}_3)_{3-n}\text{SiCH}_2\text{Y}$ with $n = 1-3$, and $\text{Y} = \text{Br}, \text{I}$, were prepared by usual procedures: iodomethylsilanes were prepared by a treatment of corresponding chloromethylsilanes with sodium iodide in dry acetone, bromomethylsilanes were obtained by the reaction of bromomethyl(chloro)methylsilanes with ethanol in the presence of pyridine or urea in dry diethyl ether. Purity of all the compounds was checked by gas-liquid chromatography and by elemental analysis. Physical constants of new compounds prepared are collected in Table I, and those for the compounds already reported agree with those found in literature. Dipole moments of $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ with $\text{Y} = \text{Br}$ and I were determined

* Part CLVIII in the series Organosilicon Compounds; Part CLVII: This Journal 43, 3179 (1978).

by measuring concentration dependence of the dielectric constant and specific volume of 10^{-2} to 10^{-3} M benzene solutions of these compounds. Dielectric constants were measured by resonance method, using the instrument after LeFèvre and Russel¹¹, and dipole moments were calculated from experimental data according to Halverstadt and Kumler¹². Proton acceptor ability of the oxygen in $(C_2H_5O)_n(CH_3)_{3-n}SiCH_2Y$ was determined from the IR spectra of hydrogen bonds of phenol due to interaction with $(C_2H_5O)_n(CH_3)_{3-n}SiCH_2Y$ in CCl_4 as described¹³.

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 groups or bonds. Provided that the molecular geometry is known, the calculation of dipole moment is carried out by vectorial combination of the partial dipole moments. The deviations of experimental values from those calculated for H_3SiCH_2Y with $Y = Cl, Br, \text{ and } I$ were attributed to nonbonded interaction between the halogen and silicon³. However, the mechanism of the α -effect was proposed¹⁴ to be $n-\sigma + \sigma_{Si-X}^*$ or $n-\sigma + \sigma_{Si-C}^*$ molecular interaction, which might possibly result in an increase in μ_{X_3Si} and/or in μ_{Si-C} values. Provided that the α -effect takes place, the total dipole moment of X_3SiCH_2Y is to be controlled by possible changes in three partial dipole moments μ_{C-Cl} , μ_{Si-C} , and μ_{X_3Si} . An analysis of the effect of the three variables on the dipole moment of X_3SiCH_2Y , μ total, can therefore provide better understanding of dipole moment data.

TABLE I

Yields and Physical Properties of $(CH_3)_3SiCH_2Y$ and $(C_2H_5O)_n(CH_3)_{3-n}SiCH_2Y$

Compound	B.p., °C/Torr	n_D^{20}	Yield, %	Ref.
$(CH_3)_3SiCH_2Br$	117	1.4464	85	6
$(CH_3)_3SiCH_2I$	141	1.4898	65	7
$C_2H_5O(CH_3)_2SiCH_2Br$	151.5	1.4420	63	8
$C_2H_5O(CH_3)_2SiCH_2I$	50/8	1.4807	30	9
$(C_2H_5O)_2CH_3SiCH_2Br$	112/78	1.4368	67	—
$(C_2H_5O)_2CH_3SiCH_2I$	65.5/4.5	1.4698	26	—
$(C_2H_5O)_3SiCH_2Br$	100/30	1.4272	43	—
$(C_2H_5O)_3SiCH_2I$	104/12	1.4572	18	10

The $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ having $\text{Y} = \text{F}, \text{Cl}, \text{Br}$ and I and isotropic trimethylsilyl group were presumed to possess undistorted tetrahedral angles, which was reported only for $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ (ref.¹⁵). A change of only a few degrees in the central angle has been however pointed out to have negligible effect on the molecular dipole moment³. Molecular dipole moments of $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ were calculated by vector addition of these bond moments: $\overrightarrow{\text{Si}-\text{C}}$ (0.6 D), $\overrightarrow{\text{H}-\text{C}}$ (0.3 D), $\overrightarrow{\text{Si}-\text{alkyl}}$ (0.2 D), (all refs¹⁶⁻¹⁸); bond moments $\overrightarrow{\text{C}-\text{F}}$ (1.49 D), $\overrightarrow{\text{C}-\text{Cl}}$ (1.57 D), $\overrightarrow{\text{C}-\text{Br}}$ (1.52 D), $\overrightarrow{\text{C}-\text{I}}$ (1.35 D) used in calculation differ from those customarily used¹⁹ due to the adjustment making $\overrightarrow{\text{C}-\text{Y}}$ moments consistent with molecular dipole moments of CH_3Y compounds¹⁹ and with recently reported¹⁸ value for bond moment $\overrightarrow{\text{H}-\text{C}}$. Calculated and experimental electric dipole moments of $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ are seen from Table II. The experimental values are always higher than those calculated and the difference between them is small - 0.10-0.16 D. Presumed that the intramolecular interaction brings about the decrease in $\mu_{\text{C}-\text{Y}}$, the total dipole moment should diminish as well. Following now the theoretical prediction of the mechanism of the α -effect¹⁴, possible changes of three partial dipole moments $\mu_{\text{C}-\text{Y}}$, $\mu_{\text{X}_3\text{Si}}$, and $\mu_{\text{Si}-\text{C}}$ affect μ_{total} value such as is illustrated in Fig. 1. We mark the values of the partial dipole moment based on those the calculation of μ_{total} was made μ_{standard} . The difference between this quantity and the value of the dipole moment considered to change (due to the α -effect), $\mu^{\text{standard}} - \mu^{\text{changed}}$, is marked as $\Delta\mu$. Fig. 1 then shows the dependence of the calculated molecular moment, μ_{total} , on the changes of partial dipole moments $\Delta\mu$; positive value of $\Delta\mu$ corresponds to the decrease and negative to the increase of the partial dipole moment. (The changes of partial dipole moments influence μ_{total} of all $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ similarly, $(\text{CH}_3)_3\text{SiCH}_2\text{F}$ is therefore arbitrarily taken to demonstrate the μ_{total} vs $\Delta\mu$ plot (Fig. 1)). Fig. 1 shows that a decrease

TABLE II
Electric Dipole Moments, $\mu(\text{D})$, of $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ in Benzene

Y	$\mu^{\text{calc.}}$	$\mu^{\text{exp.}}$	$\mu^{\text{exp.}} - \mu^{\text{calc.}}$
F	1.86	1.98 ^a	0.12
Cl	1.93	2.03 ^b	0.10
Br	1.89	1.99	0.10
I	1.72	1.88	0.16

^a Ref.²⁰, ^b ref.¹.

of the μ_{C-F} diminishes μ_{total} , which can on the other hand be compensated by an increase in μ_{Si-C} and/or μ_{C-H} . The former increase is consonant with $n-\sigma + \sigma_{Si-C}^*$ molecular interaction. Presumed that the α -effect is operative in X_3SiCH_2Y , the unlowered or higher value of experimental dipole moments of $(CH_3)_3SiCH_2Y$ compared to those calculated may thus reflect an important increase in μ_{Si-C} and μ_{C-H} bond moments.

NMR-Spectra

The proton chemical shifts of the methylene group in X_3SiCH_2Y having $Y = \text{halogen}$ bear a linear relationship to the Huggins electronegativity²¹ of the halogen, the fact having already been reported for $X = H$ (ref.²²) and alkyl (ref.²³). We have compiled $\delta(CH_2)$ values of other silylmethyl halides together with those for some of XCH_2Y with $Y = \text{halogen}$. As it is seen from Table III, the methylene proton chemical shift of all XCH_2Y move to higher field as the halogen electronegativity decreases. The $\delta(H)$ increase for the $CH_2(Si)$ protons when going from I to Cl (or F) within all the X_3SiCH_2Y with $X = H, CH_3, C_2H_5O,$ and Cl (Table III) appears to be compatible with the trend of the $\delta CH_2(O)$ values in triethoxysilylmethyl halides (δCH_2O in ppm, $Y: 3.92, Cl$ (ref.²⁷); $3.89, Br$ (ref.²⁷), $3.84, I$ (ref.¹⁰)), but controversial to the trend of the $\delta(CH_3Si)$ protons in trimethylsilylmethyl halides

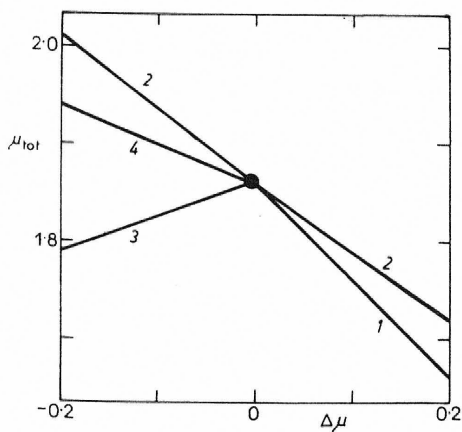


FIG. 1

The Plot of μ_{total} vs $\Delta\mu$ for Trimethylfluoromethylsilane

The curves 1 — 4 relate to the $\Delta\mu_{C-F}$, $\Delta\mu_{C-H}$, $\Delta\mu_{(CH_3)_3Si}$ and $\Delta\mu_{Si-C}$ correspondingly.

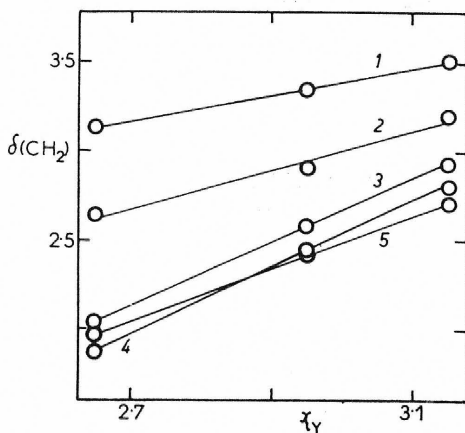


FIG. 2

The Plots of the Proton Chemical Shift $\sigma(CH_2)$ in $X-CH_2Y$ vs Halogen Electronegativity χ_Y

The lines 1—5 relate to the compounds with $X = CH_3, Cl_3Si, H_3Si, (C_2H_5O)_3Si$ and $(CH_3)_3Si$ respectively.

[$\delta(\text{CH}_3\text{Si})$ in ppm, Y: 0.07, F (ref.²⁴); 0.11, Cl (ref.²⁵); 0.13, Br (ref.²⁵); 0.17, I (ref.²⁶).]

The $\delta\text{CH}_2\text{Si}$ values in the trimethylsilylmethyl halides reveal the CH_2 group to be shielded in chloride more, in bromide about equally, and in iodide even less than in corresponding triethoxysilylmethyl halides. Bearing in consideration the isotropic character of both the silyl groups (no influence of a conformational population on the shielding of CH_2 protons) and the greater electron-donating effect of $(\text{CH}_3)_3\text{Si}$ group (Taft σ^* constant for $(\text{C}_2\text{H}_5\text{O})_3\text{Si}$ group can be evaluated on the basis of $\nu(\text{Si}-\text{H})$ for $(\text{C}_2\text{H}_5\text{O})_3\text{SiH}$ (ref.³⁴) and the plot of $\nu(\text{Si}-\text{H})$ vs Taft σ^* constant of silyl groups reported in paper³⁵ to be 0.96) one might explain these data by electronic effect variation of at least one of both the silyl groups, *i.e.* by the fact that polar effect of the silyl group(s) depends on the nature of the halogen. (Trimethylsilyl group acts as if possessing leveling effect (Fig. 2) making the CH_2 protons in $(\text{CH}_3)_3\text{SiCH}_2\text{Y}$ for $\text{Y} = \text{I}$ more acidic and for $\text{Y} = \text{Cl}$ less acidic with regard to those of corresponding $(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{Y}$.) This explanation can gain some support from the variation of polar effect of $(\text{CH}_3)_3\text{Si}$ group when it is bonded to an aromatic system^{36,37} or to $\text{CH}_n\text{Cl}_{3-n}$ group¹ and from recent report on the variation of polar effect of $\text{Cl}_n(\text{CH}_3)_{3-n}\text{Si}$ groups bonded to the oxygen^{38,39}. It can be seen (Table III, Fig. 2) that different slopes of the $\delta(\text{CH}_2)$ vs the halogen electronegativity (χ_Y) plots for silylmethyl halides represent only the case of general phenomenon. The following slopes of the $\delta(\text{CH}_2)$ vs χ_Y plot can be obtained on the grounds of the reported δCH_2 of the XCH_2Y compounds.

TABLE III

¹H — Chemical Shifts, $\delta(\text{H})$ in ppm Units, of XCH_2Y

X	Y			
	F	Cl	Br	I
$\text{H}^{a,b}$	—	2.96	2.59	2.04
$\text{H}_3\text{Si}^{a,b}$	—	2.94	2.58	2.06
$(\text{CH}_3)_3\text{Si}$	4.38 ^{c,d}	2.72 ^e	2.42 ^e	1.97 ^{c,f}
$(\text{C}_2\text{H}_5\text{O})_3\text{Si}$	—	2.82 ^g	2.45 ^g	1.87 ^h
Cl_3Si	—	3.21 ^{c,i}	2.90 ^j	2.65 ^k
CH_3	4.36 ^l	3.52 ^{c,l}	3.36 ^{c,l}	3.15 ^{c,l}
$\text{H}_3\text{Ge}^{b,m}$	—	3.06	2.63	2.10
$(\text{CH}_3)_3\text{Sn}^c$	—	2.87 ⁿ	2.55 ^o	1.90 ^o

^a Ref.²², ^b in cyclohexane; ^c in CCl_4 ; ^d ref.²⁴; ^e ref.²⁵; ^f ref.²⁶; ^g ref.²⁷; ^h ref.¹⁰; ⁱ this work; ^j ref.²⁸; ^k ref.²⁹; ^l ref.³⁰; ^m ref.³¹; ⁿ ref.³²; ^o ref.³³.

1) Organic halides: $\text{H}-\text{CH}_2\text{Y}$, 1.79 (ref.²²); $\text{CH}_3-\text{CH}_2\text{Y}$, 0.74; $\text{C}_2\text{H}_5-\text{CH}_2\text{Y}$, 0.49; $n\text{-C}_3\text{H}_7-\text{CH}_2\text{Y}$, 0.40; $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Y}$, 0.24; $\text{CH}_2=\text{CH}-\text{CH}_2\text{Y}$, 0.20; $\text{Cl}-\text{CH}_2\text{Y}$, 0.58; (all ref.³⁰).

2) Silylmethyl halides: $(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{Y}$, 1.88; $\text{H}_3\text{Si}-\text{CH}_2\text{Y}$, 1.71; $(\text{CH}_3)_3\text{Si}-\text{CH}_2\text{Y}$, 1.48; $\text{Cl}_3\text{Si}-\text{CH}_2\text{Y}$, 1.08 (all based on Table III).

3) Halides with the CH_2 group bonded to other IVb group element: $\text{H}_3\text{Ge}-\text{CH}_2\text{Y}$, 1.86; $(\text{CH}_3)_3\text{Sn}-\text{CH}_2\text{Y}$, 1.92 (both based on Table III).

It can be concluded that the slope of the $\delta(\text{CH}_2)$ vs χ_Y plot for organic halides decreases with increasing polarisability of the alkyl group, the low value for ClCH_2Y compounds reflects evidently the special features of the electronic effect transfer in geminal systems having two electronegative centers with nonbonded electrons (compare⁴⁰). The high value for the $\text{X}_3\text{SiCH}_2\text{Y}$ compounds appears to be general and since the same high values for other organometallic halides $\text{X}_3\text{MCH}_2\text{Y}$ with $\text{M} = \text{Ge}, \text{Sn}$ are observed as well, the reasons responsible for the higher slopes for all $\text{X}_3\text{MCH}_2\text{Y}$ compared to those of alkyl halides could be assumed the same.

The NMR data reported for other centers of $\text{X}_3\text{MCH}_2\text{Y}$ with $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ might be of use to explain the high sensitivity of proton chemical shift of the methylene group in silylmethyl halides to the halogen variation and it may be worthwhile to go throughout them.

Starting with chlorides, significant differences between $^{35}\text{Cl}-\text{NQR}$ frequencies of $\text{RR}'\text{R}''\text{MCH}_2\text{Cl}$ having $\text{M} = \text{Si}, \text{Ge}$ and Sn and those with $\text{M} = \text{C}$ were observed for electron donating R substituents, the difference being diminished when R was becoming more electron withdrawing in the case of $\text{M}=\text{Si}$, but not in the case of $\text{M}=\text{Ge}$ and Sn (ref.⁴). A decreased $\text{C}-\text{Cl}$ bond order in the $\text{RR}'\text{R}''\text{MCH}_2\text{Cl}$ compounds with $\text{M}=\text{Si}, \text{Ge}, \text{Sn}$ was ascribed to the electron transfer from chlorine to the atom M (the α -effect⁴). Further, no relation was found between quadrupole splitting and chemical shift in Moessbauer spectra of $\text{R}_3\text{SnCH}_2\text{X}$ compounds (X is the first row element) and the chemical nature of the substituent X , revealing thus ability of the CH_2 group to insulate the Sn atom of these compounds from the influence of the polar effect variation of the substituents X (ref.⁴¹). The proton chemical shifts, $\delta(\text{CH}_2)$ for the $\text{Cl}_3\text{SnCH}_2\text{Cl}$ and $(\text{CH}_3)_3\text{SnCH}_2\text{Cl}$ differ however noticeably³². The substituent effect of the ClCH_2 group on the ^{29}Si chemical shift varies and depends on the nature of silyl group in the $\text{XYZSiCH}_2\text{Cl}$ (ref.⁴²). Additionally, in spite of the anomalous transmission of the inductive effect of the silyl groups to chlorine⁵, the magnetic shielding of the protons of the CH_2 group appears in these compounds to be consonant with the operation of inductive effect of the silyl group⁵. The ^{119}Sn chemical shift in $(\text{CH}_3)_3\text{SnCH}_{3-n}\text{Y}_n$ with $\text{Y} = \text{Cl}, \text{Br}$ reveal the Sn atom to be always slightly more deshielded in bromide than in chloride (the greater bulk and

polarisability of the bromine was taken for explanation)⁴³. Analogous situation is encountered for silyl compounds as well; the silicon turns out from the ²⁹Si-NMR spectra of (CH₃)₃SiCH₂Y with Y = Cl, Br, to be somewhat more deshielded in trimethylsilylmethyl bromide⁴⁴. ¹H-NMR spectra of the (CH₃)₃SnCH₂F and (CH₃)₃.SnCH₂Cl show the CH₂ group less shielded and the methyl group to be more shielded in the former compound⁴⁵. The proton chemical shifts of the H₃M group in H₃MCH₂Y having Y halogen and M = Si, Ge move with the variation of halogen in the opposite direction when compared to proton chemical shifts of the methylene group^{22,30}. It seems then fair to conclude that the variation of electronic effect of the X group modifies properties of the center Y in the X₃MCH₂Y much less than expected, and the variation of electronic effect of the Y group (change of chlorine for bromine and the like) leads to the negligible changes in magnetic shielding of the M (the case of Si), or it doesn't affect magnetic shielding of this atom (the case of Sn) at all. The interposed CH₂ group and also groups X (CH₃ or H) do experience the above electronic effect variations significantly. The methylene group is thus shown to absorb changes in electronic effect of the adjacent (terminal) molecular parts of X₃MCH₂Y which is hardly to account for by an electron transfer through σ bonds but the consideration of a through space intramolecular interaction, mechanism of which can even vary when going from one compound to another, appears thus reasonable. Proceeding now to the explanation of the different slopes of $\delta(\text{CH}_2)$ vs χ_Y relationship, we make use of the fact that the silyl group has been shown by CNDO/2 and SCFMO calculations to destabilize carbonium cation^{46,47}. The similar action may be also possessed by other X₃Si (or X₃M) groups. Contrarily to the action of alkyl groups (these were reported to stabilize an electron deficient center^{48,49}), the X₃Si (or X₃M) groups can be assumed to increase the electron deficiency on the methylene group of the X₃MCH₂Y compounds, this action being more significant when the halogen electronegativity increases. Such destabilizing action of the X₃M groups should result in a steeper slope of the $\delta(\text{CH}_2)$ vs χ_Y for X₃MCH₂Y when compared to that for alkyl halides and should put the line for the plot of the X₃MCH₂Cl below the line for alkyl halides. The latter is not the case, which suggests another phenomenon increasing relative shielding of the protons of the methylene group in the X₃MCH₂Cl to be operative. It might be an intramolecular interaction between the halogen and the atom M; the $\delta(\text{CH}_2)$ in X₃MCH₂Y should be controlled together with the inductive effect of X₃M group and its destabilizing action also by an extent of the α -effect. Provided that inductive effect of the X₃Si group does not depend on the halogen we may guess the slopes of the $\delta(\text{CH}_2)$ vs χ_Y plots for the X₃SiCH₂Y compounds to be controlled by both the destabilizing action of the X₃Si group and an extent of the intramolecular interaction, these influences being directed against one another.

The IR Basicity Data

The IR absorption spectra of hydrogen bonds of phenol interacting with oxygen of R—O—R' in CCl₄ have been reported to reflect the proton acceptor ability (basicity) of the oxygen and to provide an information on the polar effects of the R and R' substituents^{40,50-51}. An examination of the IR basicity of (C₂H₅O)_n(CH₃)_{3-n}.SiCH₂Y with Y = halogen, the oxygen atom of those can be looked upon as the indicative center giving an information on the polar effect of the YCH₂ group, can be made on the basis of linear relationship between the oxygen basicity [$\Delta\nu(\text{OH})$] and $\sum\sigma^*$ parameter, which was reported earlier^{52,53} for R_nSi(OC₂H₅)_n having R groups exerting solely inductive effect. The earlier obtained parameters of the Taft equation (1)

$$\Delta\nu(\text{OH}) = \rho^* \cdot \sum\sigma^* + C \quad (1)$$

for individual R₁R₂R₃SiOC₂H₅, R₁R₂Si(OC₂H₅)₂, and R₁Si(OC₂H₅)₃ are given in ref.⁵³ and from the linear correlations evaluated inductive effect of YCH₂ group in (C₂H₅O)_n(CH₃)_{3-n}SiCH₂Y is, together with the $\Delta\nu(\text{OH})$ data for these compounds, given in Table IV. All the YCH₂ groups turn out to affect the proton acceptor ability of the oxygen in (C₂H₅O)_n(CH₃)_{3-n}SiCH₂Y by electronwithdrawing action, which is, with regard to the known -I effect of YCH₂ groups in organic compounds, reduced for all *n* and all Y. This reduction of -I effect of all YCH₂ substituents in all

TABLE IV

Wavenumber Shift, $\Delta\nu(\text{OH})$ in cm⁻¹, of Phenol Interacting with the (C₂H₅O)_n(CH₃)_{3-n}SiCH₂Y Compounds in CCl₄ and Appraised Taft Polar Constants of the YCH₂ Groups

<i>n</i>	Y	$\Delta\nu(\text{OH})$	$\sigma_{\text{YCH}_2}^*$ ^a
1	Cl ^b	238	0.57 ± 0.05
	Br	231	0.68 ± 0.05
	I	245	0.45 ± 0.05
2	Cl ^b	226	0.51 ± 0.06
	Br	226	0.51 ± 0.06
	I	230	0.44 ± 0.06
3	Cl ^b	210	0.59 ± 0.09
	Br	210	0.59 ± 0.09
	I	213	0.53 ± 0.09

^a The σ^* 's customarily used for ClCH₂, BrCH₂, and ICH₂ are 1.05, 1.00, and 0.85 respectively⁵⁴.

^b Ref.⁵.

$(C_2H_5O)_n(CH_3)_{3-n}SiCH_2Y$ clearly speaks in favour of intramolecular interaction leading to the transfer of electrons from Y to the silicon.

An intramolecular interaction earlier proposed for silylmethyl chlorides is thus also proved for other silylmethyl halides, despite that confirmatory evidence for its operation in the X_3SiCH_2Y can not be obtained from dipole moment and NMR data.

The authors wish to thank Dr M. Jakoubková for the IR basicity measurement.

REFERENCES

1. Freiser H., Charles R., Speier J., Eagle M.: *J. Amer. Chem. Soc.* **73**, 5229 (1951).
2. Steward O. W., Pierce O. R.: *J. Amer. Chem. Soc.* **83**, 4932 (1961).
3. Bellama J. M., MacDiarmid A. G.: *J. Organometal. Chem.* **24**, 91 (1970).
4. Voronkov M. G., Feshin V. P., Mironov V. F., Mikhailanc J. A., Gar T. K.: *Zh. Obshch. Khim.* **41**, 2211 (1971).
5. Pola J., Chvalovský V.: *This Journal* **42**, 3581 (1977).
6. Speier J. L.: *J. Amer. Chem. Soc.* **73**, 826 (1951).
7. Whitmore F. C., Sommer L. H.: *J. Amer. Chem. Soc.* **68**, 481 (1946).
8. Simmler W., Walz H., Niederprüm H.: *Chem. Ber.* **96**, 1495 (1963).
9. Leitheiser R. H.: *Diss. Abstr.* **17**, 225 (1957).
10. Voronkov M. G., Dyakov V. M., Lukina Y. A., Samsonova G. A., Kudyakov N. M.: *Zh. Obshch. Khim.* **45**, 2010 (1975).
11. LeFèvre R. J. W., Russel P.: *Trans. Faraday Soc.* **43**, 374 (1947).
12. Halverstadt I. F., Kumler W. D.: *J. Amer. Chem. Soc.* **64**, 2988 (1942).
13. Pola J., Chvalovský V.: *This Journal* **38**, 1674 (1973).
14. Ponec R., Chvalovský V.: *This Journal* **40**, 2309 (1975).
15. Hustings J. M., Bauer S. H.: *J. Chem. Phys.* **18**, 13 (1950).
16. Altshuler A. P., Rosenbloom L.: *J. Amer. Chem. Soc.* **77**, 272 (1955).
17. Eaborn C.: *Organosilicon Compounds*, p. 483. Butterworths, London 1960.
18. Rothenberg S.: *J. Amer. Chem. Soc.* **93**, 68 (1971).
19. Minkin V. I., Osipov O. A., Zhdanov Yu. A.: *Dipolnye Momenty v Organicheskoi Khimii*. Khimia, Moscow 1968.
20. Včelák J., Papoušková Z.: Unpublished results.
21. Huggins M. L.: *J. Amer. Chem. Soc.* **75**, 4123 (1953).
22. Bellama J. M., MacDiarmid A. G.: *J. Organometal. Chem.* **18**, 275 (1969).
23. Cavanaugh J. R., Dailey B. P.: *J. Chem. Phys.* **34**, 1099 (1961).
24. Schraml J., Včelák J., Engelhardt G., Chvalovský V.: *This Journal* **41**, 3758 (1976).
25. Cook M. A., Eaborn C., Walton D. R. M.: *J. Organometal. Chem.* **29**, 389 (1971).
26. Köbrich V. G., Nagel R.: *Chem.-Ztg.* **1970**, 984.
27. Voronkov M. G., Feshin V. P., Dyakov V. M., Romanenko L. S., Baryshok V. P., Sigalov M. V.: *Dokl. Akad. Nauk SSSR* **223**, 1133 (1975).
28. Jarvie A. W. P., Rowley R. J.: *J. Organometal. Chem.* **57**, 261 (1973).
29. Dyakov M., Lukina Y., A., Voronkov M. G.: *Zh. Obshch. Khim.* **46**, 2157 (1976).
30. Bowey F. A.: *NMR Data Tables for Organic Compounds*, Vol. 1. Interscience, New York 1967.
31. Bellama J. M., McCormick C. J.: *Inorg. Nucl. Chem. Lett.* **7**, 533 (1971).
32. Kostyanovskii R. G., Prokofiev A. K.: *Izv. Akad. Nauk SSSR* **1968**, 274.

33. Seyferth D., Andrews S. B.: *J. Organometal. Chem.* **30**, 151 (1971).
34. Thompson H. W.: *Spectrochim. Acta* **16**, 238 (1960).
35. Egorov Y. A., Morozov V. P., Kovalenko N. F.: *Ukr. Khim. Zh.* **31**, 123 (1965).
36. Soffer H., DeVries T.: *J. Amer. Chem. Soc.* **75**, 2821 (1953).
37. Soffer H., DeVries T.: *J. Amer. Chem. Soc.* **73**, 5817 (1951).
38. Pola J., Chvalovský V.: *This Journal* **43**, 746 (1978).
39. Pola J., Chvalovský V.: *This Journal* **42**, 484 (1977).
40. Pola J., Chvalovský V.: *This Journal* **43**, 760 (1978).
41. Khranov V. V., Goldanskii V. I., Prokofiev A. K., Kostyanovskii R. G.: *Zh. Obshch. Khim.* **37**, 3 (1967).
42. Schraml J., Včelák J., Chvalovský V.: *This Journal* **39**, 267 (1974).
43. Davies A. G., Harrison P. G., Kenredy J. D., Mitchell T. N., Puddephatt R. J., McFarlane W.: *J. Chem. Soc. C* **1969**, 1136.
44. School R. L., Maciel G. E., Musker W. K.: *J. Amer. Chem. Soc.* **94**, 6376 (1972).
45. Kostyanovskii R. G., Prokofiev A. K.: *Dokl. Akad. Nauk SSSR* **164**, 1054 (1965).
46. Pitt C. G.: *J. Organometal. Chem.* **61**, 49 (1973).
47. Eaborn C., Feichtmayr F., Horn M., Murrell J. N.: *J. Organometal. Chem.* **77**, 39 (1974).
48. Brauman J. I., Blair L. K.: *J. Amer. Chem. Soc.* **92**, 5986 (1970).
49. Kebarle P., Haynes R. N., Collin J. G.: *J. Amer. Chem. Soc.* **89**, 5753 (1967).
50. Koppel I. A., Payu A. I., Pikhil V. O.: *Org. Reactiv.* **10**, 921 (1973).
51. Pola J., Jakoubková M., Chvalovský V.: *This Journal* **40**, 2063 (1975).
52. Míleshkevich V. P., Nikolaev G. A., Karlin A. V., Parshina L. G.: *Org. Reactiv.* **9**, 805 (1972).
53. Pola J., Jakoubková M., Chvalovský V.: *This Journal* **43**, 753 (1978).
54. Zhdanov Y. A., Minkin V. I.: *Korrelacionnyi Analiz v Organicheskoi Khimii*. Izd. Rostov. Univ., Rostov 1966.

Translated by the author (J. P.).