

ORGANOSILICON COMPOUNDS. CI.*

 σ_p CONSTANTS OF SOME SUBSTITUTED SILYL AND GERMYL GROUPS**

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Values of σ_p constants of some substituted silyl and germyl groups of the type XYZM- (X, Y, Z = H, CH₃, F, Cl, Br, OCH₃, N(CH₃)₂; M = Si and Ge) were estimated from dipole moments and from methylic ¹³C—¹H coupling constants in nineteen substituted toluenes of the type *p*-XYZMC₆H₄CH₃; the values derived from the two independent observables are in qualitative agreement. The present estimates of the constants of the silyl groups substituted by electronegative atoms are higher and correspond better to theoretical assumptions than the values derived previously from kinetic measurements. The kinetic measurements yielded lower values apparently because of side reactions of silyl compounds or because of interactions with solvents. The present results indicate electron back-donation in Si—Cl, Si—F and Si—O bonds, the effect being most pronounced in Si—OCH₃ bond. As follows from a comparison of dipole moments, the germyl group —GeH₃ has higher +I effect than the silyl group —SiH₃, which facts suggest that the electronegativity of germanium is lower than that of silicon. In contrast, the —GeCl₃ group exhibits higher —I effect than the SiCl₃ group. This finding can be interpreted by the back-donation being less important for the Ge—Cl bond than it is for the Si—Cl bond.

In our studies of various bonds of silicon and their mutual influence¹ we had attempted to express the polar effects of substituted silyl groups by determining their Hammett δ constants. For this purpose we measured both acidity and the rate constants of esterification of silyl-substituted benzoic acids², and rate constants of bromination of silyl-substituted hydrides of the type XYZ.₂SiC₆H₄(CH₃)₂H. Since the majority of these measurements had to be conducted in highly polar solvents (dimethylformamide, pyridine) it was possible, in some cases, that complexes between silyl derivative and solvent were formed^{3,4}.

Therefore in the present paper we shall attempt to determine more accurate values of σ constants (*i.e.* not affected by solvent interactions and other factors) even, if necessary, at the expense of precision and estimate the values of the constants of some other substituted silyl and germyl groups which were not determined previously. For this purpose other methods which would allow to use non-polar solvents

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not forming complexes with the model compounds were sought. The first of the chosen methods — measurements of dipole moments — was selected despite the known uncertainty in the dipole moments calculated from the dielectric constants (corrections for atom and electron polarisation, neglect of valence angle variations and neglect of mutual interactions of moments of neighbouring bonds) because several successful correlations between dipole moments thus calculated and σ constants had been published⁵⁻⁷. For the second independent method we chose ¹H—NMR spectroscopy. Various NMR parameters have been correlated with σ constants⁸.

Among the correlations which can be used for the determination of the σ constants are the most familiar those described by Taft and coworkers⁹ for ¹⁹F chemical shifts. These correlations had already been exploited to determination of substituent constants of some silyl groups¹⁰. Similar good correlations were described for ¹³C chemical shifts¹¹; our study of ¹³C — NMR spectra of phenylsilanes is under way. Our recent experimental conditions allowed us to measure proton NMR only. Correlations of substituent constants with both proton chemical shifts and coupling constants had been described. Slopes in such correlations are usually smaller than in analogous correlations involving ¹⁹F or ¹³C nuclei. Theoretical interpretation of these empirical correlations is rather unclear except in cases when the observed chemical shift is a measure of a chemical equilibrium. A typical example of a correlation of this latter type is the correlation which holds for chemical shift of carboxylic proton of substituted benzoic acids dissolved in dry pyridine^{2,12}. Apparently due to stronger solvent and concentration dependence and to other factors the correlations involving chemical shifts are usually somewhat worse than those for coupling constants. This is the case of correlations established for chemical shifts and coupling constants ($J(^{13}\text{C}-^1\text{H})$) of protons in methyl groups of *p*-substituted toluenes¹³. Since this type of compounds is also suitable for dipole moment measurements we prepared a series of *p*-tolyl-substituted compounds of silicon and germanium and attempted to apply to them the mentioned correlations. Naturally, the values of substituent constants that will be derived from these correlations must be regarded as rough estimates more or less supplementary to information obtained by other methods.

EXPERIMENTAL

p-Tolyltrichlorosilane was prepared by Grignard synthesis starting from *p*-bromotoluene (680 g) and tetrachlorosilane (679 g) and yielding 513.2 g (57%); b.p. 132°C/17 Torr (lit.¹⁴ 125°C/50 Torr); d_{25}^{25} 1.2774 (lit.¹⁴ 1.283). *p*-Tolylmethylchlorosilane was prepared analogously from methyltrichlorosilane: b.p. 62°C/3 Torr (lit.¹⁵ 161—165°C/7 Torr — obviously in error); d_{23}^{23} 1.1500 (lit.¹⁵ d^{20} 1.2068 — also in obvious error); n_D^{20} 1.5188 (lit.¹⁵ 1.5330). *p*-Tolyl dimethylchlorosilane was prepared analogously from dimethylchlorosilane; the fraction boiling at 80°C/8 Torr was collected (lit.¹⁵ 90°C/10 Torr); d_{23}^{23} 1.0375 (lit.¹⁶ d^{25} 1.00071); n_D^{20} 1.5088 (lit.¹⁶ n_D^{25} 1.5055).

p-Tolyltrimethylsilane was prepared by the reaction of *p*-tolyltrichlorosilane with an excess of methylmagnesium chloride: b.p. 103°C/10 Torr (lit.¹⁷ 190—193°C/756 Torr); d_{23}^{23} 0.9314 (d^{20} 0.8651 (ref.¹⁷)).

p-Tolylmethyl difluorosilane was prepared from 60 g (0.29 mol) of *p*-tolylmethylchlorosilane. *p*-Tolylmethylchlorosilane was cooled and 10% excess of SbF₃ was added while maintaining the reaction mixture at temperature below 90°C and stirring for 3 h. Distillation afforded 49.7 g

(0.288 mol, *i.e.* 96.2%) of fraction boiling at 169°C. In repeated synthesis fraction boiling at 90°C/20 Torr was collected; d_{25}^{25} 1.0691, n_D^{20} 1.4556. For $\text{SiC}_8\text{H}_{10}\text{F}_2$ (172.3) calculated: 16.31% Si, 22.06% F; found: 16.20% Si, 22.13% F.

p-Tolyldimethylfluorosilane was prepared similarly as the previous compound from 56.2 g (0.3 mol) of *p*-tolyldimethylchlorosilane. Fraction boiling at 107–110°C/20 Torr yielded 49.2 g (0.26 mol, *i.e.* 92%) of the product; d_{23}^{23} 0.9639, n_D^{20} 1.4757. For $\text{SiC}_9\text{H}_{13}\text{F}$ (168.3) calculated: 16.69% Si, 11.29% F; found 16.26% Si, 11.31% F. *p*-Tolyltrifluorosilane which was prepared in an analogous way had b.p. 131–135°C (lit.¹⁴ 140°C); d_{23}^{23} 1.1705 (d_{25}^{25} 1.2412 (ref.¹⁴); n_D^{20} 1.4239 (n_D^{25} 1.4742 (ref.¹⁴)).

p-Tolylsilane was obtained by a reduction of *p*-tolyltrichlorosilane by lithium aluminium hydride in 89.7% yield. Fraction boiling at 146.5°C (lit.¹⁸ 147–148°C) was collected; (d^{20} 0.8775¹⁸); n_D^{20} 1.5131 (lit.¹⁸ 1.5112). *p*-Tolyldimethylsilane was prepared in this laboratory earlier¹⁹, the sample was rectified before use.

p-Tolyldimethoxysilane. *p*-Tolyldimethylchlorosilane (70 g, 0.37 mol) was added dropwise to 128 g (4 mol) of absolute methanol into which 8 g (0.37 mol) of finely cut sodium had been added before. The reaction was completed within two hours, the reaction mixture was heated and stirred for additional 3 h. Precipitated salts were removed by centrifugation, distillation of the liquid phase afforded 34.4 g (0.191 mol, *i.e.* 51.7%) of the product boiling at 130–132°C/3 Torr; d_{25}^{25} 1.0463, n_D^{20} 1.4900. For $\text{SiC}_{10}\text{H}_{16}\text{O}$ (180.3) calculated: 15.58% Si, 66.61% C, 8.94% H; found: 15.43% Si, 66.68% C, 8.71% H. *p*-Tolytrimethoxysilane was prepared analogously as the previous compound from 50 g of *p*-tolyltrichlorosilane in the yield 23.3 g (53.9%) as the fraction boiling at 94–95°C/3 Torr (lit.¹⁹ 135–140°C/10 Torr); d_{23}^{23} 0.7453, n_D^{20} 1.4764. *p*-Tolylmethyl-dimethoxysilane was prepared in a similar way as the two previous compounds with a yield of 52% of distillation fraction boiling at 97–98°C/8 Torr (lit.²⁰ 114–116°C/22 Torr); d_{23}^{23} 0.9883 (d^{20} 0.9980 (ref.²⁰); n_D^{20} 1.4825 (lit.²⁰ 1.4820).

p-Tolytribromosilane, prepared earlier¹⁴ was distilled before use.

p-Tolytris(dimethylamino)silane. Dimethylamine (67.5 g, *i.e.* 1.5 mol) and cyclohexane (200 ml) were placed into a three-necked reaction flask equipped with a stirrer, dropping funnel and reflux condenser cooled by a dry ice-ethanol mixture. *p*-Tolyltrichlorosilane (33.7 g, *i.e.* 0.15 mol) was added dropwise at 0°C and the reaction mixture was refluxed for 5 h till the temperature of the reaction mixture reached the boiling point of cyclohexane. Then the precipitated salts were filtered off and the liquid phase distilled affording 28 g of the product. Since the product contained still 2% of chlorine, 25 ml of cyclohexane and 4 g of dimethylamine were added to the product and the mixture was kept at 100°C for 5 h in a sealed ampoule. Rectification following a filtration and distillation afforded 25 g (0.1085 mol, *i.e.* 75.5%) of the desired product boiling at 130°C 3 Torr; d_{25}^{25} 0.9509, n_D^{20} 1.5034. For $\text{SiC}_{13}\text{H}_{25}\text{N}_3$ (251.4) calculated: 11.17% Si; found 11.25% Si.

p-Tolyltrichlorogermane was prepared from 484 g of *p*-bromotoluene and 857.7 g tetrachlorogermane by Grignard synthesis yielding 277 g (25%) of the product boiling at 97–98°C/3 Torr (lit.²¹ 115–116°C/12 Torr); d_{25}^{25} 1.5850, n_D^{20} 1.5601. *p*-Tolylgermane was prepared from *p*-tolyltrichlorogermane (80 g, 0.296 mol) by reducing it in 500 ml of ether with excess lithium aluminium hydride (14.9 g). The reaction mixture was stirred and refluxed for 4 h under nitrogen, then it was poured onto ice and the separated ether layer was dried and rectified. Fraction boiling at 166°C was obtained in the quantity of 20 g (39.8%); n_D^{20} 1.5322. For $\text{GeC}_7\text{H}_{10}$ (166.7) calculated: 43.54% Ge, 50.40% C, 6.05% H; found: 43.21% Ge, 50.31% C, 6.14% H. *p*-Tolytrimethylgermane. 1.1 mol of methylmagnesium bromide dissolved in 750 ml of ether was placed into a three necked

reaction flask and stirred while 67.5 g (0.25 mol) of *p*-tolyltrichlorogermane in 300 ml of dry ether were added dropwise. The reaction mixture was hydrolysed by dilute hydrochloric acid. The organic layer was made neutral and dried; distillation afforded 104.3 g (50%) of fraction boiling at 103°C/19 Torr; d_{25}^{25} 1.0860, n_D^{20} 1.5064. For $\text{GeC}_{10}\text{H}_{16}$ (208.8) calculated: 34.78% Ge, 57.51% C, 7.72% H; found: 34.32% Ge, 57.24% C, 7.79% H.

Dipole moments were determined according to Halverstadt and Kumler²². Concentration dependences of dielectric constants and refractive indices of benzene solutions (benzene for UV spectroscopy, Lachema, dried over molecular sieve 3 Å) were measured in concentration range of 0–0.020 weight fraction. Dielectric constants were measured by resonance method at frequency of 0.5 MHz with a precision $\Delta\epsilon/\epsilon = 1 \cdot 10^{-4}$. Construction and the measuring condenser (approx. volume 25 cm³) employed were described earlier²³. *Refractive indices* of the solutions were measured on a Zeiss immersion refractometer with the precisions of $\pm 2 \cdot 10^{-5}$; mean values of ten consecutive readings were used. Both dielectric constants and refractive indices were measured at the temperature of $25.0 \pm 0.1^\circ\text{C}$. With respect to sensitivity of the majority of the samples to air moisture the solutions were prepared in a dry box. Calculated²⁴ dipole moments of organic standards are assembled in Table I. Relative error is approximately 5 per cent.

σ_p *Constants*. Regression analysis was employed in order to establish a linear correlation between dipole moments and the σ_p constants. Least squares fit²⁵ for the standard compounds of known values of σ_p constants yielded regression line which was subsequently used to estimate σ_p constants of substituted silyl and germyl groups under study. The calculated values of the dipole moments of silyltoluenes and germyltoluenes and the estimates of substituent constants are given in Table II.

¹H NMR *spectra*. For the reasons to be explained later the spectra of the standard and studied compounds were measured under three different experimental conditions. 1) Neat compounds and their CCl_4 solutions were measured under the same conditions as described by Yoder and coworkers¹³ except for addition of 3% (vol.) of CH_2Br_2 to the measured samples. This modification was necessary in order to provide a lock signal for frequency/field stabilisation of the modified Tesla BS 477 spectrometer operating at 60 MHz. 2) Fifty percent solutions of the compounds in hexamethyldisilane containing 3% of CH_2Br_2 were measured on a Varian HA 100. 3) Measurements performed under the same condition as described under 2) except for CH_2Br_2 which was not added. Hexamethyldisilane was prepared from trimethylchlorosilane by condensation reaction with Na/K alloy in a xylene²⁶. Tetrachloromethane (Lachema, p.a.) and dibromomethane (Lachema, chemical purity grade) were dried and stored over molecular sieve Linde 4 Å, the water content was below 4 gamma/ml. Similarly as in the parallel dipole moment study the standard organic molecules were the substituted toluenes of the type *p*-X-C₆H₄-CH₃ with X = H, Cl, Br, I, NO₂, CH₃, and OCH₃.

RESULTS

Dipole moments. Electropositive methyl group in *p*-tolyl-substituted silanes and germanes increases their total dipole moments as compared to the moments of analogous phenyl derivatives (see e.g. the values of the moments of methyl-substituted²⁷ chloro-substituted²⁷, fluoro-substituted²⁸ and alkoxy-substituted²⁸ silanes and germanes²⁹). This is apparently due to an enhancement of electron back donation from benzene ring to silicon or germanium atom. Relative complexity of the substituents does not permit to apply the correlations according to Exner⁴ and therefore the simplest correlation was used, i.e. correlation of uncorrected values of dipole moments

with σ constants. Of course, the estimates of σ_p constants thus obtained are very approximative.

The dipole moments of the studied organic standards depend linearly on the published values of σ_p constants (Table I). The values of calculated correlation coefficient and standard deviation indicate a good linear relationship. The values of σ_p constants derived from the dipole moments for the studied silyl and germyl groups are collected

TABLE I
Dipole Moments of Some *p*-Substituted Toluenes at 25°C in Benzene

Substituent	CH ₃	H	Br	I	NO ₂
μ (D)	0.07	0.60	1.89	1.77	4.46

Correlation with σ constants³² gave slope $\rho = 4.69 \pm 0.58$, intercept $\mu_0 = 0.71 \pm 0.11$, correlation coefficient $r = 0.995$, standard deviation $s_{y,x} = 0.20$.

TABLE II
Dipole Moments of *p*-Silyl- and *p*-Germyl-substituted Toluenes and Calculated σ_p Constants of the Substituents

Substituent	μ , D	σ_p^a	σ_p^b
Si(CH ₃) ₃	0.48 ₅	-0.05	-0.047
Si(CH ₃) ₂ H	0.93	0.05	—
SiH ₃	1.04	0.07	—
Si(CH ₃) ₂ Cl	2.10	0.30	0.022
Si(CH ₃)Cl ₂	2.64	0.41	0.079
SiCl ₃	2.71	0.43	0.198
Si(CH ₃) ₂ F	1.76	0.23	0.170
Si(CH ₃)F ₂	2.60	0.40	0.230
SiF ₃	3.12	0.51	0.011
Si(CH ₃) ₂ OCH ₃	1.27	0.12	-0.020
SiCH ₃ (OCH ₃) ₂	1.55	0.18	0.007
Si(OCH ₃) ₃	1.60 ₅	0.19	0.134
SiBr ₃	1.98	0.27	0.406
Si(N(CH ₃) ₂) ₃	0.96	0.05	—
Ge(CH ₃) ₃	0.4	-0.06	—
GeH ₃	0.77	0.01	—
GeCl ₃	3.51	0.60	—

^a Standard deviation ± 0.05 ; ^b values derived from kinetic measurements³.

in Table II. Despite the fact that this type of correlation neglects both internal moments and charge separation⁴ the values of σ_p constants are quite plausible.

NMR spectroscopy. Measurements of the standard compounds under the conditions 1) reproduced well the values given by Yoder and coworkers¹³, and proved that the added reference compound (dibromomethane) does not affect the studied NMR parameters. Therefore the equations given in the quoted paper can be applied to the values obtained under these conditions and the substituent constants can be estimated. The results shown in Table III indicate, however, that in silyl- and germyl-derivatives the values of coupling constants and chemical shifts do not exhibit the expected trends. Moreover, application of the equations leads to absurd values of substituent constants (*e.g.* $-\text{Si}(\text{CH}_3)_2\text{OCH}_3$ would have σ constant greater than $-\text{NO}_2$ group has *etc.*). Apparently the correlation breaks down in the case of organo-silicon compounds. This may be due to specific solvent effects. Recent findings of Maire³⁰ that the slope of the linear dependence of the coupling constant ($^{23}\text{C}-^1\text{H}$ in the

TABLE III
NMR Parameters of Methyl Protons in *p*-Silyl and *p*-Germyl Substituted Toluenes and Derived σ_p Constants

Substituent	1 ^a		2 ^a	3 ^a	σ_p^d
	ν^b	J^d	J^c	J^c	
SiMe ₃	431.6	127.2	126.1	126.1	0.06
SiHMe ₂	432.3	127.2	126.0	126.1	0.06
SiH ₃	434.2	126.8	126.4	126.2	0.10
SiMe ₂ Cl	428.3	126.2	126.2	126.3	0.15
SiMeCl ₂	427.2	126.0	126.7	126.9	0.42
SiCl ₃	420.3	126.2	127.0	126.8	0.37
SiMe ₂ F	429.9	125.3	126.2	126.3	0.15
SiMeF ₂	428.1	126.7	126.5	126.6	0.28
SiF ₃	425.4	125.9 ^e	127.2	127.1	0.51
SiMe ₂ (OMe)	427.6	128.6 ^e	126.0	126.2	0.10
SiMe(OMe) ₂	423.7	126.7 ^e	126.3	126.3	0.15
Si(OMe) ₃	420.3	125.5 ^e	126.4	126.2	0.10
GeMe ₃	432.6	125.8	125.8	126.00	0.01
GeCl ₃	427.2	128.0	126.9	127.3	0.60

^a For the experimental conditions see Experimental part; ^b chemical shifts in Hz units to lower magnetic field from TMS, converted using the chemical shift of CH_2Br_2 of 285.7 Hz, standard deviation ± 0.3 Hz; ^c coupling constant $J(^{13}\text{C}-^1\text{H})$, standard deviation ± 0.1 Hz unless otherwise stated; ^d Hammett constants estimated from the values of the coupling constants determined under conditions 3); ^e only one satellite could be seen, error approx. ± 0.3 Hz.

methyl group of substituted toluenes) on the substituent constant changes its sign with a change of solvent from CCl_4 to CH_2Cl_2 , lend some support to this assertion. Our search for a suitable solvent was greatly facilitated by a recent work of Cartledge and Riedel³¹ who described a correlation between ^{13}C — ^1H coupling constant of methyl protons and Hammett constants in 50% solutions of *p*-substituted toluenes in hexamethyldisilane. This correlation has a better correlation coefficient ($r = 0.987$) than the original correlation described by Yoder and coworkers¹³. Measurements of the coupling constants in the standard compounds under the conditions 2) and 3) (the conditions 3) were identical to those given in ref.³¹) yielded values that agree within experimental errors with the values reported by Cartledge and Riedel³¹ or with the values calculated according to the correlation from the known values of the substituent constants. The only exception was *p*-methoxytoluene which had under the experimental conditions 2) the coupling constant smaller by 0.8 Hz than calculated, under the conditions 3) its coupling constant fitted the correlation. (A small solvent effect on the ^{13}C isotopic effect on proton chemical shift was also noticed but has not yet been investigated any further.) As it is evident from Table III the values of coupling constant measured under the conditions 2) and 3) differ only little. The values of σ constants were estimated from the coupling constants measured under the conditions 3) according to equation

$$\sigma = -57.212 + 0.45415 J.$$

Correlation coefficient of this correlation is $r = 0.983$ and the standard deviation $s = 0.052$.

DISCUSSION

As it can be seen from Table II and III the highest values of σ_p constants were found, in accord with our expectations, for fluoro- and chloro-substituted derivatives by both dipole moment and NMR methods. According to higher electronegativity of fluorine as compared to that of chlorine (4.0 and 3.0, resp., in Pauling scale³³) dipole moments of fluoro derivatives should be larger than those of corresponding chloro derivatives. In contrast to that monofluoro derivatives has smaller dipole moment than monochloro derivative has, the dihalogeno-substituted compounds have practically the same dipole moments. Only *p*-tolyltrifluorosilane has its dipole moment larger by 0.4 D than is the moment of *p*-tolyltrichlorosilane. Similar trends were found in dipole moments^{27,28} and relative rates of electrophilic aromatic chlorination^{34,35} of phenylfluoro- and phenylchlorosilanes. In both types of compounds $-\text{I}$ effect of halogen strengthens overlap of p_π -orbitals of the aromatic ring with $3d$ orbitals of silicon. This interaction is further increased by increasing the number of halogen atoms bonded to silicon atom. In analogous compounds contain-

ing oxygen bonded to silicon (*e.g.* methoxyderivatives) the $-I$ effect of oxygen is partially compensated by ($p \rightarrow d$)_n character of Si—O bond. Therefore, considerably lower values of dipole moments are encountered in these compounds. Of course, the lowest values of dipole moment have *p*-tolylsilane and *p*-tolyltrimethylsilane which do not contain any electronegative atom. As follows from a comparison of dipole moments of analogous silanes and germanes germyl and trimethylgermyl groups show stronger $+I$ effect than the corresponding groups of silicon. In contrast, trichlorogermyl group shows stronger $-I$ effect than trichlorosilyl group. This can be interpreted by a relatively less important electron back donation in Ge—Cl than in Si—Cl bonds.

The values of σ_p constants determined previously³ for *p*-(CH₃)_{3-n}X_nSi-groups (with X = F, Cl, Br and OCH₃) from the kinetics of bromination of silyl-substituted phenyldimethylsilanes in dimethylformamide were included into Table II for the purpose of comparison. It is evident that the values of σ_p constants are in agreement only in the case of *p*-(CH₃)₃Si-group. The difference between the two values of σ_p constants increases with the increasing number of electronegative substituents attached to silicon atom. This fact can be explained by different interactions with the solvents. While the dipole moment measurements were performed in benzene and NMR in hexamethyldisilane which cannot lower σ_p constants by coordination of electron donors to silicon the kinetics was measured in the solvent capable of such a coordination. Apparently, in the case of polar dimethylformamide, used in the quoted work³, this interaction becomes stronger as the number of electronegative substituents attached to silicon is increased. Since the estimates of σ_p constants from dipole moments are not affected by interactions with benzene they are, despite all the discussed approximations and errors, closer to the true values and correspond better to the bonding situation in the studied compounds than the values determined previously³.

REFERENCES

1. Chvalovský V.: *Pure Appl. Chem.* 13 (1—2), 231 (1966).
2. Plzák Z., Mareš F., Hetflejš J., Schraml J., Papoušková Z., Bažant V., Rochow E. G., Chvalovský V.: *This Journal* 36, 3115 (1971).
3. Mareš F., Plzák Z., Hetflejš J., Chvalovský V.: *This Journal* 36, 2957 (1971).
4. Exner O.: *This Journal* 25, 642 (1960).
5. Cukermann S. V., Čan Kuok Šon V. F.: *Ž. Fiz. Chim.* 40, 160 (1966).
6. Luckij A. E., Obuchova E. M., Češka R. S.: *Ž. Fiz. Chim.* 42, 1861 (1968).
7. Goede E. V., Ibbitson D. A.: *J. Chem. Soc.* 1960, 4265.
8. Emsley J. W., Feeney J., Sutcliffe L. H.: *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. 2. Pergamon Press, Oxford 1966.
9. Taft R. W., Price E., Fox J. R., Anderson K. K., Davis G. T.: *J. Am. Chem. Soc.* 85, 3146 (1963).
10. Kondratenko N. V., Syrova G. P., Popov V. I., Šejker Ju. N., Jagupolskij L. M.: *Ž. Obšč. Chim.* 41, 2056 (1971).

11. Levy G. C., Nelson G. L.: *Carbon-13 Nuclear Magnetic Resonance for Organic Chemistry*, p. 79. Wiley, New York 1972.
12. Kondo Y., Kondo K., Takemoto T., Ikenoue T.: *Chem. Pharm. Bull. (Tokyo)* **14**, 1332 (1966).
13. Yoder C. H., Tuck R. H., Hess R. E.: *J. Am. Chem. Soc.* **91**, 539 (1969).
14. Hradil J., Chvalovský V.: *This Journal* **32**, 171 (1967).
15. Andrianov K. A., Zubkov I. A., Semenova V. A., Michajlov S. I.: *Ž. Prikl. Chim.* **32**, 883 (1959).
16. Lewis D. W., Gainer G. C.: *J. Am. Chem. Soc.* **74**, 2931 (1952).
17. Nametkin N. S., Topčiev A. V., Gu-Chen Li, Leonova M. A.: *Dokl. Akad. Nauk SSSR* **115**, 107 (1957).
18. Hughes M. B.: *Thesis*. Iowa State University, Ames; *Dissertation Abstr.* **19**, 1921 (1959).
19. Hetflejš J., Mareš F., Chvalovský V.: *This Journal* **30**, 1643 (1965).
20. Lasocki Z.: *Bull. Acad. Polon. Sci.* **12**, 281 (1964).
21. Bauer H., Burschkies K.: *Ber.* **66**, 1156 (1933).
22. Halverstadt I. F., Kumler W. D.: *J. Am. Chem. Soc.* **64**, 2988 (1942).
23. Vaisarová V.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1967.
24. Moll F., Lippert E.: *Elektrochem.* **58**, 583 (1954).
25. Felix M. I., Bláha K.: *Matematicko-statistické metody v chemickém průmyslu*. Published SNTL, Prague 1962.
26. Wilson G. R., Smith A. G.: *J. Org. Chem.* **26**, 557 (1961).
27. Vaisarová V., Chvalovský V.: *This Journal* **33**, 859 (1968).
28. Vaisarová V., Chvalovský V.: *This Journal* **34**, 2942 (1969).
29. Vaisarová V., Hetflejš J., Chvalovský V.: *J. Organometal. Chem.* **22**, 395 (1970).
30. Maire J. C.: Private communication.
31. Cartledge F. K., Riedel K. H.: *J. Organometal. Chem.* **34**, 11 (1972).
32. Jaffé H. H.: *Chem. Revs.* **53**, 191 (1953).
33. Pauling L.: *The Nature of the Chemical Bond*, p. 58. Interscience, New York 1940.
34. Lepeška B., Chvalovský V.: *This Journal* **34**, 3553 (1969).
35. Lepeška B., Bažant V., Chvalovský V.: *J. Organometal. Chem.* **23**, 41 (1970).

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Note added in proof: After this paper had been submitted we became aware of the work of J. Lipowitz (*J. Am. Chem. Soc.* **94**, 1582 (1972)) who measured ^{19}F chemical shifts in $p\text{-FC}_6\text{H}_4\text{SiXYZ}$ compounds. His values correlate well ($r = 0.94$) with the σ constants determined here.