Synthesis of $(CH_3)_3SiD$. Diglyme was dried by distillation from lithium aluminum hydride. Over a period of 60 min, trimethylchlorosilane (83.4 g, 0.77 mol) in 100 ml of dry diglyme was added dropwise, under nitrogen, to a stirred solution of lithium aluminum deuteride (0.096 mol) in 200 ml of dry diglyme. The resulting solution was then refluxed under nitrogen for 30 min (cold water condensor) and the volatile product swept into a −78° trap by a slow purge of dry nitrogen. Distillation of the −78° trap material yielded 16.8 g (0.227 mol, 59%) of $(CH_3)_3SiD$. Mass spectral analysis indicated the product was >99.1% d_1. The infrared showed an Si–H absorption whose area was 0.69% of the Si–D absorption area.

Recovery Efficiencies of Allene, Propyne, and Tetramethylsilane from Trimethylsilane. Allene (0.167 mmol), propyne (0.137 mmol), and tetramethylsilane (0.138 mmol) were combined with trimethylsilane (~20 g, ~230 mmol or >1000-fold excess). The mixture was subjected to the normal work-up procedure for carbon vapor reactions with trimethylsilane. Vpc analysis of the appropriate fractions indicated tetramethylsilane was recovered in 88% yield and allene in 3% yield. No propyne was recovered.

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Fluorine-19 Substituent Chemical Shifts of Fluorophenylsilanes. Substituent Effects on Silicon

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Abstract: The ^{19}F substituent chemical shift (SCS) of a series of fluorophenylsilanes, FC_6H_4SiXYZ, have afforded a measure of the inductive and π components in the interaction of the silicon atom with the ring and with the substituents X, Y, and Z. Correlations of high precision have been obtained from (1) para *vs.* meta SCS ($SCS_p = \rho_1 SCS_m + \rho_2$) and (2) from para and meta SCS *vs.* the sum of inductive substituent constants, $\Sigma\sigma_I$, on silicon ($SCS = \rho_1\Sigma\sigma_I + \rho_2$). Substitution of first row donors on silicon, especially trisubstitution, leads to considerable deviations from relations 1 and 2. In the case of substitution with non-first-row donors, the extent of mesomeric interaction of silicon with para fluorine is linearly related to the electron density on silicon resulting from the inductive effects of the substituents X, Y, and Z. Use of a π substituent constant in linear combination with an inductive constant for substituents on silicon affords correlations of high precision for the full range of substituents, including first row donors. Higher precision is obtained using a π *donor* substituent content (eq 9) rather than a general resonance constant (eq 8). The *donor* substituent constant ($\sigma_p^+ - \sigma_p$) appears to be a better measure of donor ability to silicon than does $\sigma_R{}^\circ$ for first-row donors. A large variation in the inductive (or polar) effect of the tris(3,3,3-trifluoropropyl)silyl substituent with solvent has been observed. The SCS of *p*-fluorophenyl(2,2′-2′′-nitrilotriethoxy)silane, in which the electron density on silicon is increased by pentacoordination, is 5.1 ppm more shielded than is *p*-fluorophenyltriethoxysilane.

There has been much recent interest in correlating chemical and physical properties of organosilicon compounds with substituent constants of groups on the silicon atom.[1-6] The Taft σ^* parameter[7] has been most widely used in these correlations, which include infrared stretching frequencies[2a-c] and infrared intensities[2d] of silyl hydrides, rates of halogenation[3] and solvolysis[4] of silyl hydrides, ^1H nmr chemical shifts of silanols[5a] and silyl hydrides,[5b] ^{19}F nmr chemical shifts of fluorosilanes,[5c] and ^{35}Cl nqr frequencies of chlorosilanes.[6] These linear correlations do not necessarily hold for first-row substituents (O, N, F) capable of (p–d)π interactions with silicon.[2a,2c,8] Some correlations are further complicated by anisotropy effects[5a,b] or steric effects[4] of uncertain magnitude. The kinetic methods[3,4] utilized for substituent effect studies are hampered by undesirable side reactions of those first-row substituents which would be expected to exhibit unique properties on silicon.

In view of the need for a sensitive and synthetically accessible probe for the study of substituent effects on silicon, the ^{19}F substituent chemical shift (SCS) of a series of fluorophenylsilanes, FC_6H_4SiXYZ, has been utilized. The SCS has been shown[9,10] to be a sensitive

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probe for measurement of the interactions of a variety of substituents with a fluoro aromatic system.

Experimental Section

Synthesis. *p*- and *m*-fluorobromobenzene, benzyldimethylchlorosilane, and dichloromethyldimethylchlorosilane were obtained from Peninsular Chemical Research, Inc. Other chlorosilanes were readily available. The syntheses followed standard organosilicon preparation methods and are listed in Table I with the properties of the compound prepared.

The reaction of "p-FC_6H_4MgBr" and CH_3SiCl_3 in ether-toluene led to a mixture of p-$FC_6H_4SiCH_3Cl_2$, p-$FC_6H_4SiCH_3ClBr$, and p-$FC_6H_4SiCH_3Br_2$. Halogen exchange reactions between a chlorosilane and a bromo Grignard species or $MgBr_2$ have been reported previously.[11]

Infrared spectra were run in CCl_4 and CS_2 (<1300 cm^{-1}) on a Perkin-Elmer 521 spectrophotometer. Group frequency assignments are based on the correlations of Smith.[12]

The p-FC_6H_4SiXYZ series exhibits characteristic absorptions (± 10 cm^{-1}) at 1590 (s), 1500 (s), 1390 (m), 1305 (m), 1235 (m), 825 (m), 525 cm^{-1} (m). The m-FC_6H_4SiXYZ series absorbs (± 10 cm^{-1}) at 1605 (m), 1575 (s), 1475 (m), 1415 (m), 1405 (m), 1260 (m), 1215 (m), 1105 (w), 520 (m), 440 (w), 425 (w).

Proton nmr spectra were obtained at 20% concentration in CCl_4 on a Varian A-60 instrument. Mass spectral data were obtained on an AEI Model MS-12 spectrometer. Only the *m/e* value of the parent peak is reported. Isotope ratios of the parent peak and the observed fragment peaks are consistent with proposed structures.

^{19}F Substituent Chemical Shifts. SCS measurements were obtained on a Varian HA 56-60 spectrometer at 56.4 MHz on solutions of 5 vol % sample and 10 vol % C_6H_5F in reagent grade cyclohexane. The SCS is defined as the chemical-shift difference between the *p*- or *m*-fluorophenylsilane and internal fluorobenzene and is symbolized as SCS_p or SCS_m, respectively. In some cases it was necessary to use proton spin decoupling (NMR Specialties SD-60B) in order to enhance the signal-to-noise ratio and to provide an internal lock signal of sufficient intensity. SCS parameters in the *m*-fluorophenyl series were obtained using spin decoupling in all cases. The SCS values are insensitive to concentration (Table II) and should be insensitive to impurities in the samples, provided that strong specific interactions between sample and impurity do not occur.[9]

Chemical shifts of fluorine atoms on silicon and in the 3,3,3-trifluoropropyl group have been converted to Φ^* values using a Φ^* value of 113.2 ppm for C_6H_5F,[13,14] and are listed in Table I.

Results

Table II shows the small effect of concentration on the SCS of *p*-fluorophenyldimethylchloromethylsilane. The SCS values of the *m*- and *p*-fluorophenylsilanes in cyclohexane are shown in Table III. Measurements by Taft and Cohen[15] in CCl_4 and West and Harnish[16] in benzene are included in Table III. SCS measurements in cyclohexane, CCl_4, and benzene agree within 0.3 ppm, with the exception of the tris(3,3,3-trifluoropropyl)silane, $Si(Pr_f)_3$. Values for several silanes in solvents of widely different properties are listed in Table IV. The variation in SCS is small except for tristrifluoropropyl substitution. Silanes containing substituent bonds of high polarity (*e.g.*, CF, CCl, SiF) show the largest variations with solvent.

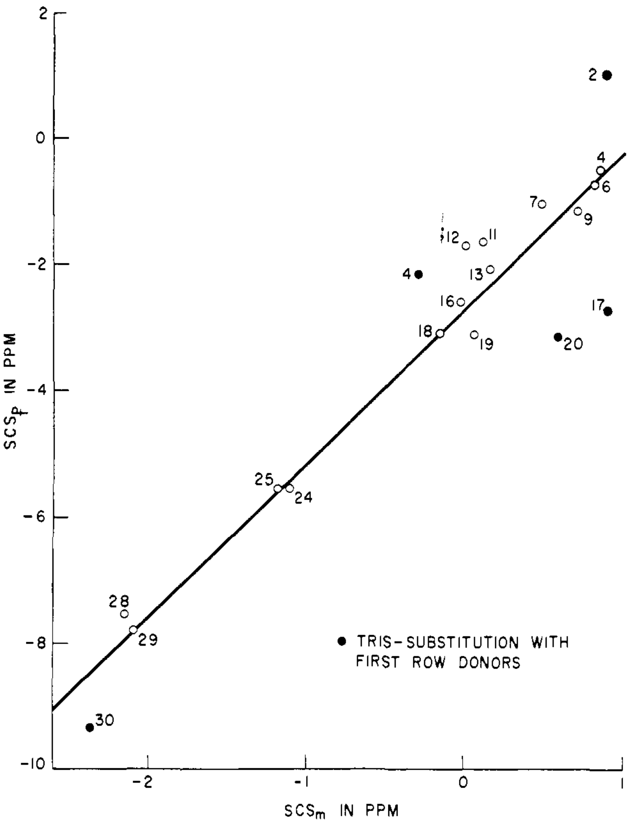

Figure 1. SCS of *p*- *vs.* m-FC_6H_4SiXYZ.

The solvent effects of *p*-fluorophenyltris(3,3,3-trifluoropropyl)silane are unusually large (Table IV) and comparable in magnitude to solvent effects in p-FC_6H_4X, in which X is a highly polar +R substituent such as CN, NO_2, or CF_3.[9b]

An approximate linearity in SCS parameters of the para and meta series is shown in Figure 1. Plots of the SCS values of the fluorophenylsilanes *vs.* the sum of the σ_I values of the substituents on silicon ($\Sigma\sigma_I$) are shown in Figures 2 (para series) and 3 (meta series).

Discussion

SCS Correlations with Inductive Effects of Non-First-Row Donors on Silicon. The SCS of para substituted fluorobenzenes has been interpreted predominantly in terms of mesomeric effects with a lesser contribution resulting from inductive effects.[9b,17] In a family of closely related substituents, a linearity between para and meta shielding parameters is often observed.[9b] Such a correlation in the silane series of slope 2.4 is shown in Figure 1. The substituents showing the largest deviations from linearity in Figure 1 are those in which the silicon atom is substituted with three first-row donor atoms containing p or π electrons, specifically $Si(C_6H_5)_3$, $Si[N(CH_3)_2]_3$, $Si(OCH_3)_3$, $Si(OC_2H_5)_3$, and SiF_3. The C_{sp^2} and N substituents lie above the least-squares line whereas the O and F substituents lie below the line. Both O and F are appreciably more electronegative than is C_{sp^2} or N.[18] In the case of substituents on para sili-

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(14) Some uncertainty in Φ^* will occur due to solvent effects since cyclohexane rather than CCl_3F was used as solvent.

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Table I. Syntheses of $\mathrm{FC_6H_4X}$

X	Method[a]	Bp, °C (P, mm)	Glpc % purity	Ir,[b] cm^{-1}	^{1}H nmr[c]	Mass spectrum[d]	Ref
p-$\mathrm{Si(CH_3)_2H}$	A	156–158	>99	ν_{SiH} 2123	$\mathrm{CH_3}$, 9.70, 6.0, 2 H, 5.56, 0.9, 7 J_{HH} = 3.8		*e*
m-$\mathrm{Si(CH_3)_2H}$	A	165–166	>99	ν_{SiH} 2124	$\mathrm{CH_3}$, 9.67, 6.0, 2 H, 5.59, 1.0, 7 J_{HH} = 4	154	*f*
p-$\mathrm{Si(CH_3)_2Cl}$	B	190–192	82[g]	ν_{SiCl} 492	$\mathrm{CH_3}$, 9.36, 5.5, 1		*h*
m-$\mathrm{Si(CH_3)_2Cl}$	B	110–111 (61)	98[g]	ν_{SiCl} 495	$\mathrm{CH_3}$, 9.35, 5.8, 1	188	
p-$\mathrm{Si(CH_3)_2F}$	C	160–161		ν_{SiF} 880	$\mathrm{CH_3}$, 9.59, 6.2, 2 J_{HF} = 7.2		*i*
m-$\mathrm{Si(CH_3)_2F}$	C	160–162		ν_{SiF} 870	$\mathrm{CH_3}$, 9.55, 6.0, 2 J_{HF} = 7.0	172	
p-$\mathrm{Si(CH_3)_2CHCl_2}$	A	98–102 (3)	97	δ_{CH} 1190, 1130	$\mathrm{CH_3}$, 9.49, 5.5, 1 CH, 4.78, 0.95, 1	236	*j*
m-$\mathrm{Si(CH_3)_2CHCl_2}$	A	86–92 (2)	90[k]		$\mathrm{CH_3}$, 9.66, –, 1 CH, 4.83, –, 1	236	
p-$\mathrm{Si(CH_3)_2C_2H_5}$	A	197–200	92	$\mathrm{SiC_2H_5}$, 1010, 960	$\mathrm{CH_3}$, 9.78, 5.4, 1 $\mathrm{C_2H_5}$, 9.1, 4.9, m		
p-$\mathrm{Si(CH_3)_2OCH_3}$	F	*l*	90[m]	ν_{SiO} 1090	$\mathrm{CH_3}$, 9.67, 6.2, 1 $\mathrm{OCH_3}$, 6.72, 3.2, 1		
p-$\mathrm{Si(CH_3)_2Br}$	B	93–94 (24)	86[g]	ν_{SiBr} 410	$\mathrm{CH_3}$, 9.21, 5.8, 1		
p-$\mathrm{Si(CH_3)_2OCOCH_3}$	G	69–72 (6)	97	$\nu_{\mathrm{C=O}}$ 1713 SiOC, 1220 (sh), 940	$\mathrm{CH_3}$, 9.48, 5.9, 1 $\mathrm{OCH_3}$, 8.01, 2.8, 1		*n*
p-$\mathrm{Si(CH_3)_2(CH_2)_2CF_3}$	A	73 (8)	97	*o*	$\mathrm{CH_3}$, 9.70, 5.8, 1 $\mathrm{SiCH_2}$, 9.1, 2.1, m $\mathrm{CH_2CF_3}$, 8.0, 2.1, m[q]		*p*
m-$\mathrm{Si(CH_3)_2(CH_2)_2CF_3}$	A	101–102 (30)	94[s]	*o*	$\mathrm{CH_3}$, 9.69, 5.8, 1 $\mathrm{SiCH_2}$, 9.1, 2.2, m $\mathrm{CH_2CF_3}$, 8.0, 2.2, m		
p-$\mathrm{Si(CH_3)_2CH_2Cl}$	A	107 (24)	97	$\mathrm{SiCH_2Cl}$, 1175 (sh)	$\mathrm{CH_3}$, 9.86, 6.0, 1 $\mathrm{CH_2}$, 7.40, 2.0, 1		*r*
m-$\mathrm{Si(CH_3)_2CH_2Cl}$	A	109–111 (24)	97[s]		$\mathrm{CH_3}$, 9.60, 5.6, 1 $\mathrm{CH_2}$, 7.14, 1.9, 1		
p-$\mathrm{Si(CH_3)_2CH_2C_6H_5}$	A	75–76 (0.1)	93		$\mathrm{CH_3}$, 9,78, 5.9, 1 $\mathrm{CH_2}$, 7.79, 1.9, 1 $\mathrm{C_6H_5}$, 2.8, 5.0, m		
p-$\mathrm{Si(CH_3)_2CH{=}CH_2}$	A	71–76 (34)	>99	$\mathrm{SiCH{=}CH_2}$, 950, 1005	$\mathrm{CH_3}$, 9.68, 6.3, 1 $\mathrm{CH{=}CH_2}$, 4.1, 3.1, m		
m-$\mathrm{Si(CH_3)_2CH{=}CH_2}$	A	92–93 (32)	97[s]	$\mathrm{SiCH{=}CH_2}$, 950, 1005	$\mathrm{CH_3}$, 9.75, 6.0, 1 $\mathrm{CH{=}CH_2}$, 4.0, 3.0, m		
p-$\mathrm{Si(CH_3)_2C_6H_5}$	A	*t*	98	$\mathrm{SiC_6H_5}$, 1110 (sh)	$\mathrm{CH_3}$, 9.50, 6.3, 1 $\mathrm{C_6H_5}$, 2.8, 5.0, m		*u*
p-$\mathrm{Si(CH_3)_2CH(CH_3)_2}$	E	73–75 (30)	97	$\mathrm{SiCH(CH_3)_2}$, 1470 (sh), 1000, 880	$\mathrm{CH_3}$, 9.78, 6.1, 1 $\mathrm{CH(CH_3)_2}$, 9.06, 7.2[v]		
p-$\mathrm{SiCl_2(C_6H_4F}$-$p)$	A	144–150 (1)	98			288	*w*
p-$\mathrm{SiCl_2CH_3}$	A	88–91 (10)	93[x]	$\nu_{\mathrm{SiCl_2}}$ 555, 495	$\mathrm{CH_3}$, 9.01, 3.1, 1	208	*y*
m-$\mathrm{SiCl_2CH_3}$	A	76 (8)	93[z]			208	*aa*
p-$\mathrm{SiClBrCH_3}$	A	95–98 (10)	71[bb]	ν_{SiClBr} 530, 440	$\mathrm{CH_3}$, 8.87, –, 1	252	
p-$\mathrm{SiBr_2CH_3}$	A	100–110 (7)	34[cc]		$\mathrm{CH_3}$, 8.72, –, 1	296	
p-$\mathrm{SiCH_3(OCH_3)_2}$	D	65–68 (3.5)	99	ν_{SiO} 1080, ν_{OCH} 2840	$\mathrm{CH_3}$, 9.74, 3.0, 1 $\mathrm{OCH_3}$, 6.54, 5.9, 1	200	*dd*
p-$\mathrm{SiF_2CH_3}$	C	*l*	86				
p-$\mathrm{SiCl_3}$	A	82 (9)	>99	$\nu_{\mathrm{SiCl_3}}$ 590, 495		228	*ee*
m-$\mathrm{SiCl_3}$	A	69 (6)	>99			298	*ff*
p-$\mathrm{Si(OCH_3)_3}$	D	78–81 (2)	99	ν_{SiO} 1190, 1090, ν_{OCH} 2840	$\mathrm{OCH_3}$, 6.45, 9.0, 1	216	*gg*
m-$\mathrm{Si(OCH_3)_3}$	D	*l*	98	ν_{SiO} 1190, 1090, ν_{OCH} 2850	$\mathrm{OCH_3}$, 6.45, 9.0, 1	216	
p-$\mathrm{SiF_3}$	C	100–102				180	
p-$\mathrm{Si(OCH_2CH_2)_3N}$	H	195–196.5 (mp) (needles, $\mathrm{CH_3OH}$)			$\mathrm{NCH_2}$, 7.12, 6.0, 3 $\mathrm{OCH_2}$, 6.29, 6.0, 3, J_{HH} = 5.7		*hh*
p-$\mathrm{Si(CH_2CH_2CF_3)_3}$	A	110–115 (1)	98		$\mathrm{SiCH_2}$, 8.9, 6.4, m $\mathrm{CH_2CF_3}$, 8.0, 6.4, m[ii]		*jj*

[a] Synthetic methods: A, addition of "$\mathrm{FC_6H_4MgBr}$" in ether to an ether solution of the chlorosilane (ref 1a, p 10); **B**, halogenation of the silyl hydride in $\mathrm{CCl_4}$ (J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 556 (1950); C, fluorination of the chlorosilane with $\mathrm{SbF_3}$ or $\mathrm{ZnF_2}$ (H. F. Emeleus and C. J. Wilkins, *J. Chem. Soc.*, 454 (1944); D, methoxylation of the chlorosilane with methyl orthoformate (M. S. Schorr, *J. Amer. Chem. Soc.*, **76**, 1390 (1954)); E, alkylation of the chlorosilane with isopropyllithium (ref 1a, p 19); F, methanolysis of the silyl hydride with Pt/C (R. L. Merker and M. J. Scott, *J. Org. Chem.*, **28**, 2717 (1963); G. H. Barnes and N. E. Daughenbaugh, *ibid.*, **31,** 885 (1966); G, reaction of the chlorosilane with sodium acetate (H. A. Schuyten, J. W. Weaver, and J. D. Reid, *J. Amer. Chem. Soc.*, **69,** 2110 (1947)); H, reaction of $\mathrm{FC_6H_4Si(OCH_3)_3}$ and triethanolamine (C. L. Frye, G. E. Vogel, and T. A. Hall, *ibid.*, **83,** 996 (1961)). [b] Cm^{-1}, group

Footnotes to Table I (*Continued*)

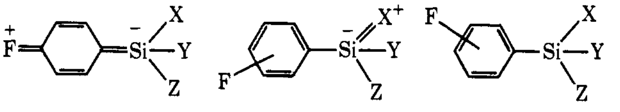
frequency assignments of Smith, ref 12. [c] Assignment, τ value, relative area, multiplicity (m = multiplet). The fluorophenyl signal is centered at τ 2.6–2.8. Integrated areas are relative to a fluorophenyl area of 4. *J* values are in hertz. [d] *m/e* of parent peak. [e] P. Reich and H. Kriegsmann, *Z. Anorg. Allgem. Chem.*, **334**, 272 (1965); bp 45–46.5° (10 mm), n^{20}D 1.4800, ν_{SiH} 2127 (neat). [f] Calcd for $C_8H_{11}FSi$: C, 62.3; H, 7.19; active H, 0.65. Found: C, 63.0; H, 7.11, active H, 0.67. [g] The impurity was identified as $[p\text{-}FC_6H_4(CH_3)_2Si]_2O$ by infrared, ^1H, and ^{19}F nmr spectroscopy. [h] Z. S. Shashkova, K. P. Grinwich, and K. A. Andrianov, *Sov. Plast.*, 18 (1962). [i] Φ^*_{SiF} = 159.0 ppm, Ar*F*/Si*F* = 1.05 (integrated area). [j] Calcd for $C_9H_{11}Cl_2FSi$: C, 45.6; H, 4.68; Si, 11.84. Found: C, 46.6; H, 5.10; Si, 11.40. [k] Impurities are the para isomer and $[Cl_2CH(CH_3)_2Si]_2O$. [l] Flash evaporated at low pressure. [m] The impurity is the corresponding disiloxane. [n] G. Schott and V. Bondybey, *Chem. Ber.*, **100**, 1773 (1967), bp 72–73° (1 mm). [o] Characteristic infrared absorptions for the $Si(CH_2)_2CF_3$ group. [p] Calcd for $C_{11}H_{14}F_4Si$: C, 52.8; H, 5.64. Found: C, 52.7; H, 5.96. [q] $\Phi^*_{CF_3}$ = 69.9 ppm, CF_3/Ar*F* = 3.1 (integrated area). [r] S. G. Mairanovskii, V. A. Ponomarenko, N. V. Baroshkova, and M. A. Kadina, *Izv. Akad. Nauk USSR, Ser. Khim.*, 1951 (1964), bp 74–76° (2 mm), n^{20}D 1.5042. [s] The impurity is the para isomer. [t] Purified by preparative glpc. [u] Reference 16, p 42, n^{25}D 1.5447. [v] The chemical shifts of the methine and methyl protons of the isopropyl group on silicon are almost identical. At 50-Hz sweep width, two singlets of unequal height can be observed. [w] Reference 15, p 117, bp 102–110° (1 mm). [x] Impurity is $p\text{-}FC_6H_4SiCH_3ClBr$, identified by ^1H nmr and mass spectroscopy. [y] K. A. Andrianov, I. A. Zubkov, K. P. Grinevich, Z. S. Shashkov, and M. A. Kleinovskaya, *J. Gen. Chem. USSR*, **30**, 3345 (1960), bp 196–198° (758 mm), n^{20}D 1.5050. [z] The major impurity is $m\text{-}FC_6H_4SiCH_3ClBr$, identified by mass spectroscopy. [aa] G. N. Mal'nova, E. P. Mikeev, A. L. Klebanskii, and N. P. Filimonova, *Dokl. Chem.*, **123**, 693 (1958). [bb] Impurities are $p\text{-}FC_6H_4SiCl_2CH_3$ (17 mol %) and $p\text{-}FC_6H_4SiBr_2CH_3$, identified by ^1H nmr and mass spectroscopy. [cc] Impurities are $p\text{-}FC_6H_4SiCl_2CH_3$ (8 mol %) and $p\text{-}FC_6H_4SiClBrCH_3$ (58 mol %). [dd] Calcd for $C_9H_{13}FO_2Si$: C, 54.0; H, 6.54; Si, 14.0. Found: C, 54.2; H, 6.52; Si, 14.0. [ee] Reference 15, bp 40–42° (1 mm). [ff] Calcd for $C_6H_4Cl_3FSi$: Cl, 46.3. Found: Cl, 46.0. N. G. Maksimova and V. F. Mirnov, USSR Patent 183,746 (1966); *Chem. Abstr.*, **66**, 38044 (1967), bp 74° (10 mm). [gg] Calcd for $C_9H_{13}FO_3Si$: C, 50.0; H, 6.06; Si, 13.0. Found: C, 50.2; H, 6.12; Si, 13.0. [hh] Calcd for $C_{12}H_{16}FNO_3Si$: C, 53.5; H, 5.99; N, 5.20. Found: C, 53.4; H, 6.14; N, 5.14. [ii] $\Phi^*_{CF_3}$ = 69.7 ppm, CF_3/Ar*F* = 9.0 (integrated area). [jj] Calcd for $C_{15}H_{16}F_{10}Si$: C, 43.5; H, 3.89; Si, 6.78. Found: C, 45.0; H, 4.18; Si, 6.60.

Table II. Effect of Concentration on the SCS of $p\text{-}FC_6H_4Si(CH_3)_2CH_2Cl$

X^a	SCS_P, ppm
90	−2.07
45	−2.07
10	−2.06
8	−2.07
5	−2.07

[a] *X* vol % sample, 10 vol % C_6H_5F, (90 − *X*) vol % cyclohexane.

con which do not contain p or π electrons, the mesomeric structure **1** is expected to make a large contribution to the shielding parameter.[9b]



1 2 3

Evidence for a (p–d)π interaction of aromatic C_{sp^2} and Si, which is enhanced by R groups in the para position (**1**), has been established by dipole moment studies,[19] acidities of benzoic acids, phenols, and anilines,[20] reactivities,[20,21] ^{19}F nmr,[9b,10b,15,16] ^1H nmr,[5a] and ultraviolet measurements.[22] A similar (p–d)π interaction in vinylsilanes has been invoked to explain anti-Markovnikov additions,[23] anomalous spectroscopic measurements,[24] ionization potentials,[25] and reduction potentials.[26]

The perturbation of the mesomeric interaction **1** introduced by substitution of first-row donors on silicon, involving participation of the silicon d orbitals as electron acceptors, should be most pronounced upon trisubstitution. This (p–d)π interaction with first-row

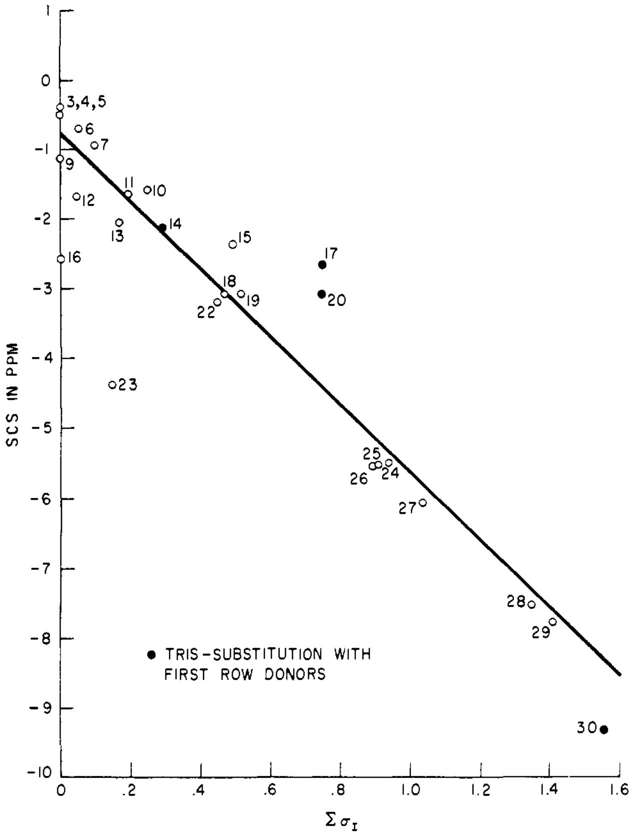


Figure 2. SCS of $p\text{-}FC_6H_4SiXYZ$ *vs.* $\Sigma\sigma_I$.

(19) J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Amer. Chem. Soc.*, **71**, 2923 (1949); H. Soffer and T. DeVries, *ibid.*, **73**, 5817 (1951); A. M. Coleman and H. Freiser, *ibid.*, **83**, 4130 (1961); E. L. Reilly, C. Curran, and P. A. McCusker, *ibid.*, **76**, 3311 (1954); H. Freiser, M. V. Eagle, and J. L. Speier, *ibid.*, **75**, 2821 (1953).

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(26) H. Bock and H. Alt, *Angew. Chem., Int. Ed. Engl.*, **6**, 941 (1967).

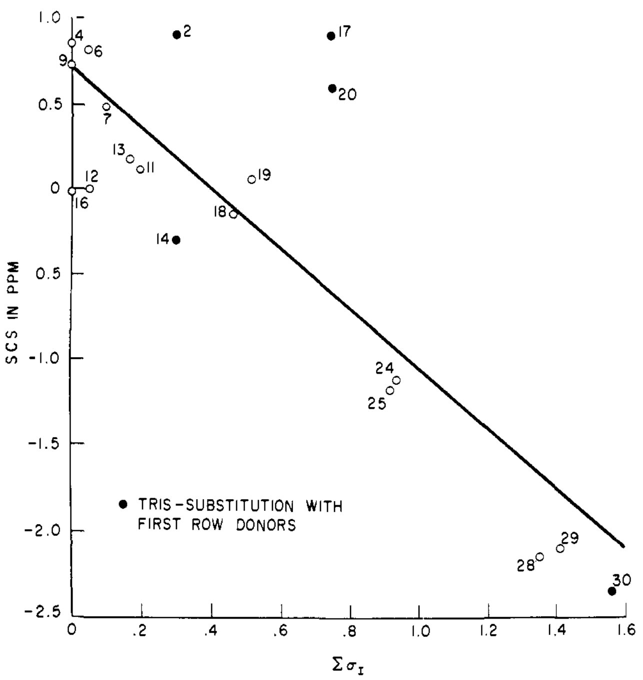

Figure 3. SCS of *m*-FC_6H_4SiXYZ *vs.* $\Sigma\sigma_I$.

Table III. ^{19}F SCS of FC_6H_4SiXYZ[a]

No.[b]	SiXYZ	SCS_p[c]	SCS_m[c]
1	$Si\text{-}(OCH_2CH_2\text{-})_3N$	+2.43[d]	
2	$Si[N(CH_3)_2]_3$	(+0.99)[e]	(+0.90)[e]
3	$Si(CH_3)_2C_2H_5$	−0.43	
4	$Si(CH_3)_3$	(−0.50)[e]	(+0.85)[e]
5	$Si(CH_3)_2CH(CH_3)_2$	−0.50	
6	$Si(CH_3)_2CH{=}CH_2$	−0.73 (−0.85)[h]	+0.82
7	$Si(CH_3)_2C_6H_5$	−0.96 (−1.06)[f]	(+0.48)[f]
8	$Si(CH_3)_2CH_2C_6H_5$	−0.98	
9	$Si(CH_3)_2H$	−1.16	+0.72
10	$Si(CH_3)_2OCH_3$	−1.60	
11	$SiCH_3(C_6H_5)_2$	(−1.63)[f]	(0.11)[f]
12	$Si(CH_3)_2(CH_2)_2CF_3$	−1.70	0
13	$Si(CH_3)_2CH_2Cl$	−2.07	+0.16
14	$Si(C_6H_5)_3$	(−2.13)[f]	(−0.30)[f]
15	$SiCH_3(OCH_3)_2$	−2.43	
16	SiH_3	(−2.60)[e]	(−0.02)[e]
17	$Si(OC_2H_5)_3$	(−2.70)[e]	(+0.90)[e]
18	$Si(CH_3)_2Cl$	−3.08	−0.15
19	$Si(CH_3)_2F$	−3.09	+0.06
20	$Si(OCH_3)_3$	−3.12	+0.59
21	$Si(CH_3)_2CHCl_2$	−3.22	
22	$Si(CH_3)_2Br$	−3.23	
23	$Si[(CH_2)_2CF_3]_3$	−4.39	
24	$SiCH_3Cl_2$	−5.52	−1.11
25	$SiCH_3ClBr$	−5.53	−1.18
26	$SiCH_3Br_2$	−5.56	
27	$SiCH_3F_2$	−6.08	
28	$SiBr_3$	(−7.55)[e]	(−2.15)[e]
29	$SiCl_3$	−7.79 (−7.90)[e]	−2.10 (−2.10)[e]
30	SiF_3	−9.32 (−9.57)[g]	(−2.35)[g]

[a] 5 vol % sample, 10 vol % C_6H_5F, in cyclohexane. [b] Compound number, used in Figures 1–3. [c] SCS in parts per million (±0.02) with respect to internal fluorobenzene. [d] In acetone. [e] Reference 15; in CCl_4. [f] Reference 16; in benzene. [g] Private communication from Professor R. W. Taft; in CCl_4. [h] Reference 101; in cyclohexane.

donors has been extensively reviewed.[1a,27] Thus, additional resonance interactions, **2**, should appreciably contribute to the ground state of C_{sp^2}, N, O, and F substituents and perturb the linearity of the σ_I–σ_R relationship of the SiXYZ group, destroying the linearity of the para–meta shielding relationship. The weakly inductively withdrawing first-row substituent, dimethylamino, appears to increase electron density on Si (relative to CH_3 on Si) upon trisubstitution. That is, the "backbonding" effect of this group more than compensates for its inductive withdrawing effect.

Structure **3** is intended to represent the inductive effects operable through the Si-X and Si-Y and Si-Z bonds and transmitted to the fluorine atom by an inductive or polar mechanism. The effect on SCS_p as a result of this inductive or polar effect should be smaller than that resulting from the mesomeric effect.[9] The combined inductive effect of the substituents will affect the magnitude of the larger (p–d)π mesomeric effect, **1**, in the case of para substitution by a perturbation of electron density on the silicon atom. That is, a decrease of electron density on the silicon atom as a result of inductively withdrawing substituents will tend to contract the atomic d orbitals and thus increase overlap with the aromatic π system.[28] This implies a correlation between the inductive (σ_I) and resonance (σ_R) parameters of the SiXYZ group (eq 1). Furthermore, a correlation between the sum of the inductive effects of the substituents X, Y, and Z ($\Sigma\sigma_I$) with σ_I for the SiXYZ group as a whole is implied (eq 2).[29] Since the meta shielding parameter is believed to be predominantly a measure of the inductive effect of the SiXYZ group[9a] (eq 3) and the para shielding parameter is composed of inductive and mesomeric components[9b] (eq 4), a linear relationship between σ_I and σ_R (eq 1) will result in a linear relationship between the para and meta SCS (eq 5). The generality of linear para *vs.* meta relationships in closely related families of substituents is a consequence of linear $\sigma_I - \sigma_R$ relationships resulting from common interaction mechanisms.[9b,10b,31]

$$\sigma_R = a\sigma_I + b \qquad (1)$$

$$\sigma_I = c\textstyle\sum\sigma_I + d \qquad (2)$$

$$SCS_m = -7.1\sigma_I + 0.6 \qquad (3)$$

$$SCS_p = -29.5\sigma_R + SCS_m \qquad (4)$$

$$SCS_p = (4.16a + 1)SCS_m - (2.49a + 29.5b) \qquad (5)$$

The deviations of the silanes substituted with C_{sp^2}, N, O, or F substituents from this linear relationship may then result from significant "backbonding" interactions of these substituents with silicon. That is, the proportionality between the mesomeric interaction of SiXYZ with aromatic fluorine (the major contributor

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(27) (a) Reference 1b, Chapter 1; (b) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 228; (c) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955); (d) E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements," Vol. I, Part I, A. G. McDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, Chapter I.

(28) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954); D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956).

(29) Aliphatic σ_I values are given by Ritchie and Sager.[30] A σ_I value of 0.05 for 3,3,3-trifluoropropyl was calculated from σ_I of CF_3, using an attenuation factor of 2.8 per methylene group. The σ_I value of isopropyl was assumed to be 0, as for the methyl and ethyl substituents.

(30) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964).

(31) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961); N. L. Bauld, Abstracts, 139th National Meeting of the American Chemical Society, March 1961, p 21-O; C. Y. Meyers, B. Cremonini, and L. Maioli, *J. Amer. Chem. Soc.*, **86**, 2944 (1964).

Table IV. Solvent Effects on the SCS of p-FC_6H_4SiXYZ[a]

XYZ	Cy[b]	CCl_4	$CHCl_3$	Dioxane	CH_3CN	DMSO[c]	C_6H_6	85% aq acetone
$(CH_3)_2(CH_2)_2CF_3$	−1.70	−1.79	−1.65	−1.38	−1.41			
$(CH_3)_2CH_2Cl$	−2.07	−2.23	−2.21	−1.91	−2.08	−1.92		
$(CH_3)_2CH{=}CH_2$	−0.73	−0.74	−0.88	−0.84	−0.99	−1.06	−0.92	−1.10
$(CH_3)_2CH_2C_6H_5$	−0.98	−1.09	−1.03	−0.90	−1.10	−1.06	−1.04	−1.18
$(CH_3)_3$	(−0.50)[d]	(−0.50)[d]						
$(CH_3)_2C_6H_5$	−0.96						−1.06 (−1.06)[e]	
Cl_3	−7.79	(−7.90)[f]						
F_3	−9.32	(−9.57)[g]						
$(CH_2CH_2CF_3)_3$	−4.39	−4.53	−4.24	−3.34	−2.97	−2.59	−3.88	−3.15

[a] 5 vol % sample + 10 vol % C_6H_5F. [b] Cyclohexane. [c] Dimethyl sulfoxide. [d] Reference 9b. [e] Reference 16. [f] Reference 15. [g] R. W. Taft, private communication.

Table V. Correlations of the SCS of FC_6H_4SiXYZ

Correlation[a]	N[b]	Coefficients ρ_1	ρ_2	ρ_3	SD[c]	r[d]	Δ[e]	RMS[f]
$SCS_p = \rho_1 SCS_m + \rho_3$	19	+2.44		−2.70	0.94	0.941	10.31	4.18
$SCS_p = \rho_1 SCS_m + \rho_3$	14[g]	+2.44 (+2.66)[k]		−2.53 (−2.32)[k]	0.40	0.987	7.29	3.94
$SCS_p = \rho_1 \Sigma\sigma_I + \rho_3$	27	−4.86		−0.76	1.08	0.907	10.31	4.01
$SCS_p = \rho_1 \Sigma\sigma_1 + \rho_3$	20[g−i]	−5.10 (−5.10)[k]		−0.68 (−0.73)[k]	0.35	0.989	7.36	3.86
$SCS_m = \rho_1 \Sigma\sigma_I + \rho_3$	19	−1.75		+0.71	0.59	0.837	3.25	1.06
$SCS_m = \rho_1 \Sigma\sigma_I + \rho_3$	13[g,i]	−1.96 (−1.92)[k]		+0.66 (+0.60)[k]	0.24	0.973	3.00	1.03
$SCS_p = \rho_1 \Sigma\sigma_I + \rho_2 \Sigma\sigma_R{}^0 + \rho_3$	21	−5.26	−2.69	−2.53	0.51	0.984	10.31	4.16
$SCS_m = \rho_1 \Sigma\sigma_I + \rho_2 \Sigma\sigma_R{}^0 + \rho_3$	13	−2.03	−1.24	0	0.33	0.970	3.25	1.19
$SCS_p = \rho_1 \Sigma\sigma_1 + \rho_2 \Sigma(\sigma_p{}^+ - \sigma_p) + \rho_3$	22	−4.66	−1.75	−2.27	0.26	0.996	10.31	4.26
$SCS_m = \rho_1 \Sigma\sigma_1 + \rho_2 \Sigma(\sigma_p{}^+ - \sigma_p) + \rho_3$	13	−1.67	−0.71	+0.06	0.39	0.955	3.25	1.17
$SCS_m = \rho_1 \Sigma\sigma_I + \rho_2 \Sigma(\sigma_p{}^+ - \sigma_p) + \rho_3$	12[j]	−1.74	−0.51	−0.11	0.18	0.991	3.25	1.19

[a] Summation is over the substituents X, Y, Z. [b] Number of points. [c] Standard deviation. [d] Correlation coefficients. [e] Total range of the SCS (parts per million). [f] Root-mean-square SCS. [g] Excluding trisubstituted first-row donors. [h] Excluding the tris(3,3,3-trifluoropropyl)silane point. [i] Excluding the SiH_3 point. [j] Excluding the trimethoxysilane point. [k] Calculated.

to SCS_p) and the inductive or polar effect of SiXYZ (the major contributor to SCS_m) will be perturbed by (p–d)π interactions with first-row donors on silicon. This perturbation is most pronounced in the cases of substitution by three first-row donors on silicon. The linear correlation between the para and meta SCS is shown in Table V. Elimination of the five trisubstituted first-row donor points results in a significantly improved correlation. The correlation coefficient increases from 0.941 to 0.987, and the statistical criteria of fit used by Taft,[10e] SD/RMS, decreases from 0.225 to 0.101.

Using eq 1–4, linear relationships (eq 6 and 7) between the meta or para SCS and $\Sigma\sigma_I$, for non-first-row donors on Si, can be derived.

$$SCS_m = -7.1c\sum\sigma_I - 7.1d + 0.6 \qquad (6)$$

$$SCS_p = (-29.5ac - 7.1c)\sum\sigma_I - (29.5ad + 29.5b + 7.1d - 0.6) \qquad (7)$$

Equations 5, 6, and 7 have been derived from the Taft[9] equations (3 and 4), the necessary condition (eq 1) for linearity in the para *vs.* meta series, and the assumed equation, 2. The coefficients of eq 5, 6, and 7 can be equated to the least-squares coefficients (ρ_i) obtained from SCS values for the analogous equations in Table V. Coefficients of least-squares equations which exclude trisubstituted first-row donor points have been used. Six equations in four parameters (a–d) are thus generated.

Good agreement with least-squares coefficients (ρ_i) in Table V can be obtained with $d = 0$ and the following values: $a = 0.40$, $b = 0.045$, $c = 0.270$. The calculated coefficients (Table V) are within 10% of experimental coefficients. Thus, the assumption of linearity between σ_I of the SiXYZ group and $\Sigma\sigma_I$ of the substituents X, Y, and Z (eq 2) is valid as a first approximation, with $\sigma_I = 0.27\Sigma\sigma_I$. The assumption holds with greatest precision for substituents which do not include first-row donor atoms bonded to silicon. Greater deviations progressively occur as one, two, and three first-row donors are bonded to silicon. In the case of trisubstitution, deviations from linearity increase in the order $C_6H_5 < F < OCH_3 < N(CH_3)_2$. Linear relationships with $\Sigma\sigma_I$ are shown in the para (Figure 2) and meta (Figure 3) series, with trisubstituted first-row donors showing the largest deviations from linearity. The statistical fits of these correlations are shown in Table V. The correlation with $\Sigma\sigma_I$ is significantly improved in the para and meta series by exclusion of the trisubstituted first-row donors. The correlation coefficient in the para series increases from 0.907 to 0.989 and SD/RMS decreases from 0.269 to 0.091. The tris(3,3,3-trifluoropropyl)silane point has been excluded for reasons that will be explained in the subsequent discussion. The correlation coefficient in the meta series is improved from 0.837 to 0.973 and SD/RMS decreases from 0.56 to 0.23. Although the latter SD/RMS value is not good by Taft's criteria,[10e] the SD of 0.24 ppm is approximately the SCS variation to be expected for moderately polar substituents in the meta series in the solvents cyclohexane, carbon tetrachloride, and benzene.[9a]

Correlations Including First-Row Donors. The statistical fit to the two-parameter Taft[10e] eq 8 with inclusion of trisubstituted first-row donors is improved (Table V) over eq 6 and 7 in that the $\sigma_R{}^0$ parameter, which is highly negative for the first-row donors F, O, and N, provides an additional degree of freedom. The correlation coefficients and SD/RMS values in the para and meta series are 0.984, 0.125 and 0.970, 0.277, respectively. The corresponding values in the correlation with $\Sigma\sigma_I$ are 0.907, 0.270 and 0.837, 0.556, respectively.

$$\mathrm{SCS} = \rho_1 \sum \sigma_I + \rho_2 \sum \sigma_R{}^0 + \rho_3 \qquad (8)$$

The (p–d)π interaction of substituents on silicon has invariably been formulated as one in which the substituent functions as an electron *donor*. A parameter which reflects the ability of a substituent to function only as a π donor is the parameter $\sigma_p{}^+ - \sigma_p$, used in the Yukawa–Tsuno equation.[32] The fit to a linear combination of σ_I and $\sigma_p{}^+ - \sigma_p$ (eq 9) is shown in Table V. The values of $\sigma_p{}^+$ and σ_p used are those listed by Leffler and Grunwald.[33] The standard deviation of eq 9 in the para series is of the same order as the variation in SCS with solvents used in this series. In the meta series, the $Si(OCH_3)_3$ substituent deviates to a much greater extent than do the other substituents. The standard deviation without incorporation of this point is within the variation in SCS with solvent. Use of eq 9 in the para series offers a substantial improvement in precision over the Taft equation (8) which uses the same number of dependent variables. A marked improvement is obtained over eq 8 in the meta series with exclusion of the $Si(OCH_3)_3$ substituent.

$$\mathrm{SCS} = \rho_1 \sum \sigma_I + \rho_2 \sum (\sigma_p{}^+ - \sigma_p) + \rho_3 \qquad (9)$$

The Magnitude of the (p–d)π Effect. Although the concept of (p–d)π interaction between first-row donors (and possibly second-row donors) and silicon is well established, the magnitude of the effect in the ground state is uncertain.[27] Recent evidence, summarized by Ebsworth,[27d] indicates that stabilization energies resulting from ground-state (p–d)π interactions are quite small. That is, thermodynamic properties and bond energy measurements indicate little, if any, stabilization attributable to (p–d)π effects. On the other hand, reaction rates, equilibrium constants, and low-energy spectroscopic effects which are markedly affected by small energy changes show substantial effects attributable to (p–d)π interactions.

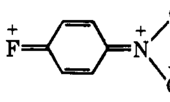
The SCS results are compatible with a small ground-state contribution from the (p–d)π mesomeric effect (**1**). The similarity of the para and meta SCS of the tris(dimethylamino)silanes indicates little, if any, contribution of mesomeric structure **1** to the ground state of *p*-fluorophenyltris(dimethylamino)silane. Using the approximate relationship (eq 10) between SCS and π charge[9b] and the total range of the para and meta SCS, the total change in π charge density on the fluorine atom [$\Delta q_{(F)}$] is less than 0.01 in the silane series.

$$\mathrm{SCS_p} = \mathrm{SCS_m} - 1200\Delta q_{(F)} \qquad (10)$$

Thus, the contribution of mesomeric structure **1** to the ground-state description of the silanes is small in all cases, although **1** is expected to make a predominant contribution to the para SCS.

A Large Solvent Effect in Tris(3,3,3-trifluoropropyl)silane. The non-first-row donor 3,3,3-trifluoropropyl (Pr_f) substituent exhibits a large deshielding effect in the para trisubstituted silane (Figure 2). This is the only substituent for which a large deshielding effect (−2.9 ppm) is observed in the para series over that predicted from the $\Sigma\sigma_I$ value.

The large solvent effects (Table IV) observed for this compound are comparable in magnitude to those observed by Taft[9b] for molecules containing +R substituents (CN, NO, NO_2) in which dipolar resonance forms such as **4** are expected to make large ground-state contributions. The observed decrease in shielding with increasing solvent polarity observed by Taft was attributed to an increase in the ground-state contribution of dipolar resonance forms such as **4** in polar solvents. The aromatic F of the tristrifluoropropylsilane exhibits solvent effects in the opposite sense. That is, a decrease in shielding occurs with decreasing solvent polarity. No such dipolar resonance forms can be postulated in this case. It should be pointed out that this silane exhibits solvent effects opposite in direction but of even greater magnitude than the highly polarizable CF_3 substituent. Trifluoropropyldimethylsilane and the other silanes in Table IV exhibit relatively small solvent effects which do not correlate with any obvious solvent parameter. These solvent effects are being studied more closely to determine the cause of the effect and the nature of the substituent required to observe this effect.



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It appears that the electron-withdrawing nature of the trifluoropropyl group whether on Si or C is strongly dependent on the polarity of the solvent. The apparent σ^* value of a trifluoropropyl group varies from 0.32 in H_2O to 0.54 in 70% aqueous acetone to a value greater than 1 in nonpolar solvents.[34] The increase in the apparent σ^* value with decreasing solvent polarity is consistent with the pronounced solvent effect shown in Table IV. This pronounced solvent dependence is striking in that highly polar substituents such as OH, F, and Cl exhibit σ_I values which are not as strongly solvent dependent.[9a]

Shielding Parameter Evidence for Pentacoordinate Bonding in *p*-Fluorophenyl(2,2′,2′′-nitrilotriethoxy)silane. The SCS of *p*-fluorophenyl(2,2′,2′′-nitrilotriethoxy)silane (**5**, R = $p\text{-}FC_6H_4$) is 5.1 ppm more shielded

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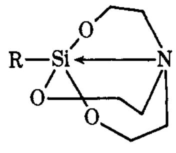
[32] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965, 971 (1959).

[33] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, p 204.

[34] A σ_I value of about 0.23 in cyclohexane, corresponding to a σ^* value of 1.4, would be appropriate for a trifluoropropyl group on Si by inspection of Figure 2. Unpublished SCS values of $p\text{-}FC_6H_4X$ [X = $C(OH)(Pr_f)_2$, $C(Br)(Pr_f)_2$], hydrogen bonding studies of carbinols and silanols,[35] and redistribution studies of silanes[36] indicate a σ^* value of ~1–1.4 would best fit LFE correlations in CCl_4 or cyclohexane. We have obtained a σ^* value for Pr_f of 0.54, based on the hydrolysis rate of ethyl γ,γ,γ-trifluorobutyrate in 70% aqueous acetone.

[35] R. H. Baney, private communication.

[36] R. H. Baney and R. J. Shindorf, *J. Organometal Chem.*, **6**, 660 (1966).



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than is the "model" compound p-fluorophenyltriethoxysilane[37] and indeed is more highly shielded than any of the silanes measured. This is a consequence of high-electron density on the silicon atom resulting from a partial $N^+ \rightarrow Si^-$ donor–acceptor bond. Evidence for some $N^+ \rightarrow Si^-$ interaction in the "triptych" compounds (**5**, R = C_6H_5) includes diminished basicity of the N and association in solution,[38a] high dipole moment (5.98D),[38b] a Si–N distance of 2.19 Å (1.3 Å less than the van der Waals radii), and distorted trigonal-bipyrimidal geometry about the silicon atom.[38c]

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(37) The shielding parameter of the "model" compound was obtained in CCl_4[15] whereas **5**, which is insoluble in CCl_4, was measured in acetone.

(38) (a) See Frye, *et al.*, Table I, footnote *a*; (b) M. G. Voronkov *Pure Appl. Chem.*, 13, 35 (1966); (c) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 90, 4026 (1968).

Cation–Anion Combination Reactions. V. Correlation of Reactivities of Nucleophiles with Diazonium Ions and with Triarylmethyl Cations[1a,b]

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Abstract: New data concerning rates and equilibria of reactions of diazonium ions with azide, cyanide, methoxide, and thiophenoxide ions in methanol solution and reactions of three triarylmethyl cations with thiophenoxide ion in methanol are presented. The new data and previously reported data on reactions of nucleophilic systems with both diazonium ions and triarylmethyl cations clearly show that the selectivities of the two different cation classes are nearly identical. The data cannot be accommodated by current concepts of nucleophilicities or of reactivity–selectivity relationships.

In the previous papers of this series, we have reported the results of our studies of the reactions of aryldiazonium ions with hydroxide, cyanide, and azide ions in aqueous solution and have made comparisons with the earlier results of studies of reactions of triarylmethyl cations with the same nucleophiles. The present paper deals with reactions of aryldiazonium ions and of triarylmethyl cations with nucleophiles in methanol solution.

The reactions of Malachite Green (MG, bis(p-dimethylaminophenyl)phenylmethyl cation), p-Nitro Malachite Green (PNMG, (bis(p-dimethylaminophenyl)-p-nitrophenylmethyl cation), and Crystal Violet (CV, tris(p-dimethylaminophenyl)methyl cation) with azide and methoxide ions in methanol solution were studied earlier. We now report the results of studies of reactions of MG, PNMG, and CV with thiophenoxide ion, and reactions of a series of aryldiazonium ions with azide, cyanide, methoxide, and thiophenoxide ions, all in methanol solution.

As we have explained in the earlier papers of this series, the goal of the studies of cation–anion combination reactions is an understanding of the factors affecting the relative nucleophilicities of anions in this type reaction. We believe that the present results have brought us quite close to this goal and allow an unusual insight into the general problems of nucleophilicity and solvent effects.

Results

Reactions of Diazonium Ions with Azide Ion in Methanol. The reactions of aryldiazonium ions with azide ion produce aryl azides and aryl pentazoles as the initial observable products.[2,3] In the present studies, we have followed the rates of disappearance of the diazonium ions in low buffered concentrations of azide ion in methanol solution. The measured rate constants are the sum of the rate constant for formation of aryl azide and that for formation of aryl pentazole. The techniques are detailed in the Experimental Section.

In all cases studied, the decomposition of the aryl pentazole to aryl azide was sufficiently slower than the formation reaction that it did not interfere with calculations of the fast reaction rate constants. In only one case, that of p-benzoylbenzenediazonium ion, did we measure the rate constant for decomposition of the

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(1) (a) Previous paper in this series: C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, *93*, 6574 (1971). (b) This work was supported by a grant from National Institutes of Health, U. S. Public Health Service, Grant GM-12832, and National Science Foundation Grant No. GP-10414. (c) On leave from Department of Chemistry, University of Oulu, Oulu, Finland.

(2) I. Ugi and R. Huisgen, *Chem. Ber.*, 90, 2914 (1957).

(3) C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, 93, 2429 (1971), and earlier references cited there.