

¹⁹F SUBSTITUENT CHEMICAL SHIFTS OF THE FLUOROPHENYLDIPHENYLSILANES AND THE CARBON ANALOGS

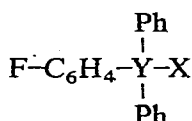
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SUMMARY

Substituent chemical shifts in the

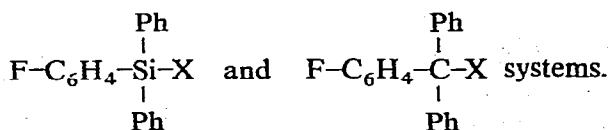


system, where Y = Si, C and X is H or a donor type atom or group, have been measured by ¹⁹F NMR techniques. The σ_1 parameters from the *meta* shifts by the method of Taft are small for both the silicon and carbon series. The *para* ¹⁹F chemical shifts for the silicon compounds are downfield with respect to the carbon analogs indicating important silicon-phenyl resonance interaction in the ground state. Subtle changes in substituents at the central atom affect the *para* shielding, the *para* shielding order being H > NH₂ > OEt > OH > Cl ≈ N₃ > Br > F in the carbon compounds and NH₂ > H > OH ≈ OEt > Cl ≈ Br > F ≈ N₃ for the silicon series. Changes for H and N₃ have been interpreted as possibly resulting from Si-X π interactions.

INTRODUCTION

Nuclear magnetic resonance spectroscopy has been used in recent years to examine substituent effects in aromatic and other conjugated systems¹⁻¹⁰. ¹⁹F NMR has been used extensively^{2,3,5,8-10} to monitor changes in electron density at the *meta* and *para* ring positions. Hammett substituent constants obtained by this method have been demonstrated in many cases to agree rather well with those obtained by chemical and instrumental methods^{2,3,11-13}. In the course of his investigation of ¹⁹F shielding correlation with Hammett substituent constants, Taft³ found evidence for a *p* → *d* π-bond between Si and an aromatic ring. Other workers using a variety of techniques have concluded similar results for Si-Ph systems.

This work utilizes the sensitive ¹⁹F probe to compare the effect of substituent changes in the



EXPERIMENTAL SECTION

General

The fluorophenyldiphenylsilanes reported in this work have not been previously described. Of the fluorophenyldiphenylmethanes, the *para*²³ and *meta*³⁰ carbinols, the *para*²³ and *meta*³⁰ chlorides, and *meta* fluorophenyldiphenylmethane³¹ have appeared in the literature. All of the preparations closely follow literature procedures usually for the triphenyl derivatives. Since relatively small amounts of material were needed for the NMR studies, no attempt was made to achieve maximum yields.

TABLE 1

MELTING POINT AND BOILING POINT DATA^a FOR $FC_6H_4\begin{matrix} Ph \\ | \\ Y-X \\ | \\ Ph \end{matrix}$

X	<i>para</i> $FC_6H_4\begin{matrix} Ph \\ \\ Y-X \\ \\ Ph \end{matrix}$		<i>meta</i> $FC_6H_4\begin{matrix} Ph \\ \\ Y-X \\ \\ Ph \end{matrix}$	
	Y=C	Y=Si	Y=C	Y=Si
NH ₂	60-62	(150/0.45)	67-69	(70/0.1)
H	57-58	(113/0.06)	36-37 95 ^b	(65-70/1)
OH	120-121 121-122 ^c	110-112	117 115-116 ^d	104-105
OEt	65-66	62.5-65	59-61	(200-210/10)
Cl	85-87 91-92 ^c	85-89	75-77 84-84.5 ^d 113.5 ^b	95-96 (132/0.07)
F	46-48	39-40	75-77	(140/0.1)
N ₃	59-60	67.5-68.5	(150/0.6)(decomp.)	59.5-60
Br	113-114	96-100	110-111	79-82

^a Melting points, °C; boiling points, (°C/mmHg). ^b Ref. 31. ^c Ref. 23. ^d Ref. 30.

Melting points are uncorrected (Table 1). Analyses were by MHW Laboratory, Garden City, Michigan, and Micro-Analysis Incorporated, Wilmington, Delaware (Table 2). The structures of the compounds were verified by mass spectrometry, ¹H NMR, and infrared analyses. The ¹⁹F NMR spectra were recorded in benzene and in chloroform-*d* at approximately 0.1 M concentration using a Varian HR 60 operating at 56.4 MHz. In benzene, the internal reference was 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (2% volume) for reasons discussed by Taft². Trichlorofluoromethane (4% volume) was the reference used in chloroform-*d*. All ¹⁹F shifts were then recalculated relative to internal fluorobenzene².

Syntheses

(a) *para* and *meta* Fluorophenyldiphenylsilanes. The *para* and *meta* fluorophenyldiphenylchlorosilanes were prepared by a procedure analogous to that of Gilman¹⁴. The appropriate Grignard reagent was added under anhydrous conditions

TABLE 2
ELEMENTAL ANALYSES, FOUND (CALCD.) (%)

X	<i>para</i> Compound			<i>meta</i> Compound		
	C	H	Other	C	H	Other
	$\begin{array}{c} \text{Ph} \\ \\ \text{FC}_6\text{H}_4\text{Si-X} \\ \\ \text{Ph} \end{array}$					
NH ₂	73.43 (73.68)	5.37 (5.50)	4.50 ^a (4.77)			4.19 ^a (4.77)
H	77.62 (77.66)	5.59 (5.43)		77.45 (77.66)	5.53 (5.43)	
OH	73.71 (73.46)	4.87 (5.10)		73.38 (73.46)	5.04 (5.10)	
OEt	73.97 (74.52)	5.85 (5.94)		73.0 (74.5)	5.6 (5.9)	
Cl	67.10 (69.09)	4.26 (4.52)	10.74 ^b (11.33)			
F	73.04 (72.94)	4.87 (4.76)		72.74 (72.94)	4.82 (4.76)	
N ₃	67.99 (67.69)	4.33 (4.42)	12.95 ^a (13.15)	67.75 (67.69)	4.37 (4.42)	13.20 ^a (13.15)
Br			21.52 ^c (22.41)			22.43 ^c (22.41)
	$\begin{array}{c} \text{Ph} \\ \\ \text{FC}_6\text{H}_4\text{C-X} \\ \\ \text{Ph} \end{array}$					
NH ₂			4.90 ^a (5.05)			
H	86.89 (87.00)	5.66 (5.73)		86.89 (87.00)	5.70 (5.73)	
OH	82.28 (82.01)	5.38 (5.40)		81.99 (82.01)	5.46 (5.40)	
OEt	82.35 (82.35)	6.15 (6.21)		81.6 (82.3)	5.9 (6.2)	
Cl	77.12 (76.89)	4.76 (4.72)		77.07 (76.89)	4.76 (4.72)	
F	81.35 (81.43)	5.24 (5.00)				13.36 ^d (13.57)
N ₃	75.46 (75.24)	4.70 (4.62)	13.81 ^a (13.86)	75.05 (75.24)	4.58 (4.62)	13.66 ^a (13.86)
Br			23.30 ^c (23.46)	67.20 (66.86)	4.19 (4.10)	22.43 ^c (23.46)

^a Nitrogen. ^bChlorine. ^c Bromine. ^d Fluorine.

to an ethereal solution of diphenyldichlorosilane at reflux. The resulting *para* and *meta* fluorophenyldiphenylchlorosilanes were recrystallized from hexane and sublimed. Rather poor elemental analyses (see Table 2) were obtained with the chlorides due to exchange of halogen (Br for Cl) in the Grignard reaction. Yields of crude products were 50% of theory for each isomer.

para and *meta* Fluorophenyldiphenylsilyl azides were prepared by the method of Thayer¹⁵. Under anhydrous conditions the *para* and *meta* fluorophenyldiphenylchlorosilanes were added to sodium azide and catalytic amounts of aluminum chloride in tetrahydrofuran. The mixtures were held at reflux for 75 hours. The THF was removed and the products were recrystallized from hexane and sublimed. The *para* fluorophenyldiphenylsilyl azide was recovered in 55% yield and the *meta* compound in 65% yield.

para and *meta* Fluorophenyldiphenylsilanol were prepared by hydrolysis of the chlorides in acetone as described by Dilthey¹⁶. The silanols were recrystallized from petroleum ether. The yields of unrecrystallized products were 80% of theory.

para and *meta* Fluorophenyldiphenylethoxysilanes were prepared by a procedure similar to that used by Gilman¹⁷ to make tri-*o*-tolylethoxysilane. The *para* and *meta* ethoxy compounds were made by addition at room temperature of the fluorophenyldiphenylchlorosilanes to anhydrous ethanol. The products were distilled under vacuum. The *para* isomer was obtained in 35% yield and 20% of the *meta* compound was recovered.

para and *meta* Fluorophenyldiphenylfluorosilanes were prepared by the procedure of Eaborn¹⁸. The fluorides were prepared by treatment of the *para* and *meta* fluorophenyldiphenylchlorosilanes with aqueous ethanol/hydrofluoric acid solutions for 3 days at room temperature. The *para* compound was recrystallized from hexane and sublimed. The *meta* isomer was vacuum distilled. The *para* fluorophenyldiphenylfluorosilane was prepared in 75% of the calculated value, and 30% of the *meta* isomer was recovered.

para and *meta* Fluorophenyldiphenylbromosilanes were prepared by the method of McCusker¹⁹. The *para* and *meta* bromides were made under anhydrous conditions by treating *para* and *meta* fluorophenyldiphenylsilanol with tetrabromosilane in ether. The solutions were stored at room temperature for 8 days in sealed vials. After filtering and removal of solvent the products were obtained by sublimation from the crude solids. 20% of the theoretical amount of each isomer was recovered after sublimation.

para and *meta* Fluorophenyldiphenylsilanes were prepared by the procedure used by Finholt *et al.*²⁰ utilizing the reduction of the chlorides by lithium aluminum hydride in anhydrous ether held at reflux for 1 h. The reaction mixture was slowly poured into a water-ice mixture. An equal volume of ether was added and the ethereal layer separated. The ether was stripped off and the products distilled under vacuum. Both the *para* and *meta* fluorophenyldiphenylsilanes were prepared in about 40% yield.

para and *meta* Fluorophenyldiphenylsilyl amines were prepared by the method of Kraus²¹ under anhydrous conditions by addition of liquid ammonia to the chlorides. After storing the reaction mixture in Dry Ice for 5 h, the ammonia was boiled off. Anhydrous ether was added and the solutions were filtered. The ether was then removed and the products distilled. Because of easy hydrolysis the amines were recovered in approximately 15% yield.

(b). *para* and *meta* Fluorophenyldiphenylmethanes. *para* and *meta* Fluorophenyldiphenylcarbinols were prepared by conventional procedures^{22,23}. The Grignard reagents were added to anhydrous cold ethereal solutions of benzophenone. The solutions remained under N₂ for 2h at room temperature. The reaction mixture was

then poured into a 10% H₂SO₄ solution. The ether layer was separated, washed with NH₄Cl solution and water, then dried and evaporated. The products were recrystallized from hexane and sublimed at reduced pressure. Yields for both the isomers were near 80%.

para and *meta* Fluorophenyldiphenylchloromethanes were prepared by the method of Blicke²⁴ from carbinols by treatment with acetyl chloride in benzene at room temperature under nitrogen for 3 days. The precipitated products were washed with petroleum ether and sublimed. The *para* fluorophenyldiphenylchloromethane was prepared in 70% yield while 50% of the *meta* fluorophenyldiphenylchloromethane was obtained.

para and *meta* Fluorophenyldiphenylbromomethanes were prepared in 50% yields by the procedure described by Fieser²⁵. The carbinols were dissolved in glacial acetic acid and treated with 48% hydrobromic acid to produce the *para* and *meta* fluorophenyldiphenylbromomethanes. The products were recrystallized from petroleum ether.

para and *meta* Fluorophenyldiphenylazidomethanes were prepared from the carbinols by the procedure of Sanders²². To a solution of the carbinol in chloroform was added excess sodium azide in water. Concentrated sulfuric acid was added slowly over 10 min, and the mixture was stirred 1 h at room temperature. The mixtures were neutralized with concentrated NaOH solution. The chloroform layer was collected, dried, and evaporated. The *para* compound was recovered in 60% yield from petroleum ether. The *meta* fluorophenyldiphenylazidomethane was distilled with some decomposition to give 20% of the theoretical yield.

para and *meta* Fluorophenyldiphenylmethanes were prepared by the method of Trevo²⁶ by the reduction of the fluorophenyldiphenylchloromethanes with lithium aluminum hydride in anhydrous ether at reflux for 1 h. The solutions were poured into an ice-water mixture, and an equal volume of ether added. The etheral layer was separated and the ether removed by distillation. The products were purified by sublimation, in approximately 80% of calculated yield. Beynon and Bowden³¹ give a melting point of 95°C (see Table 1) for the *meta* isomer. By several methods of investigation our compound which melted at 36°C was shown to have the desired structure.

para and *meta* Fluorophenyldiphenylethoxymethanes were prepared in about 50% yields by the method of Fieser²⁵. Warming the *para* and *meta* fluorophenyldiphenylbromomethanes with anhydrous absolute ethanol produced the ethoxymethanes. The products were recrystallized from ethanol.

para and *meta* Fluorophenyldiphenylfluoromethanes were prepared by the procedure of Blicke²⁴ from the carbinols by treatment with acetyl fluoride in benzene. The solutions were kept in sealed ampoules for 10 days. The benzene was removed and the products were recrystallized from hexane and sublimed. Apparent hydrolysis of the products kept the yields of pure products to 15% for the *meta* compound and 10% for the *para* isomer.

para and *meta* Fluorophenyldiphenylaminomethanes were prepared according to Kornblum²⁷ by bubbling ammonia through a solution of the appropriate bromide in dry benzene at room temperature. The NH₄Br was filtered off, the benzene stripped, and the products sublimed. Both isomers were obtained in 35% yields.

RESULTS AND DISCUSSION

Previous investigators have found straight line *para vs. meta* ^{19}F shift relationships for series of structurally related compounds, *i.e.*, $\text{C}_6\text{H}_4\text{CH}_2\text{X}^{2,3,9}$. These linear relationships have been discussed by Taft^{2,3,8}. In our work, a least squares fit of the *para vs. meta* silanes ^{19}F SCS* data (Fig. 1) shows linearity, while the plot for the carbon compounds in chloroform-*d* shows wide scattering (Fig. 2)**. A somewhat better fit is obtained in benzene for the carbon series.

Inductive parameters, σ_I (Table 3) calculated by the method of Taft³ from the *meta* ^{19}F shifts (Table 4) are small in both the silicon and carbon series. Thus it is inferred from the small σ_I parameters that the inductive effects operating through the σ -structure of the molecule are small for both the silicon and carbon compounds. If the *meta* SCS data obtained in benzene are compared for the two series (Table 4), it is seen that the range for the silicon compounds is much larger (1.0 ppm) than for the carbon analogs (0.2 ppm). Since the *meta* SCS have been correlated with inductive effects^{2,3,9} these results would suggest silicon is better able to transmit substituent inductive effects; however, recent studies suggest caution should be used in interpretation of *meta* SCS²⁸.

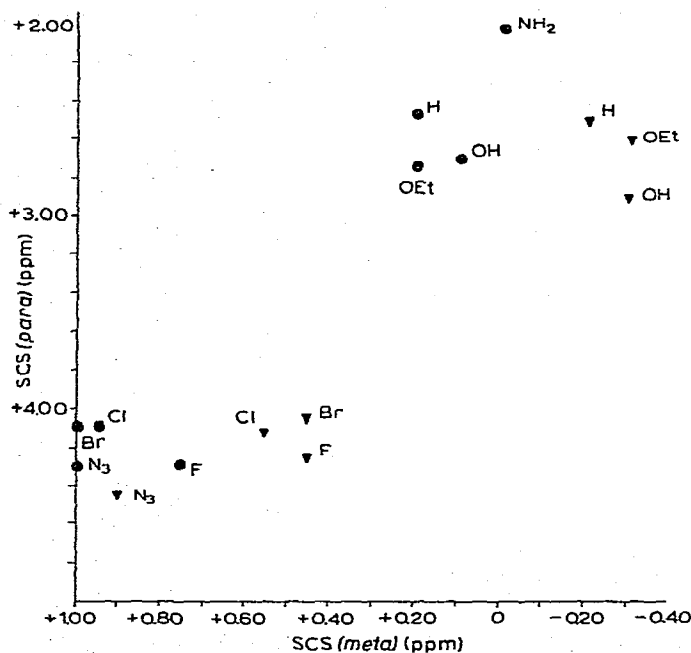


Fig. 1. *para vs. meta* Substituent chemical shifts for the fluorophenyldiphenylsilanes. ● Represents points taken in benzene, ▼ those in chloroform-*d*. A least squares fit of the data in benzene produces a line of slope 2.08 (standard deviation 0.24), intercept 2.24 (standard deviation 0.16), and a correlation coefficient of 0.961. In chloroform-*d* the slope is 1.68 (standard deviation 0.22), the intercept 3.17 (standard deviation 0.11), and a correlation coefficient of 0.958.

* SCS=substituent chemical shift.

** A referee has pointed out that since CDCl_3 is not an "inert" solvent perhaps this solvent is interacting with basic centers in some molecules.

As seen in the σ_R^0 parameters obtained by the method of Taft^{2,3} (Table 3) for the SiPh₂X substituents, these substituents are all electron withdrawing by resonance. Withdrawing of electron density into vacant Si acceptor orbitals (presumably 3d) is

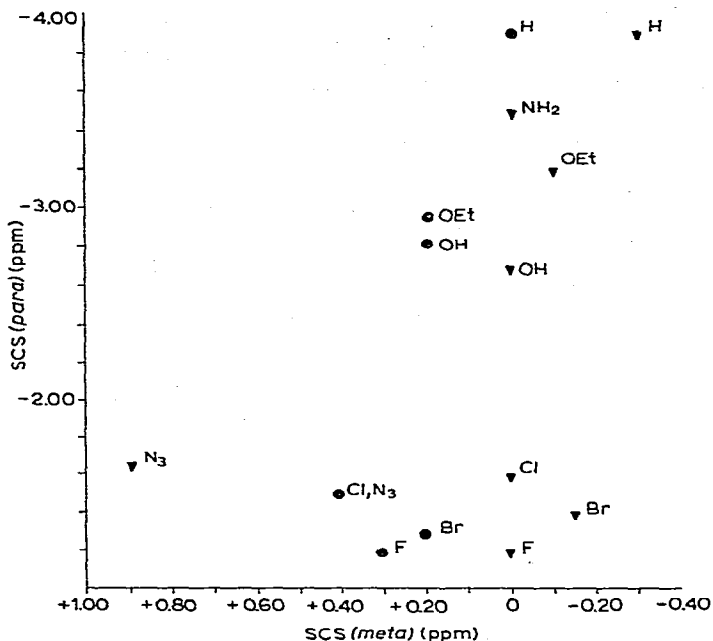


Fig. 2. *para* vs. *meta* Substituent chemical shifts for fluorophenyldiphenylmethanes. ● Represents points taken in benzene, ▼ those in chloroform-*d*. A least squares fit of the data in benzene produces a line of slope 6.05 (standard deviation 1.95), intercept -3.63 (standard deviation 0.54), and a correlation coefficient of 0.807.

TABLE 3

SUBSTITUENT CONSTANTS^a FROM ¹⁹F NMR IN C₆H₆

X	$\begin{array}{c} Ph \\ \\ -Si-X \\ \\ Ph \end{array}$		$\begin{array}{c} Ph \\ \\ -C-X \\ \\ Ph \end{array}$	
	σ_I	σ_R^0	σ_I	σ_R^0
NH ₂	0.08	0.06	0.11	-0.14
H	0.10	0.08	0.08	-0.13
OH	0.09	0.08	0.10	-0.11
OEt	0.10	0.08	0.10	-0.12
Cl	0.18	0.11	0.12	-0.06
F	0.16	0.11	0.11	-0.05
N ₃	0.22	0.10	0.12	-0.06
Br	0.22	0.11	0.10	-0.05

^aAfter Taft Refs. 2, 3: $\frac{-SCS(meta) - 0.60}{-7.1} = \sigma_I$; $\frac{-SCS(para) + SCS(meta)}{-29.5} = \sigma_R^0$.

TABLE 4

^{19}F CHEMICAL SHIFT OF $\text{FC}_6\text{H}_4\text{Y-X}$ IN ppm RELATIVE TO $\text{PhF}^{a,b}$

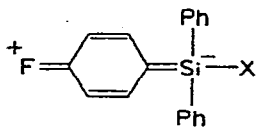
$\begin{array}{c} \text{Ph} \\ | \\ \text{FC}_6\text{H}_4\text{Y-X} \\ | \\ \text{Ph} \end{array}$

No extensive studies were undertaken to determine effects of concentration, however the X=H, OH, and F substituents were measured at various concentrations and the shifts were found to be parallel.

X	<i>para</i> $\text{FC}_6\text{H}_4\text{Si-X}$		<i>meta</i> $\text{FC}_6\text{H}_4\text{Si-X}$		<i>para</i> $\text{FC}_6\text{H}_4\text{C-X}$		<i>meta</i> $\text{FC}_6\text{H}_4\text{C-X}$	
	δCDCl_3	δPh	δCDCl_3	δPh	δCDCl_3	δPh	δCDCl_3	δPh
NH ₂		+2.00	-0.40	-0.10	-3.50	-3.70	0	
H	+2.50	+2.45	-0.20	+0.20	-3.90	-3.90	-0.30	0
OH	+2.90	+2.70	-0.30	+0.10	-2.70	-2.80	0	+0.20
OEt	+2.60	+2.75	-0.30	+0.20	-3.20	-2.95	-0.10	+0.20
Cl	+4.10	+4.10	+0.55	+0.95	-1.60	-1.50	0	+0.40
F	+4.25	+4.30	+0.45	+0.75	-1.20	-1.20	0	+0.30
N ₃	+4.45	+4.30	+0.90	+1.00	-1.65	-1.50	+0.90	+0.40
Br	+4.05	+4.10	+0.45	+1.00	-1.40	-1.30	-0.15	+0.20

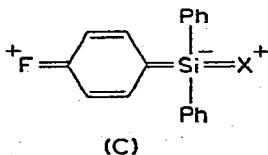
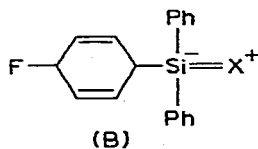
^a Rounded to nearest 0.05 ppm (experimental error). ^b (-) Indicates signal to high field of reference.

probably responsible for deshielding around the ^{19}F in the *para* fluorophenylsilicon series compared with the *para* fluorophenylcarbon analogs (Structure A).



No similar resonance form can be written for the carbon compounds.

Resonance forms involving silicon *d* orbital interaction with filled orbitals on the X substituent (Structure B), or forms involving donation to two silicon *d* orbitals from the phenyl groups and the X substituent (Structure C) are also possible.

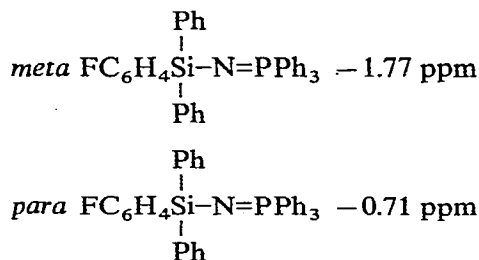


If Si-X interactions represented by (B) and (C) exist at the expense of the structure described by (A), then σ_R^0 (*para* SCS) for the silicon series should be affected by an amount proportional to the ability of the X substituent to effect a π -bond with silicon. From Table 3 it can be seen that as the substituents are changed from NH₂ through halogen to the pseudohalogen N₃, though the *para* silicon series is displaced downfield relative to the carbon analogs, no obvious trends in σ_R^0 are evident. Therefore, no firm conclusion can be drawn from σ_R^0 as to which resonance form (A, B, C) is more important. However, one finds the *para* shielding order for carbon to be H > NH₂ > -OEt > OH > Cl \approx N₃ > Br > F, which is similar to the order of σ_1^0 values for the X substituent given by Ritchie and Sager²⁹. A least squares fit produces a straight line relationship in benzene for the *para* SCS *vs.* the σ_1 of X, of slope 5.76 (standard deviation 0.38), intercept -4.14 (standard deviation 0.14), and a correlation coefficient of 0.987 (97.4% correlation). A straight line relationship confirms that resonance interactions are not important in the carbon compounds. On the other hand, a poorer fit is obtained for the *para* SCS values for the silanes *vs.* the σ_1 of X (slope = 4.67, standard deviation 0.72; intercept 1.89, standard deviation 0.26; correlation coefficient 0.935; 87.4% correlation) which could indicate some ground state resonance interaction.

The shielding order for the *para* ¹⁹F silicon compounds, NH₂ > H > OH \approx OEt > Cl \approx Br > F \approx N₃, shows two changes when compared with the *para* carbon series which we believe are significant. The greater relative deshielding for H in the silicon series can be accounted for if one accepts electron donation to Si by the donor type substituents thereby reducing the importance of the resonance form represented by structure (A) (*i.e.*, the Si-phenyl interaction). The relative deshielding for the azide in the silicon series may indicate a smaller contribution from the resonance forms of structures (B) and (C) for this substituent.

However, since the changes in SCS required for reversal of the substituent shielding order are relatively small, this explanation is by no means exclusive. The difficulty in assessing the importance of such factors as changing from silicon to the smaller carbon central atom and the ensuing effect on the aromatic π system, makes necessary more conclusive studies.

Preliminary results for the Si compounds, where X is -N=PPh₃, show this group to be a strong electron donor. Initial results in chloroform-*d* are:



A subsequent publication will provide details of these compounds and of long range substituent effects in silylphosphinimines and the carbon analogs.

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