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THE ELECTRONIC EFFECT OF SILYL SUBSTITUENTS BY ^{19}F AND ^{13}C NMR : d-ORBITAL PARTICIPATION VERSUS HYPERCONJUGATION.

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Numerous studies[1] have clearly established that simple silyl substituents ($SiH_n(CH_3)_{3-n}$, where n = 0 to 3) function as weak electron acceptors by a conjugative mechanism (+M)[2] when directly attached to π-electron systems. Current interest centers on the nature of this interaction. In this connection, much speculation exists concerning the role of 3d and σ* orbitals on the silicon substituent. Although a $(p\rightarrow d)_\pi$ model[1a-h,j,n] has been traditionally favoured over a hyperconjugative one $(p\rightarrow\sigma^*)_\pi$, support for the latter[1h,i,k,m,o,p] has more recently emerged mainly on the basis that CNDO/2 calculations reproduce the effect of silyl substituents without explicit inclusion of d-orbitals in the basis set. However, it has been pointed out[3] that, as a result of parameterization difficulties, such calculations are often unreliable and, thus, support for a hyperconjugative model must be viewed as being insecure.

An operational criterion for drawing a distinction between the two possible models is based on their respective conformational dependencies; whereas hyperconjugation has the conformational requirement that the σ-bond (Si-C or Si-H) overlap significantly with the orbital to which it is to interact,[1h,4] the extent of p_π-d_π interactions are angularly independent due to the number and symmetry of the d-orbitals involved.[5] Hence if one considers the effect of successive replacements of hydrogen atoms in SiH_3 with CH_3 groups on the π-acceptor ability of this substituent, the following predictions emerge from a consideration of the preferred rotameric forms of SiH_2CH_3 and $SiH(CH_3)_2$ recently determined by nmr techniques[6] : (i) for a hyperconjugative model only, since the energy differential between π_{HOMO} and $\sigma^*_{Si-C(H)}$ is increased on replacing H with CH_3[1k], the effect of the first two replacements will be to reduce the π-acceptor capacity by approximately two equal amounts.[1h] However, to a first approximation, the third replacement to give $Si(CH_3)_3$ should not have any further effect since the third Si-C bond would be in the plane of the ring and, therefore, unable to hyperconjugate[7]; (ii) for a $(p\rightarrow d)_\pi$ model only, since H is more electronegative than CH_3, successive replacement of the former with the latter in SiH_3 should lead to a decrease in the positive charge on silicon with a concomitant increase in the energy and radial component of the d-orbitals[5,8]. On the other hand, d-orbital energies for SiH_4 and $Si(CH_3)_4$ have been suggested to be essentially constant.[1k] Thus, the π-acceptor capacity should either progressively decrease in a monotonic fashion or remain constant for the three replacements.

The key to a solution of this problem hinges on sensitive and reliable methodology for quantitatively estimating mesomeric or resonance parameters. In this regard, we have recently employed ^{19}F substituent chemical shift (SCS) data of 6- and 7-substituted (X) β-fluoronaphthalenes (1 and 2 respectively),[9,10] ^{13}C data of C6 and C7 as well as C10 in β-substituted (X) naphthalenes (3)[10] and their respective dual substituent parameter (DSP) correlative equations.[9,11] Accordingly, we have synthesized 1, 2, and 3 ($X = SiH_n(CH_3)_{3-n}$, where n = 0 to 3) and measured their ^{19}F and ^{13}C nmr spectra respectively.[12] The results are shown in Table 1. Substituent parameters dissected from this data by means of the appropriate DSP equation[13] are set out in Table 2.

Table 1. ^{19}F and ^{13}C SCS (ppm) for $SiH_n(CH_3)_{3-n}$-Substituted Naphthalenes (1, 2, and 3)

	^{19}F SCS^{a,b,c}				^{13}C SCS^{a,b,d}		
	Benzene		DMF		$CDCl_3$(3)		
Substituent, X.	1	2	1	2	C6	C7	C10
SiH_3	1.77	0.84	1.87	0.97	1.02	0.41	0.49
SiH_2CH_3	1.40	0.60	1.50	0.72	0.79	0.28	0.50
$SiH(CH_3)_2$	1.05	0.38	1.09	0.44	0.59	0.15	0.46
$Si(CH_3)_3$	0.77	0.17	0.71	0.21	0.38	0.04	0.27
	(0.77)^e	(0.19)^e	(0.70)^e	(0.21)^e			

a. A positive sign implies deshielding. b. Accurate to ±0.03 ppm. c. Relative to β-fluoronaphthalene. d. Naphthalene ($CDCl_3$; relative to TMS) : 127.90 (C1); 125.82 (C2); 133.56 (C9). e. W. Adcock, S.Q.A. Rizvi, and W. Kitching, J.Am.Chem.Soc., 94, 3658 (1972).

Table 2. Substituent Parameters for $SiH_n(CH_3)_{3-n}$ Substituents

	^{19}F nmr (1 and 2)				^{13}C nmr (3; $CDCl_3$)		
	Benzene		DMF		C6,7		C10
Substituent, X.	σ_I	$\sigma_R^{\,o}$	σ_I	$\sigma_R^{\,o}$	σ_I	$\sigma_R^{\,o}$	$\sigma_R^{\,o}$
SiH_3	0.16	0.05	0.19	0.04	0.14	0.06	0.04
SiH_2CH_3	0.12	0.04	0.14	0.04	0.09	0.06	0.04
$SiH(CH_3)_2$	0.07	0.04	0.08	0.03	0.05	0.05	0.04
$Si(CH_3)_3$	0.02	0.03	0.03	0.03	0.01	0.04	0.02

Several important conclusions follow from these results. Firstly, it can be seen (Table 1) that, except for the resonance dominated C(10) position of system 3, the electron withdrawing power of SiH_3 is substantially reduced on successive replacement of the H atoms with CH_3 groups. Moreover, it is clear (Table 2) that this change has its origin in the polar term (σ_I) and not mesomerism ($\sigma_R^{\,o}$). In fact, the $\sigma_R^{\,o}$ values remain essentially constant within experimental error (±0.01) and, thus, are completely in accord with expectations based on a $(p\rightarrow d)_\pi$ model and not a hyperconjugative one (vide supra). This conclusion is strongly corroborated by the identical $\sigma_R^{\,o}$ values obtained by Katritzky and Topsom's ir technique[14a] for SiH_3 (+0.02)[14b] and $Si(CH_3)_3$ (+0.02).[14c,d]

Secondly, it is important to stress that there is no dichotomy between the observed positive σ_I values (Table 2) implying electron withdrawal and the accepted classification of these groups as electropositive substituents (-I; electron donation by a σ-inductive effect).

The inductive parameter (σ_I) provides a measure of the field effect (F) of a substituent[15] and, thus, does not necessarily mirror the direction of the σ-inductive effect (I) acting directly on the substrate.[16] In this connection, the direction of the molecular moment (0.73D) of methylsilane ($H_3C\text{-}SiH_3 \overset{+}{\rightarrow}$)[16] is worth noting. However, the electronegativity effect ($C^{\delta}_{sp^2} \leftarrow Si^{\delta+}$) of $SiH_n(CH_3)_{n-3}$ substituents has been clearly demonstrated by physical methods (charge transfer, uv, and pe spectroscopy; polarography)[1] which concern the electronic levels of molecules. Thus, $SiH_n(CH_3)_{3-n}$ groups should be classified as +F-I+M rather than -I+M substituents[2] i.e. the groups have opposing field (F) and inductive effects (I).It is of interest to note, that recently[1p], CNDO/2 calculations with Si d-orbitals in the basis set have been reported which indicate that SiH_3 should exhibit opposing field and σ-inductive effects.

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(13) (a) ^{19}F SCS = $5.4\sigma_I + 19.3\sigma_R^{o}$ (1; benzene) and ^{19}F SCS = $4.5\sigma_I + 2.2\sigma_R^{o}$ (2; benzene); ^{19}F SCS = $6.0\sigma_I + 18.4\sigma_R^{o}$ (1; DMF) and ^{19}F SCS = $4.6\sigma_I + 2.2\sigma_R^{o}$ (2; DMF). These equations have been derived utilizing a new DSP treatment (DSP-2) which removes the constraint in the previous analysis[9] of a single resonance susceptibility parameter (ρ_R). We are grateful to Professor R.W. Taft for this information prior to publication; (b) ^{13}C SCS = $4.01\sigma_I + 7.74\sigma_R^{o}$ (C6; $CDCl_3$) and ^{13}C SCS = $2.85\sigma_I + 0.37\sigma_R^{o}$ (C7; $CDCl_3$)[11]; (c) ^{13}C SCS = $0.41\sigma_I + 11.23\sigma_R^{o}$ (C10; $CDCl_3$)[11]. Resonance parameters for weak polar groups can be determined directly from this equation by ignoring the small inductive contribution in this position.

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