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ELECTRON-DONATION BY METHYLPOLYSILANYL GROUPS: σ^+ CONSTANTS FROM ^{13}C NMR SPECTROSCOPY

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Summary

Carbon-13 NMR spectra have been determined for some methylpolysilanylbenzenes and trimethylsilylmethylbenzenes. Relative electron-release of these groups toward the benzene ring was calculated as σ^+ constants from the chemical shift of the *para* carbon atom. The orders of electron-donation found are $(Me_3Si)_3Si > (Me_3Si)_2SiMe \sim$ cyclo-$Si_5Me_9 \sim$ cyclo-$Si_6Me_{11} > Me_5Si_2 \sim Me_3Si(SiMe_2)_2 \sim$ cyclo-$Si_5Me_9SiMe_2 \sim Ph(SiMe_2)_2 \sim Ph(SiMe_2)_3 > Me_3Si > PhMe_2Si$; and $(Me_3Si)_2CH > (Me_3Si)_3C > Me_3SiCH_2 > CH_3$.

Like simple organosilyl substituents, polysilane groups are electron-releasing toward aromatic rings by inductive and/or field effects, and electron-attracting by π—σ^* (or π—d) backbonding [1]. In addition, polysilane substituents can donate electron density to benzene rings by σ—π hyperconjugation from the Si—Si bonding orbitals [2]. In substituted benzene anion-radicals, the groups Me_3Si, Me_5Si_2, and $(Me_3Si)_3Si$ all act quite similarly as moderate electron-withdrawing substituents [3]; ESR studies show little difference in spin distribution among these three anions. However Sakurai has shown that as a substituent on neutral cyclopentadienyl radicals, Me_3Si is weakly electron-withdrawing while Me_5Si_2 is electron-releasing [4]. Reaction rate studies also indicate electron-release by Me_5Si_2 and other polysilanyl groups [5].

The effect of substituents which donate charge to benzene rings by conjugation can be measured by σ^+ constants [6,7]. However, the few studies of σ^+ (or the related $\sigma_R{}^0$) constants for polysilanes have given rather discordant results. We therefore decided to investigate the σ^+ values for a variety of polysilanyl benzenes **5**—**12** by ^{13}C NMR spectroscopy. Some silylmethyl benzenes (**2**—**4**) and diphenylpolysilanes (**13**—**15**) were also studied; the ^{13}C results for these compounds are also interpreted.

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$(Me_3Si)_nCH_{3-n}Ph$

(1, n = 0;
2, n = 1;
3, n = 2;
4, n = 3)

$Me_3Si(SiMe_2)_nPh$

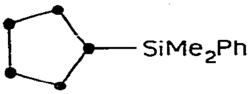
(5, n = 0;
6, n = 1;
9, n = 2)

$(Me_3Si)_2SiMePh$

(7)

$(Me_3Si)_3SiPh$

(8)



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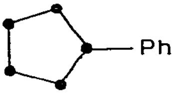

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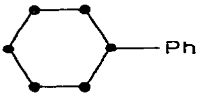

(12)

$Ph(SiMe_2)_nPh$

(13, n = 1;
14, n = 2;
15, n = 3)

Experimental

Phenyl- and benzyl-silanes were available from previous investigations in these laboratories [3,8,9] with the exception of compounds **10**—**12** which were synthesized by published methods [10,11].

Carbon-13 NMR spectra were obtained with a Jeol JNM-FX 60 NMR spectrometer operating in the FT mode at 15.04 MHz. An internal deuterium ($CDCl_3$) lock was employed with broad-band proton decoupling. Concentrations varied between 3—10 mole percent in $CDCl_3$. Chemical shifts (ppm) were measured relative to internal TMS, positive shifts being downfield. A study of **3** at 4, 10 and 16 mole percent showed no significant change in chemical shifts with concentration. Previous work has indicated that phenylsilane resonances are only very slightly affected by much larger changes in concentration than encountered here [12]. Spectral reproducibility was typically 0.06 ppm.

Chemical shift assignments for each of the compounds listed in Table 1 were made in part on the basis of previous assignments for **1**, **2**, **5** and **13** as well as the general trends noted in these earlier studies [12—15]. Relative peak intensities were also useful. Assignments for the silyl methyl carbons were greatly aided by comparison with the permethylated polysilane analogues [16]. A high degree of internal consistency for the ^{13}C chemical shifts was found among the compounds studied.

The *ortho-* and *meta*-carbon assignments for compounds **3** and **4** are tentative, but interchange seems unlikely based on the smaller shifts generally observed for meta carbons. Also, for compounds **11** and **12** the polysilane ring methyl carbons C_β and $C_{distant}$ cannot be separated unequivocally.

TABLE 1

^{13}C NMR CHEMICAL SHIFTS

Compound	*ipso*	*ortho*	*meta*	*para*	C_α [a]	C_β	$C_{distant}$
1	137.70	128.97	128.14	125.22	21.36	—	—
2	140.34	127.97	127.97	123.83	27.05	—1.93	—
3	143.05	128.69	128.03	123.28	29.71	0.28	—
4	143.10	131.50	127.42	123.50	21.53	4.25	—
5	140.39	133.21	127.64	128.69	—1.16	—	—
6	139.56	133.65	127.64	128.19	—4.03	—2.26	—
7	137.63	134.43	127.6	127.6	—9.00	—1.05	—
8	135.48	136.53	127.64	127.25	—	1.21	—
9	139.90	133.66	127.64	128.19	—3.09	—6.79	—1.54
10	140.78	133.60	127.64	128.24	—0.94	—11.54	—3.86, —5.68, —5.91 —6.35
11	137.96	134.87	127.6	127.6	—7.34	—	—5.41, —6.07, —6.40 [b]
12	137.80	134.70	127.58	127.75	—6.13	—	—4.75, —4.46, —6.35, —6.51, —6.79 [b]
13	138.19	134.10	127.70	128.97	—2.42	—	—
14	138.85	133.77	127.64	128.36	—3.86	—	—
15	139.56	133.65	127.64	128.24	—3.26	—6.46	—

[a] C_α is either attached to the phenyl ring, or is bonded to silicon attached to the ring. [b] Includes C_β.

Results and discussion

The ^{13}C chemical shifts * and assignments are listed in Table 1. From these data the σ^+ values for substituents were calculated using the relationship $\sigma^+ = -0.1081\ (128.24 - \delta^p)$ where δ^p is the chemical shift for the carbon atom *para* to the substituent. This formula has been used to obtain the σ^+ constants for a number of phenylsilanes [17]. Although its limitations have been pointed out [18], this method provides values for substituent constants which agree quite well with those determined from other kinds of studies. The σ^+ constants obtained by this approach are shown in Table 2.

A. Silylmethylbenzenes. The well-known electron-releasing effect of substituents like Me_3SiCH_2 is accounted for by σ—π hyperconjugation, in which an appropriate component of the C—Si σ bond interacts with and perturbs the π-system [14,19—22]. Hyperconjugative electron release in benzylsilanes is subject to conformational constraints [15]. σ—π interaction is maximized when the Si—C bond is normal to the plane of the benzene ring, and follows a $\cos^2$ function of the angle between the benzene π orbitals and the z-component of the σ bond [20,21]. The results for silylmethylbenzenes 2—4, summarized in Table 2, show the expected electron-release by these silylmethyl substituents.

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[*] *Note added in proof.* ^{13}C NMR data which are in good agreement with our results for compounds 2—4 have recently been reported for a number of benzylsilanes. See C. Eaborn, A.R. Hancock and W.A. Stańczyk, J. Organometal. Chem., 218 (1981) 147.

TABLE 2

σ^+ CONSTANTS FROM ^{13}C NMR

Compound	Substituent	σ^+	σ^+ (lit.)	Ref.
1	CH_3	−0.33	−0.31	22
2	Me_3SiCH_2	−0.48	−0.50	17
			−0.54	22
3	$(Me_3Si)_2CH$	−0.54	−0.62	22
4	$(Me_3Si)_3C$	−0.51	−0.52	22
5	Me_3Si	+0.04	0.00	25
			+0.01 [a]	5
			+0.02	7, 17
6	$Me_3SiSiMe_2$	−0.01	−0.03 [a]	5
			(−0.23)	25
7	$(Me_3Si)_2SiMe$	−0.07	−0.05 [a]	5
8	$(Me_3Si)_3Si$	−0.11	−0.06 [a]	5
9	$Me_3Si(SiMe_2)_2$	−0.01		
10	cyclo-$Si_5Me_9SiMe_2$	0.00		
11	cyclo-Si_5Me_9	−0.07		
12	cyclo-Si_6Me_{11}	−0.05		
13	$PhSiMe_2$	+0.08		
14	$Ph(SiMe_2)_2$	+0.01		
15	$Ph(SiMe_2)_3$	0.00		

[a] Calculated from rate data in Ref. 5.

The σ^+ constant decreases most markedly going from **1** to **2** and then less so from **2** to **3** as the number of C—Si bonds adjacent to the benzene ring increases from zero to one to two. A small increase is observed from **3** to **4**, which has three C—Si bonds adjacent to the ring. This trend can be understood, at least in part, in terms of the probable conformations of the molecules. For **2** the favored conformation is probably the one with the C—Si bond perpendicular to the ring, leading to minimum steric repulsion. In **3** the sterically favored conformation is the one with the two C—Si bonds each at 60° to the ring plane. Both of these conformations produce maximum σ—π overlap but in agreement with the calculated σ^+ constants the relative increase in C—Si hyperconjugation with the benzene π orbitals should be greater for **1** to **2** than for **2** to **3**.

If these conformations are correct, the lack of an increased electron release in **4** compared to **3** can be accounted for because the third C—Si bond could not increase conjugation to the ring. The small change in σ^+ actually observed going from **3** to **4** may possibly result from more subtle steric effects, such as bond lengthening or bending in the overcrowded $(Me_3Si)_3C$ group in **4**. Unexpectedly low electron-release by $(Me_3Si)_3C$ has been observed in other studies of aryl compounds, and rationalized similarly [19]. Chemical shift data for the *ortho* phenyl carbons in compounds **1** through **4** can also be understood provided a second and dominant $\cos^2$ term is introduced to account for steric interaction between trimethylsilyl groups and ortho protons [23].

B. Polysilanylbenzenes. Our results confirm earlier findings [4,5] that polysilanyl groups are more electron-releasing to benzene than Me_3Si. Increasing the number of silicon atoms attached to the α silicon increases electron-releasing power somewhat. The σ^+ value decreases by 0.05 going from Me_3Si to Me_5Si_2, and compounds **7**, **11** and **12**, all with the Si_2Si—Ph structure, show further decrease of σ^+ by about 0.06. Compound 8 with three silicon atoms on the α silicon shows a still lower σ^+ value by about 0.04. On the other hand, lengthening of the polysilane chain beyond two silicon atoms has no discernable effect; compounds 6, 9 and 10 all show essentially identical σ^+ values (zero or —0.01).

Our values are consistent with the results of Cook, Eaborn and Walton, who studied the relative rates of acid cleavage of aryltrimethylstannanes *para*-substituted with Me_3Si, Me_5Si_2, $(Me_3Si)_2SiMe$ and $(Me_3Si)_3Si$ groups [5]. Using their rate data, σ^+ constants can be calculated for these four groups to be +0.01, —0.03, —0.05 and —0.06. The trend is in good agreement with ours although the total spread is somewhat less. Our results are also in qualitatively good agreement with a study of infrared intensities, interpreted in terms of $\sigma_R{}^0$ constants, which showed rather small differences between Me_3Si, Me_5Si_2 and $(Me_3Si)_2SiMe$ substituents ($\sigma_R{}^0$ = zero, ±0.04 and ±0.06 respectively) [24].

A previous study of σ^+ for Me_3Si and Me_5Si_2 based on infrared frequency shifts of *p*-substituted acetophenones gave values of 0.00 and —0.23 respectively [25]. The value for Me_3Si agrees with ours, and with other data in the literature [5,7], but that for Me_5Si_2 does not. The infrared method may be unreliable since it depends on measurement of very small changes in frequency, which may be influenced by other vibrational properties of the molecule. From another study, based on measurement of charge transfer spectra, σ^+ values of —0.22, —0.62, —0.77 and —0.81 for Me_3Si, Me_5Si_2, $Me_3Si(SiMe_2)_2$ and $(Me_3Si)_2SiMe$ were reported [26]. These values are all much more negative than ours, or than other literature values.

The electron-release by polysilanyl groups presumably results mainly from σ—π conjugation of Si—Si bonding orbitals with the benzene ring π system. Our results are consistent with this view, except for the decrease in σ^+ going from $(Me_3Si)_2SiMe$ (compound 7) to $(Me_3Si)_3Si$ (8). No difference is expected on the basis of a purely hyperconjugative model, suggesting that other effects may contribute to electron donation in 8 and perhaps in other polysilylarylbenzenes.

C. Diphenylpolysilanes. The results for the compounds in this class (13—15) are again summarized in the form of σ^+ constants in Table 2. The $PhSiMe_2$ substituent, with σ^+ = +0.08, is electron-attracting toward benzene compared with Me_3Si, as expected. The effect of the second benzene ring is rapidly muted as it becomes more remote, so that the $PhSiMe_2SiMe_2$ and $PhSiMe_2(SiMe_2)_2$ groups are essentially indistinguishable from Me_5Si_2 or $Me_3Si(SiMe)_2$.

In a study of ^{13}C and ^{29}Si NMR spectra of halogen-substituted permethylpolysilanes, we found that substituent effects of Cl and F do not extend beyond the third silicon atom from the site of substitution [27]. The present results confirm this conclusion for the case of phenyl substitution, and thereby cast further doubt on the theory of long-range electronic transmission in the ground state of polysilanes [28].

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