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HYPERCONJUGATIVE vs. *d* ORBITAL EFFECTS IN UNSATURATED SILANES

II*. THE RADICAL ANIONS OF *para*-SILYL-SUBSTITUTED ANILINES

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Summary

The radical anions of a series of *para*-silyl substituted *N,N*-dimethylanilines; p-$SiH_nMe_{3-n}C_6H_4NMe_2$ (n = 0-3) have been studied by electron spin resonance spectroscopy. When $n = 0$ or 1 the primary radicals may be generated by either electrolytic or metal reduction. For $n = 2$ or 3 reduction with potassium immediately gives secondary paramagnetic species resulting from loss of hydride from silicon. Primary radicals for the $n = 2$ or 3 compounds may be obtained electrolytically. The ESR spectra show increasing spin delocalization into the silyl group as n increases, to the point that the spin distribution in the p-SiH_3 compound approaches that of p-nitro-*N,N*-dimethylaniline radical anion. A tentative analysis of the secondary and tertiary spectra is given. The results, coupled with CNDO/2 calculations for the radical anions, indicate that the primary interaction between silicon and the aromatic system involves the σ^* levels of the silyl substituents and the π^* orbitals of *N,N*-dimethylaniline.

Introduction

The trends of the energy levels produced by *para* silyl substituents in *N,N*-dimethylanilines reported in the preceding paper were interpreted in terms of variations in the interactions of the σ^* system of the silyl substituent with the aniline π system. These interactions increased as the number of hydrogens on silicon increased [1]. If this conclusion is correct, then the lowest lying vacant molecular orbitals in the silyl substituted anilines should have significant σ^*(Si—H) character. We have recently reported the finding that the trimethylsilyl substituent sufficiently enhances electron affinity of the *N,N*-dimethylaniline system to permit reduction to the radical anion [2]. To test the relative importance of

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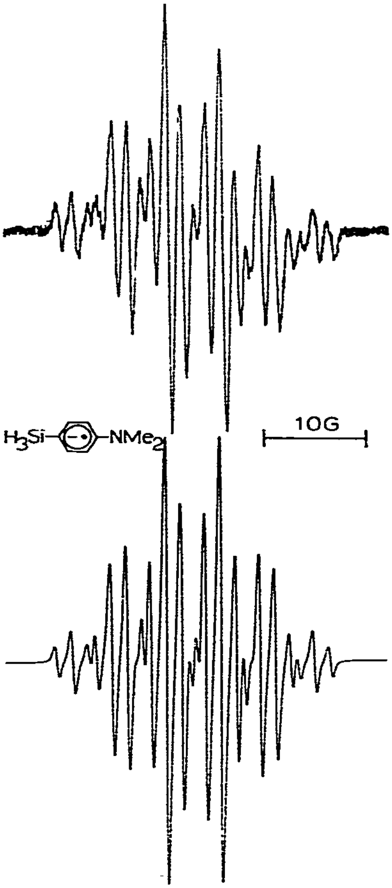
* For part I see ref. 1.

σ^* hyperconjugative and *d* orbital interactions we have examined how the replacement of methyl groups on silicon by hydrogen affects *para* silyl substituted *N*,*N*-dimethylaniline radical anions.

There have been several reports of the ESR spectra of aromatic radical anions containing silicon—hydrogen bonds [3], which have been summarized in a recent paper by O'Brien et al. [4]. Widely differing values for silyl hydrogen coupling constants appear in these reports, apparently because the investigators were observing paramagnetic species resulting from reactions of the parent radical anions [4]. In this paper we report the primary ESR spectra of *para* silyl substituted *N*,*N*-dimethylaniline radical anions and preliminary results on the secondary and tertiary spectra which result from subsequent reactions of these radical anions.



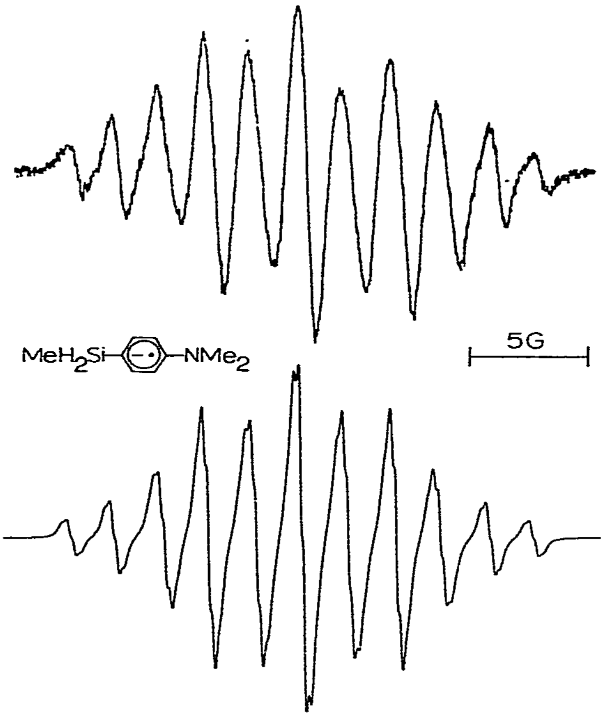


Fig. 1. ESR spectrum of the radical anion of *p*-silyl-*N*,*N*-dimethylaniline, generated electrolytically, THF, —96°C; upper, experimental; lower computer simulated using Lorentzian line shapes and a line width of 0.25 G.

Fig. 2. ESR spectrum of the radical anion of *p*-methylsilyl-*N*,*N*-dimethylaniline, generated electrolytically, THF, —90°C; upper, experimental; lower computer simulated using Lorentzian line shapes and a line width of 0.20 G.

Results and discussion

In Fig. 1 is shown the ESR spectrum of the radical anion of *p*-silyl-*N*,*N*-dimethylaniline generated electrolytically in THF solution at —96°C with tetrabutylammonium perchlorate as the supporting electrolyte. This spectrum cannot be obtained by potassium reduction. Using potassium metal as the reducing agent the spectrum shown in Fig. 6 is obtained. The primary (electrolytic) spectrum consists of a quartet splitting due to the silyl protons of 5.35 G, and two triplet splittings of 3.94 and 1.59 G which are assigned to the protons *meta* and *ortho* to the dimethylamino group, respectively, by analogy to the coupling constants of *p*-trimethylsilyl-*N*,*N*-dimethylaniline radical anion [5]. No coupling due to nitrogen or the protons of the dimethylamino group were resolved for *p*-silyl-*N*,*N*-dimethylaniline radical anion. However, the line width of 0.8 G is considerably larger than that observed for the trimethylsilyl substituted anilines, viz. 0.15 G [2]. This broadening might be attributed to the unresolved couplings with the dimethylamino group. The fit of the simulated spectrum could be improved by using a line width of 0.25 G, and adding splittings of 0.10 G and 0.05 G for the nitrogen and the methyl protons.

The spectrum of *p*-methylsilyl-*N*,*N*-dimethylaniline radical anion, generated electrolytically, is shown in Fig. 2. The spectrum consists of three triplet splittings of 4.02, 3.81 and 1.78 G. The smallest triplet coupling is assigned to the protons *ortho* to the dimethylamino group. The 4.02 and 3.81 G splittings are assigned to the *meta* protons and the silyl protons, respectively. It is possible for the assignments of these two couplings to be reversed. However, the trend of the splittings for the couplings of the *meta* protons to increase from *p*- silyl- to *p*-trimethylsilyl-, Table 1, supports the assignment given.

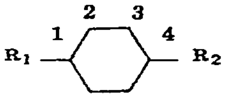
Potassium reduction of *p*-dimethylsilyl-*N*,*N*-dimethylaniline in 2/1 THF/DME solution at —90°C gave a greenish yellow solution which had the ESR spectrum shown in Fig. 3. The spectrum consists of a doublet splitting of 3.08 and two triplet splittings of 4.07 and 2.39 G which are assigned as indicated in Table 1. An expanded spectrum permits the measurement of a smaller splitting of 0.18 G arising from the methyl protons on silicon. Electrolytic reduction gave a similar, but much weaker spectrum.

The hyperfine couplings for these radical anions are collected in Table 1, along with previously reported couplings for similar radical anions. The couplings due to nitrogen or the methyl protons on nitrogen in the silylaniline radical anions were not resolved in any of the cases studied. The line width, which may be attributed to interaction of the unpaired electron with the dimethylamino group, increases with increasing number of hydrogens on silicon. However, O'Brien et al. observed line broadening in phenylsilane radical anions as the number of hydrogens on silicon increased [4]. Other workers have observed that for a series of dimethylsilyl substituted aromatic radical anions, line width variations are observed depending on solvent and method of generation [6]. Nevertheless, by attributing the line broadening to spin density delocalized on the dimethylamino group, maximum possible values for the nitrogen and dimethylamino protons may be estimated. These have been included in Table 1.

Inspection of the results given in Table 1 shows that the ring proton coupling constants are larger, and the silyl proton splittings smaller than those

TABLE 1

HYPERFINE COUPLING CONSTANTS OF SILYL SUBSTITUTED AROMATIC RADICAL ANIONS



Substituents		Hyperfine splittings (Gauss)					
R_1	R_2	a(N—Me)	a_{R_1}	a_{H_2}	a_{H_3}	a(Si—H)	a(Si—Me)
NMe_2	$SiMe_3$			3.25	4.55		0.15
NMe_2	$SiHMe_2$			2.39	4.07	3.08	0.18
NMe_2	SiH_2Me	0.03[a]	0.05[a]	1.78	4.02[b]	3.81[b]	0.20
NMe_2	SiH_3	0.05[a]	0.10[a]	1.59	3.94	5.35	
NMe_2	NO_2[c]	0.71	1.13	1.10	3.33		
H	$SiHMe_2$[d]		8.15	0.86	2.72	7.20	0.11
H	SiH_2Me[d]		8.40	0.64	2.76	6.33	0.20[a]
H	SiH_3[d]		8.46	0.52	3.08	8.04	

[a] Estimated. [b] These two assignments might be interchanged. [c] Ref. 20; $a(NO_2) = 12.0$ G [d] Ref. 4.

for the corresponding silyl benzene radical anions. As we have suggested elsewhere, this is probably a result of the competition between the dimethylamino group whose electron-donating effect tends to favor the antisymmetric state for the radical anion and the silicon substituent, whose electron-withdrawing effect

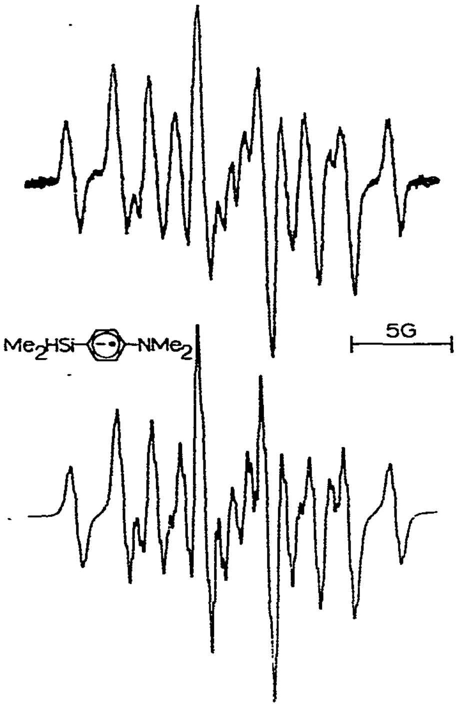


Fig. 3. ESR spectrum of the radical anion of p-dimethylsilyl-N,N-dimethylaniline, generated by potassium reduction, 2/1, THF/DME, −90°C; upper, experimental; lower, computer simulated using Lorentzian line shapes and a line width of 0.18 G.

tends to favor the symmetric state [5,7]. The π^* symmetric character of the occupied orbital in the radical increases as methyl groups on silicon are replaced by hydrogen. Down the series there is a decrease in the ring proton coupling constants and an increase in the splittings due to the silyl protons. The effect of the silyl group approaches that of the nitro group in terms of the spin distribution in the radical anions. The results clearly indicate that the interaction of the silyl substituent with the π^* orbital of the radical increases as methyl groups on silicon are replaced with hydrogen.

In order to gain a better understanding of the bonding interactions between the silyl substituents and the ring π system, CNDO/2 calculations [8] for the radical anions have been performed. For these calculations standard bond lengths and angles were employed [9]. For the initial calculations, a silicon—hydrogen bond was held coplanar with the ring, as was suggested by NMR studies of silyl substituted aromatic systems [10]. The total calculated electronic energy and the spin distributions were not affected to a large extent by rotation of the silyl substituent. For *p*-silyl-*N*,*N*-dimethylaniline the total electronic energy for the configuration with one Si—H bond perpendicular to the ring was about 83 cal/mol more stable than the configuration with one hydrogen in the ring plane [11]. For the methylsilyl and dimethylsilyl substituents the calculations again predicted the lowest energy configuration of the silyl substituent to be one with a Si—H bond perpendicular to the ring.

In the calculations reported here the lower energy configuration of the silyl substituent, that with one Si—H bond perpendicular to the ring was employed.

Our CNDO/2 calculations were far more sensitive to the orientation of the dimethylamino group. In our earlier work we found that the only configuration of the dimethylamino group which gave reasonable agreement with experiment was that in which it was sp^2 hybridized and planar with the ring [12]. Recently crystallographic studies have shown that in 5-*p*-*N*,*N*-dimethylaminophenyl-10,11-dihydro-5H-dibenzo[b,f]silepin the *para*-dimethylamino group is, in fact, nearly planar with the benzene ring [13]. However, with a planar configuration for the dimethylamino group in *p*-silyl-*N*,*N*-dimethylaniline radical anion, the highest occupied orbital is calculated to be a σ^* orbital involving the silyl group, while the experimental hyperfine splittings indicate the occupied orbital to be of symmetric π^* symmetry. If, in the CNDO/2 calculation, the dimethylamino group is treated as tetrahedral the calculation correctly gives an orbital of π^* symmetry as the HOMO in the radical anion. As we have pointed out [2], it is conceivable that in systems where the additional electron occupies an aromatic π^* orbital, electron repulsion between the unpaired electron and the nitrogen lone pair results in a distortion of the molecule so as to remove the lone pair from conjugation. This is supported by the fact that the CNDO/2 calculations predict the tetrahedral configuration of the dimethylamino group in *p*-silyl-*N*,*N*-dimethylaniline radical anion to be about 29 kcal/mol more stable than the planar configuration [11]. The total energy of the system also decreases to a smaller extent as the lone pair is rotated from the position perpendicular to the ring plane. For the results given here the dimethylamino group was treated as tetrahedral with a dihedral angle between the nitrogen lone pair and the plane of the ring of 30°, a geometry which is indicated by our calculations to be close

TABLE 2

CNDO/2 RESULTS FOR THE *para*-SILYL-*N*,*N*-DIMETHYLANILINE RADICAL ANIONS

Substituent	Energy HOMO^a	π spin densities^b							HOMO coefficients	
		N	H				Si		Si	
			1	2	3	4	p	d	p_π	d_π
$SiMe_3$	0.0275	−0.005	0.332	−0.084	0.180	0.087	0.105	0.195	−0.314	0.429
$SiHMe_2$	0.0231	−0.005	0.331	−0.088	0.186	0.077	0.105	0.207	−0.325	0.443
SiH_2Me	0.0219	−0.004	0.303	−0.089	0.185	0.049	0.143	0.196	−0.387	0.432
SiH_3	0.0157	−0.004	0.313	−0.094	0.190	0.052	0.162	0.184	−0.401	0.419

^{a}In atomic units. $^b\alpha$ spin—β spin; numbering as in Table 1.

to the minimum energy orientation of the group [11]. As with our calculations on the trimethylsilyl-*N*,*N*-dimethylaniline radical anions [5], reasonable agreement between experimental and calculated π spin densities using a McConnell type relation [14] was obtained. The cogent CNDO/2 results are given in Table 2.

In the radical anions, the energy of the HOMO decreases from *p*-trimethylsilyl- to *p*-silyl-*N*,*N*-dimethylaniline, following the same trend observed for the ground state energies [1]. The p_π spin density on silicon increases down the series while the d_π spin density decreases slightly. Similarly, the HOMO coefficients for silicon's *p* orbital of π symmetry increase significantly as methyls are replaced by hydrogen while the d_π coefficients decrease. Generally hydrogens on silicon accept electron density better than methyl groups [15]. The silicon—hydrogen bond ($Si^{\delta+}H^{\delta-}$) is more polar than the silicon—carbon bond [16]. One might anticipate that the replacement of methyl groups on silicon by hydrogen would increase the positive charge on silicon, lower the energy of the *d* orbitals, and increase the interaction between the *d* orbitals and the π system. While increasing *d* orbital interaction as methyl groups are replaced with hydrogen could be used to rationalize the ESR results, such an explanation is not consistent with the CNDO/2 results. The CNDO/2 results are consonant with the increase in the energy of the *d* level going from tetramethylsilane to silane, discussed in the preceding paper [1]. As the energy of the *d* level increases, the interaction between the aniline π system and the *d* orbitals decreases as the calculations suggest. While the calculations indicate that both p_π and d_π interactions are involved in these radical anions, only the variation of the silicon *p* orbital parameters follow the experimentally observed trends. The combination of the silicon p_π orbitals with the aniline π system which we obtain in our calculations is antibonding with respect to silicon's other substituents. This in agreement with calculations by Hollebone which show that the lowest lying π acceptor orbital for the silyl group and the trimethylsilyl group is a σ^* orbital originating with silicon's 3*p* level [17]. The CNDO/2 calculations therefore indicate that it is a hyperconjugative interaction between a σ^* level of the silyl group and the aniline π system which accounts for the trends observed in the aniline radical anions. This finding is consistent with the suggestion by Pitt that interactions between silicon σ^* levels and π systems could be significant [18]. In addition, Bock has recently reported that CNDO/2 calculations, including 3*d* orbitals for silicon in the basis set, overemphasize d—p_π back bonding and that 3*d* silicon orbitals need not be considered explicitly to rationalize either the different dipole moments of methyl- and silyl-acetylenes or the general photoelectron spectroscopic pattern of the silicon compounds [19].

Secondary and tertiary spectra

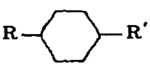
After obtaining the primary spectrum of *p*-dimethylsilyl-*N*,*N*-dimethylaniline radical anion, Fig. 3, the solution was again brought into contact with the potassium mirror at —78°C. Spectra II, or III, (Fig. 4) were obtained from the resulting solution. Species II appeared after 15 to 20 h, and species III 1 to 2 days after spectrum II was obtained. Spectrum II could not be obtained from the primary radical without further reaction at the potassium mirror. Spectrum II is a doublet of quintets. The doublet splitting of 7.05 G is comparable to the couplings for the silyl hydrogens of either 1,4-bis(dimethylsilyl)benzene radical anion or 1-phenyldimethylsilyl-4-dimethylsilylbenzene radical anion [4]. The quintet coupling of 1.85 G in spectrum II is similar to the couplings observed for benzene radical anions substituted at the 1,4 positions with organosilyl substituents [4]. The coupling constants of II suggest that it is a 1,4-bis(disilyl)benzene radical anion bearing one silyl hydrogen. Considering that species II is formed in the reduction of *p*-dimethylsilyl-*N*,*N*-dimethylaniline, and the path proposed by O'Brien for the further reactions of arylsilyl radical anions [4], species II may be tentatively identified as 4-dimethylsilyl(*p*-dimethylaminophenyl)dimethylsilylbenzene radical anion. Couplings for the methyl protons on silicon were not resolved. Formation of this species requires silicon—hydrogen bond cleavage in the dimethylsilyl precursor.

Spectrum III consists of a quintet (1.78 G). The additional peaks at the ends are probably due to remaining II. The absence of silyl hydrogen coupling in species III again suggests silicon—hydrogen bond cleavage occurs during the reaction of species II to form III. A tentative structure for III is given in Table 3.

Potassium reduction of *p*-methylsilyl-*N*,*N*-dimethylaniline at —78°C does not give the primary spectrum shown in Fig. 2. Instead a yellow solution is produced within 5 min of reduction which gives the spectrum of species IV, Fig. 5. The spectrum consists of a triplet of quintets. The triplet splitting of 7.21 G is presumably due to two silyl hydrogens, and the quintet of 1.75 G due to the four ring protons of a 1,4-bis(disilyl)benzene ring. A tentative structure is given in Table 3.

TABLE 3

RADICAL ANIONS PRODUCED BY FURTHER REACTIONS OF *para* SILYLANILINES WITH POTASSIUM

Starting compounds	Radical anions 		Coupling constants (Gauss)			
	R	R'	a(Si—H)	a_{aryl}	a(Si—CH$_3$)	Species
p-$Me_2HSiC_6H_4NMe_2$	Me_2HSi	$SiMe_2C_6H_4NMe_2$	7.05	1.85	0.16^a	II
II	Me_3Si	$SiMe_2C_6H_4NMe_2$		1.78	0.16^a	III
p-$MeH_2SiC_6H_4NMe_2$	Me_2HSi	$SiHMeC_6H_4NMe_2$	7.21	1.75	0.14^a	IV
p-$SiH_3C_6H_4NMe_2$	MeH_2Si	$SiH_2C_6H_4NMe_2$	6.05	1.70	0.15^a	V

^{a} Estimated.

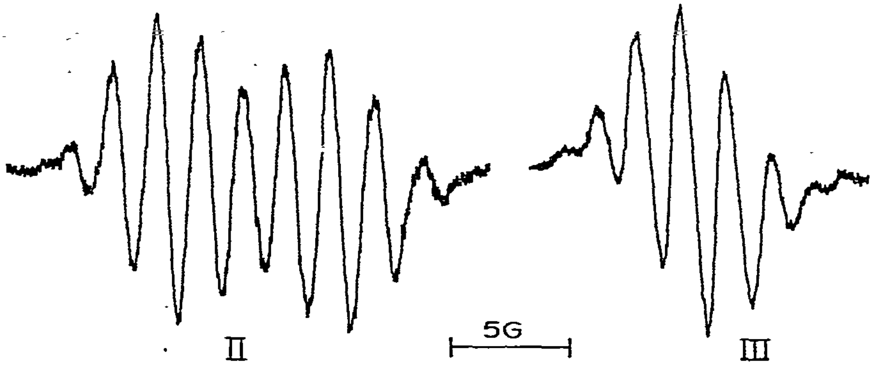


Fig. 4. ESR spectra of the secondary (II) and tertiary (III) radical anions obtained from potassium reduction of *p*-dimethylsilyl-*N*,*N*-dimethylaniline; −95°C, 2/1, THF/DME.

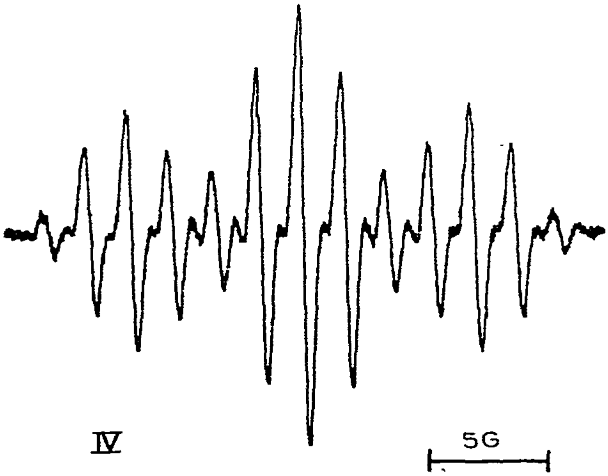


Fig. 5. ESR spectrum of the secondary (IV) radical anion obtained by potassium reduction of *p*-methylsilyl-*N*,*N*-dimethylaniline; −95°C, 2/1, MeTHF/DME.

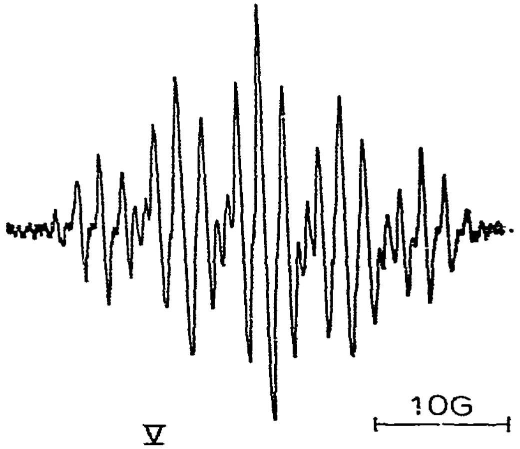


Fig. 6. ESR spectrum of the secondary (V) radical anion formed by potassium reduction of *p*-silyl-*N*,*N*-dimethylaniline; −95°C; 2/1, MeTHF/DME.

Potassium reduction of *p*-silyl-*N*,*N*-dimethylaniline gave the spectrum V, shown in Fig. 6, consisting of a quintet of quintets. The 6.05 G coupling may be assigned to four silyl hydrogens and the 1.70 G coupling to four equivalent ring protons. This species V is tentatively identified a 4-methylsilyl(*p*-dimethylaminophenyl)silylbenzene radical anion.

The ESR spectral characteristics of these secondary and tertiary species, along with tentative structure assignments are collected in Table 3. The unpaired electron is apparently localized on the ring substituted at the 1,4 positions with silicon substituents. This ring would be expected to have a higher electron affinity than the rings bearing dimethylamino substituents. The splitting patterns and coupling constants for these species bear a striking resemblance to those reported by O'Brien for the secondary and tertiary species produced on the reduction of phenylsilanes [4].

While a great deal of very interesting chemistry remains to be done in firmly characterizing these secondary and tertiary species and their mode of formation, the main point bearing on our bonding studies is clear. In both O'Brien's and our systems the secondary and tertiary species produced by metal reduction of aryl silanes bearing silicon—hydrogen bonds arise through loss of hydride from silicon. This is clear chemical evidence that the reduction of these arylsilanes results in the population of an electronic level which has significant σ^*(Si—H) character. Furthermore, the order of stability of the radical anions towards the loss of hydride ($Me_2HSi > MeH_2Si > H_3Si$) suggests that the interaction of the σ^*(Si—H) level with the aromatic π^* system increases as methyl groups on silicon are replaced by hydrogen.

Thus, it appears, on the basis of consideration of energy levels [1], ESR spectra of the radical anions, CNDO/2 analyses, and chemical reactions of the radical anions, that the predominant interaction between silyl substituents and the *N*,*N*-dimethylaniline π system is of the hyperconjugative type, involving the σ^* orbitals of the silyl groups.

Experimental

The synthesis and characterization of the compounds involved in this study have been described previously [1].

Metallic reductions were carried out in vacuo by allowing approximately 10^{-3} *M* solutions of the appropriate silyl aniline dissolved in 2/1 mixtures of tetrahydrofuran (THF): dimethoxyethane (DME) or 2-methyltetrahydrofuran (MeTHF): dimethoxyethane to react with a potassium mirror at —78°C. The details of our method of metal reduction have been described previously [2]. ESR spectra were recorded with the resulting radical anion solutions contained in side arm sample tubes, not in contact with the metal mirror, in the temperature range —90°C to —95°C.

Electrolytic reductions were performed using a sample cell containing two platinum electrodes, designed to fit in the variable temperature probe of the spectrometer. The cathode was located within the cavity, while the anode was outside and above the cavity. No reference electrode was employed. Polarographic grade tetrabutylammonium perchlorate (10^{-2} *M*) was used as the supporting electrolyte in tetrahydrofuran solvent. The anion radicals were generated directly in the ESR cavity at about —90°C using a Heathkit ID-32 dc power source.

The spectra were recorded using a Varian V-4502-13 spectrometer with 100 kHz field modulation.

Acknowledgement

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