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HYPERCONJUGATIVE INTERACTIONS IN SILYLANILINES

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The ground states and lower lying excited states for a series of ortho and para $\text{Me}_n\text{H}_{3-n}\text{M}$ (M = C or Si, n = 0-3) substituted N,N-dimethylanilines have been examined for the bonding interactions between the substituents and the ring π system.

In the para series of compounds the ionization potentials, determined by cyclic voltammetry, are higher for the silicon compounds than for their carbon analogs. The ionization potential decreases as the number of methyl groups on the substituent increases in both the silicon and carbon series, but the effect is much larger for the silicon compounds. Based on correlations between the ultraviolet spectra and the ground state energies, the excited states of the silicon compounds exhibit larger stabilizations than the ground states. Further evidence for the strong interaction between the silyl substituents and the excited states is the fact that the radical anions of the silyl substituted N,N-dimethylanilines may be generated by electrolytic or metal reduction. The same techniques fail to produce any radicals for the carbon compounds. The silyl substituted radicals represent the first examples of aniline radical anions which do not bear strongly electron-withdrawing ring substituents.

The hyperfine coupling constants (hfcc) for the radical anions, unambiguously assigned by labelling experiments, indicate that the lowest lying antibonding orbital is predominantly a π^* orbital symmetric with respect to the plane defined by the point of silicon substitution on the ring. The electron donating effect of the dimethylamino group is greatly diminished in the radical anions, evidently due to repulsion between the nitrogen lone pair and the additional electron. The ring proton hfcc of the para substituted silylaniline radical anions decreases with increasing number of hydrogens on silicon. A concomitant increase in the hfcc for the silyl hydrogens indicates that the interaction of the silyl substituent with the π^* orbital of the radical increases as methyl groups on silicon are replaced by hydrogen.

When potassium is used as the reducing agent, the radical anions undergo further reactions involving loss of hydride from the silicon, to eventually produce new paramagnetic species. Coupled with CNDO/2 calculations, the results provide the first experimental evidence for the importance of $p_{Si}-\pi^*$ as opposed to $d_{Si}-\pi^*$ interaction in the excited states of unsaturated organosilicon molecules.

For the ortho substituted N,N-dimethylanilines the rotational angle of the dimethylamino group has been determined spectroscopically. In general, the angle is greater for the silicon compounds than for their carbon analogs. However,

a linear correlation between the ionization potentials and the rotational angles suggests that the ground state energy of the molecules is predominantly a function of the extent of lone pair conjugation with the ring. No evidence for a through space interaction between the nitrogen lone pair and the vacant silicon d orbitals was found.

Overall, the study indicates that d orbital involvement in the interactions of organosilicon substituents with unsaturated systems is much less significant than is generally held. The importance of $p_{Si}-\pi$ and $p_{Si}-\pi^*$ hyperconjugative interactions between silicon σ^* orbitals and π system in producing the effects of silicon substitution on unsaturated systems has become more apparent.

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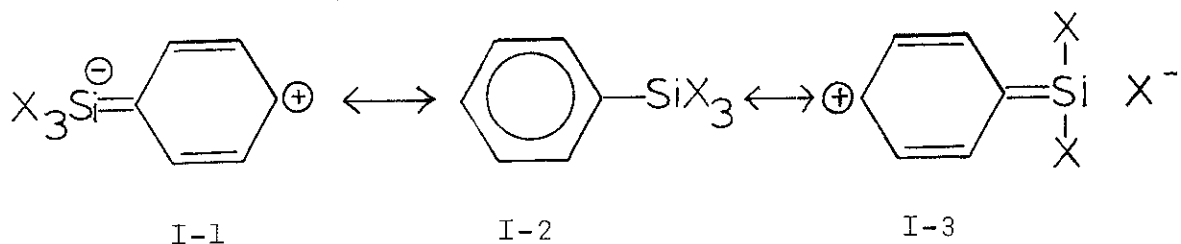
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CHAPTER I

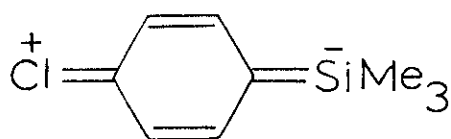
INTRODUCTION

The substituent effects of silyl groups on unsaturated systems have been the subject of numerous investigations, and an excellent review on this subject is available (1). When silicon is attached to a π system, two effects become apparent: silicon, being more electropositive than carbon, has an inductive effect, releasing electron density to the σ system (+I effect); and silicon withdraws electron density from the π system (-M effect). A number of observations have been reported in the literature which indicate that silicon has a small +I effect and higher -M effect (1).

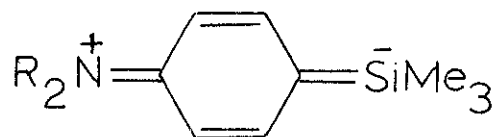
In the early investigations of the interactions between Group IV substituents and the benzene π systems, dipole moment measurements were used. Curram *et al.* (7) measured the dipole moments for the compounds, $\text{Ph}_n\text{X}_{4-n}\text{M}$ (M = C and Si, X = halogen), and observed higher values for the silicon compound than for the corresponding carbon compound.



This was attributed to a combination of d- π bonding (I-1) and negative hyperconjugation (I-3). In similar studies Softer and de Vries (18) reported the dipole moments for phenyltrimethylsilane and its derivatives, substituted with dimethylamino, fluoro, chloro, bromo, methyl, and nitro group. They concluded that while d- π bonding was not important in phenyltrimethylsilane, it did occur in cases where the phenyl ring was substituted with the strongly electron donating groups (I-4, I-5).



I-4



I-5

These results are consistent with the kinetic data reported by Gilman and Marshall (10) for the acid-catalyzed ring carbon-silicon cleavage reactions. They demonstrated that the difficulty of cleavage of the trimethylsilyl group increased in the order: p-anisyl, p-dimethylaminophenyl, p-tolyl, phenyl, p-chlorophenyl, benzyl. Benkeser and Krysiak (3) also noted that the cleavage reaction was facilitated by a strong electron-donating substituent at a ring position where it could furnish high electron density to the aryl carbon-silicon bond.

Webster (19) measured the proton nmr spectra of a series of alkyl and aryl substituted silanes and their carbon analogs. The progressive replacement of methyl groups by the more electronegative phenyl groups resulted in a progressive deshielding for the protons in the substituents. The shift was larger for the protons on the carbon than for those on silicon. This was explained by d-p π bonding between the silicon and the phenyl ring, which increased the electron density on silicon. Sakurai and Ohtzura (16) correlated the chemical shifts of methyl protons of phenyltrimethylsilane derivatives with the σ^+ constants of Brown (6). The σ^+ constants also correlated well with the dipole moment data of Sofer and de Vries (18). They used the applicability of the σ^+ constants as evidence for d-p π bonding between the ring π systems and the silicon.

Benkeser and Krysiak (2) reported the pKa values for a series of Group IV substituted anilines, dimethylanilines, phenols, and benzoic acids. Their results showed that p-trimethylsilylaniline and p-trimethylsilyl-N,N-dimethylaniline were weaker bases and p-trimethylsilylphenol was a stronger acid, compared to unsubstituted or alkyl substituted compounds. They interpreted these results in terms of d-p π bonding (I-5).

Whether d-p π interactions lower the ground state energy of silicon substituted benzene derivatives can not be

determined quantitatively by the above-mentioned methods of measurement. Ionization potentials for such series of compounds have been used in order to determine the energy differences. Bock and Alt (5) investigated the ground state energies for silicon and carbon substituted benzene systems by measuring the vertical ionization potentials of the compounds from intermolecular charge transfer band maxima of suitable donor-acceptor complexes. The observed ionization energy was greater for the silicon compound than that of the carbon analog when silicon was attached directly to the aromatic ring. They explained this in terms of electron withdrawal by silicon via $d-p\pi$ interactions. Lower ionization energy was observed when silicon was attached β to the ring, where $d-p\pi$ interactions were not possible. The reason for this was suggested to be the greater +I effect of silicon relative to carbon. An alternative explanation to this effect was proposed by Pitt (14) and Traylor (11). They suggested that $\sigma-\pi$ hyperconjugative interaction between the ring π system and the C-Si sigma bond could account for the electron release.

Jones (12) has shown that the electrolytic oxidation potentials may be related to the ionization energy of a molecule in cases where direct measurements of the ionization energies are rather difficult and expensive to obtain. He has obtained a better linear relationship

between the ionization potentials measured by photoelectron spectroscopy and the electrolytic potentials then between the photoelectron data and the charge transfer band maxima. The oxidation potentials also correlate well with pKa values for the compounds. The results indicate a small stabilization of the highest filled molecular orbital (MO) when silicon is substituted for carbon in the para position of N,N-dimethylaniline (12). Based on CNDO/2 calculations, the stabilization of the ground state was indicated to be due to a combination of d-p π interactions and p-p π interaction, with d-p π interactions the major perturbation (8).

The CNDO/2 approximation has recently been the object of several critical papers. Worley (20) points out that ionization potentials calculated using Koopman's theorem (13) are usually about 4.0 eV too high. Bock (9) has recently reported that CNDO/2 calculations including 3d orbitals for silicon in the basis set overemphasize d-p π back-bonding and that 3d silicon orbitals need not be considered explicitly in order to explain the general photoelectron spectroscopic pattern of silylacetylenes. However, Bloor and Breen (4) have shown that while CNDO/2 generally gives poor results for ionization potentials of substituted benzenes, relative values for a series of closely related compounds are more reliable.

Jones (8) has demonstrated that CNDO/2 (15) calculations can be usefully applied in bonding studies of Group IV

substituted anilines. They give good correlation with experimentally determined ionization potentials for the ground states and coupling constants for radical cations in Group IV substituted N,N-dimethylanilines. The CNDO/2 charge densities calculated by Jones have been shown to correlate well with changes in ^{13}C chemical shifts (17).

The purpose of the present work is to study the bonding interactions between the substituents and the ring π system for a series of ortho and para $\text{Me}_n\text{H}_{3-n}\text{M}$ ($\text{M} = \text{C}$ or Si , $n = 0-3$) substituted N,N-dimethylaniline. Both ground and excited-state interactions were studied and their magnitudes determined. The experimental data were then used in conjunction with molecular orbital calculations to differentiate among inductive, hyperconjugative, and d-p π interactions on the ground and excited states.

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CHAPTER II

ENERGY LEVELS

The ionization energies of a series of closely related molecules provide a basis for comparing substituent effects on their ground state orbitals (21). The mass spectroscopically determined ionization energies (5) and the vertical ionization potentials from intermolecular charge transfer band maxima of suitable donor-acceptor complexes (6) were used for the bonding informations on the relative energies of the highest filled molecular orbitals (MO) in silyl- and alkylbenzenes. Higher ionization energy was observed for silicon compounds than for carbon analogs, when silicon was attached directly to the aromatic ring. This was explained by electron withdrawal of the silyl group via d-p π bonding. Lower ionization energies were observed when silicon attached β to the ring where d-p π bonding was not possible. The reason for this was thought to be the greater +I effect of silicon relative to carbon, but later an alternative approach to this effect was proposed by Pitt (32) and Traylor (18), which was σ - π hyperconjugative interaction between the ring π system and the carbon silicon sigma bond. Coulson (9) provided theoretical support for a type of σ - π interaction in the form of rehybridization of silicon d-orbitals.

Jones (21) has obtained a better linearity of ionization potentials measured by photoelectron spectroscopy with electrolytic oxidation potentials than with the intermolecular charge transfer spectra band maxima of suitable donor-acceptor complexes, particularly the Group IV substituted anilines. The linearity yields the equation 2.1,

$$I = 2.59 E_{p/2} + 5.44 \quad \text{eq. 2.1}$$

where I is given in electron volts and $E_{p/2}$ is in volts vs. s.c.e. The slightly higher ionization energy, calculated from equation 2.1, using the oxidation potentials measured by cyclic voltammetry in acetonitrile solution, using tetrabutylammonium perchlorate as the supporting electrolyte, has been observed for *p*-trimethylsilyl- than *p*-tert-butyl-*N,N*-dimethylaniline. This stabilization of the ground state observed for *p*-trimethylsilyl-*N,N*-dimethylaniline is attributed to a combination of $d-p\pi$ interaction and hyperconjugative $p-p\pi$ interaction, with the $d-p\pi$ interaction the major perturbation, based on CNDO/2 calculations (12).

Drews and Jones (11) have recently constructed the relative energy levels of the lower-lying excited states, using the ground state energies and solution ultraviolet spectra of *p*-tert-butyl- and *p*-trimethylsilyl-*N,N*-dimethylaniline. They have observed that the trimethylsilyl group perturbs the excited states to a much larger extent than the ground states.

The corresponding substituent effects for ortho Group IV substituted N,N-dimethylanilines have not been previously studied in detail. The previous investigations dealt mostly with trimethylsilyl substituted compounds and their carbon analogs. We have investigated both the ground states and the low-lying excited states of a whole series of ortho and para Group IV substituted N,N-dimethylanilines, including o- and p-silyl-, -methylsilyl-, -dimethylsilyl-, -trimethylsilyl-N,N-dimethylaniline and their carbon analogs.

The object of this study was to determine how the progressive replacement of methyl groups in the trimethylsilyl group with hydrogen affects the bonding interactions between the silicon group and the ring π system.

Results and Discussion

Para Group IV Substituted N,N-dimethylanilines

The oxidation potentials listed in Table 2.1 for the para series of compounds were determined by cyclic voltammetry in acetonitrile solution, using tetrabutylammonium perchlorate as the supporting electrolyte. The ionization energies calculated from equation 2.1, using the oxidation potentials, have also been included in the table. Assuming Koopman's theorem (24), these ionization energies reflect the relative ground state energies for the compounds.

Higher ionization energies are observed for the silicon compounds than for the carbon components. The trend of

TABLE 2.1

HALF-PEAK OXIDATION POTENTIALS AND IONIZATION ENERGIES
FOR PARA GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	$E_{p/2}^a$ V vs. sce	Ionization energy ^b eV
-H	0.74 ^c	7.62 ^c
-CH ₃	0.70 ^d	7.50 ^c
-CH ₂ Me	0.70	7.50
-CHMe ₂	0.71	7.53
-CMe ₃	0.68 ^c	7.44 ^c
-SiH ₃	0.86	7.98
-SiH ₂ Me	0.85	7.95
-SiHMe ₂	0.83	7.89
-SiMe ₃	0.78 ^c	7.74 ^c

^aDetermined in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte.

^bCalculated from eq. 2.1.

^cRef. 21.

^dRef. 27.

increasing ionization energies from carbon compounds to silicon analogs may be interpreted in terms of a stabilization of the highest filled MO by silyl groups. This stabilization can only result from the electron density in the ring being reduced. The lower ground-state energies observed for silicon compounds indicate that silyl groups are either electron-withdrawing or less electron-donating than alkyl groups. Stabilization of the ground-state orbitals is commonly observed in unsaturated organosilicon compounds and has generally been attributed to d-orbital interactions with the bonding π orbitals (1). However, Bock (14) has recently reported that silicon 3d orbitals need not be considered in order to rationalize the higher ionization potentials of silyl acetylenes over the corresponding carbon analogs. Inductive effects and hyperconjugative interactions between the methyl or silyl group and acetylene are sufficient to explain the ordering of ground-state MO's. A methyl group has a higher hyperconjugative effect than a silyl group (3). It has also been reported that photoelectron spectroscopic data (4) indicate that the silicon-carbon or silicon-hydrogen σ orbitals are more localized than the corresponding carbon-carbon or carbon-hydrogen orbitals in Group IV substituted ethylenes.

Ionization energies generally increase from p-tert-butyl- to p-methyl-N,N-dimethylaniline, as well as from p-

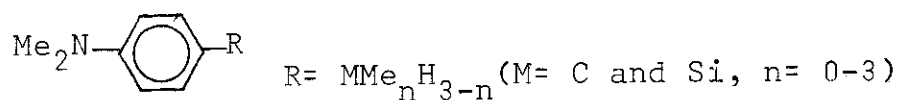
trimethylsilyl- to p-silyl-N,N-dimethylaniline. This is consistent with the higher inductive effect of a methyl group compared with hydrogen (36). The effect is larger for silicon compounds than for carbon compounds. This suggests that π type interactions, as well as σ inductive effects, exist between the silicon and the ring π system.

Nuclear magnetic resonance (nmr) spectroscopy has been widely applied for the study of substituent effects. The chemical shifts for the series of substituted aromatic systems provide information about the electronic nature of the substituents (13). The proton chemical shifts for para Group IV substituted N,N-dimethylanilines are listed in Table 2.2. The chemical shifts for aromatic protons and the dimethylamino protons in the silicon compounds are shifted downfield compared to the carbon compounds. This is consistent with the fact that the silyl groups are electron-withdrawing or less electron-donating than the alkyl groups, as indicated by the ionization energies observed for these compounds.

In the silicon series of compounds the chemical shifts for the aromatic and dimethylamino protons are slightly shifted downfield as the methyl groups on silicon are replaced by hydrogen, while the opposite trend is observed for the chemical shifts of silyl hydrogens. Both trends suggest that the electron-accepting ability of the silyl group increases as the number of hydrogens on silicon increases. This is

TABLE 2.2

NMR DATA FOR PARA GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES



Substituent (R)	Chemical shifts ^a						
	M-H	(J ^b)	M-CH ₃	N-CH ₃	H _o	(J ^b)	H _m
-H	-		-	2.85			6.76
-CH ₃	2.23		-	2.91	6.54	(8)	6.92
-CH ₂ Me	2.56	(6)	1.18	2.92	6.57	(8)	6.94
-CHMe ₂	2.74	(7)	1.15	2.76	6.40	(8)	6.80
-CMe ₃ ^c	-		1.30	2.90	6.70	(8)	7.24
-SiH ₃	4.26		-	3.00	6.68	(8)	7.42
-SiH ₂ Me	4.38	(4)	0.34	3.02	6.68	(8)	7.39
-SiHMe ₂	4.46	(4)	0.27	2.95	6.66	(8)	7.34
-SiMe ₃ ^c	-		0.20	2.90	6.58	(9)	7.25

^aMeasured in carbon tetrachloride solution with tetramethylsilane as an internal reference, in δ .

^bIn hz.

^cRef. 40.

consistent with the ordering of the ground states observed for the compounds.

In order to gain a better understanding of the bonding interactions between Group IV substituents and the ring π system, reflected by the ground states and nmr data, CNDO/2 calculations have been performed for the ground states of these molecules.

In the calculations the dimethylamino groups were held planar for the ground states of these molecules, allowing maximum conjugation with the ring π system (12). This value is reasonably close to the electron diffraction data for N,N-dimethylaniline, where the C-N-C intervalence angle at nitrogen is 116° (37). It was also reported that an electron-withdrawing ring substitution increased the angle and the angle approached 120° (37). The rotational orientation of silyl groups with respect to the aromatic ring was varied to determine the most stable configuration. The orientation of the silyl group with one of the silyl hydrogens in the plane of the ring was found to give the lowest total electronic energy. This configuration was about 1.15 kcal/mole more stable than that with the silyl hydrogen perpendicular to the ring for p-silyl-N,N-dimethylaniline (see Appendix I). This is in good agreement with the conformation analysis reported for arylsilanes, which showed the preferred conformation of the silyl hydrogen was coplanar with the aromatic

ring (31). The same orientation of alkyl groups was used for the carbon compounds.

In Tables 2.3 and 2.4, the numbering given below was used.

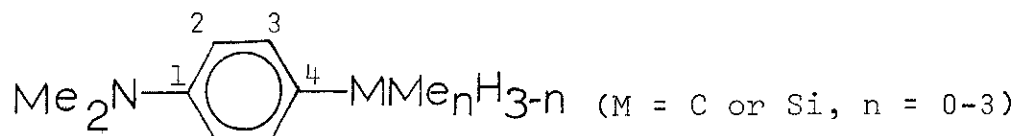


Table 2.3 gives the energy and the atomic orbital coefficients for the highest filled MO. Lower energy of the orbital is observed for silicon compounds than for carbon compounds. The energy also decreases as the number of methyl groups in the substituent increases for both the silicon and carbon series of compounds. This trend is consistent with the ordering of ground states, as indicated by oxidation potentials. Figure 2.1 clearly illustrates that there is a quite good linear relationship between the CNDO/2 calculated energy of the highest filled MO and the oxidation potentials for para Group IV substituted N,N-dimethylanilines.

In Table 2.3 it can be seen that the highest filled MO is clearly a π symmetric orbital with significant nitrogen lone-pair character. It is interesting that the MO has a node between the nitrogen and the ring and a node between the alkyl substituent and the ring, but there is no node between the silyl substituent and the ring. The general trend observed is for the energy of the highest filled MO to decrease as the coefficient of the nitrogen $p\pi$ orbital

TABLE 2.3

CNDO/2 π COEFFICIENTS AND THE ENERGY FOR THE HIGHEST FILLED MOLECULAR ORBITAL OF PARA GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES^a

Substituent	Energy -au	Atoms				Si		
		N	1	2	3	4	p	d ^b
-H ^c	0.3923	0.658	-0.265	-0.321	0.119	0.399		
-CH ₃ ^c	0.3727	0.575	-0.301	-0.293	0.181	0.408	-0.136	
-CH ₂ Me	0.3787	0.609	-0.295	-0.306	0.165	0.408	-0.111	
-CHMe ₂	0.3772	0.606	-0.297	-0.304	0.168	0.408	-0.123	
-CMe ₃ ^c	0.3774	0.605	-0.296	-0.304	0.166	0.406	-0.127	
-SiH ₃	0.4156	0.663	-0.217	-0.347	0.070	0.367	0.029	-0.182
-SiH ₂ Me	0.4070	0.651	-0.229	-0.350	0.084	0.374	0.017	-0.170
-SiHMe ₂	0.4008	0.643	-0.241	-0.319	0.096	0.382	0.014	-0.158
-SiMe ₃ ^c	0.3975	0.640	-0.234	-0.318	0.098	0.382	0.010	-0.158

^aIn as much as this is a π symmetric orbital for all the molecules, these are coefficients of the atomic orbitals of π symmetry. None of the other atomic orbitals contribute significantly to this MO.

^bIn the set-up of the overlap integrals the orientation of this $d\pi$ orbital is such that a negative coefficient indicates positive overlap.

^cRef. 12.

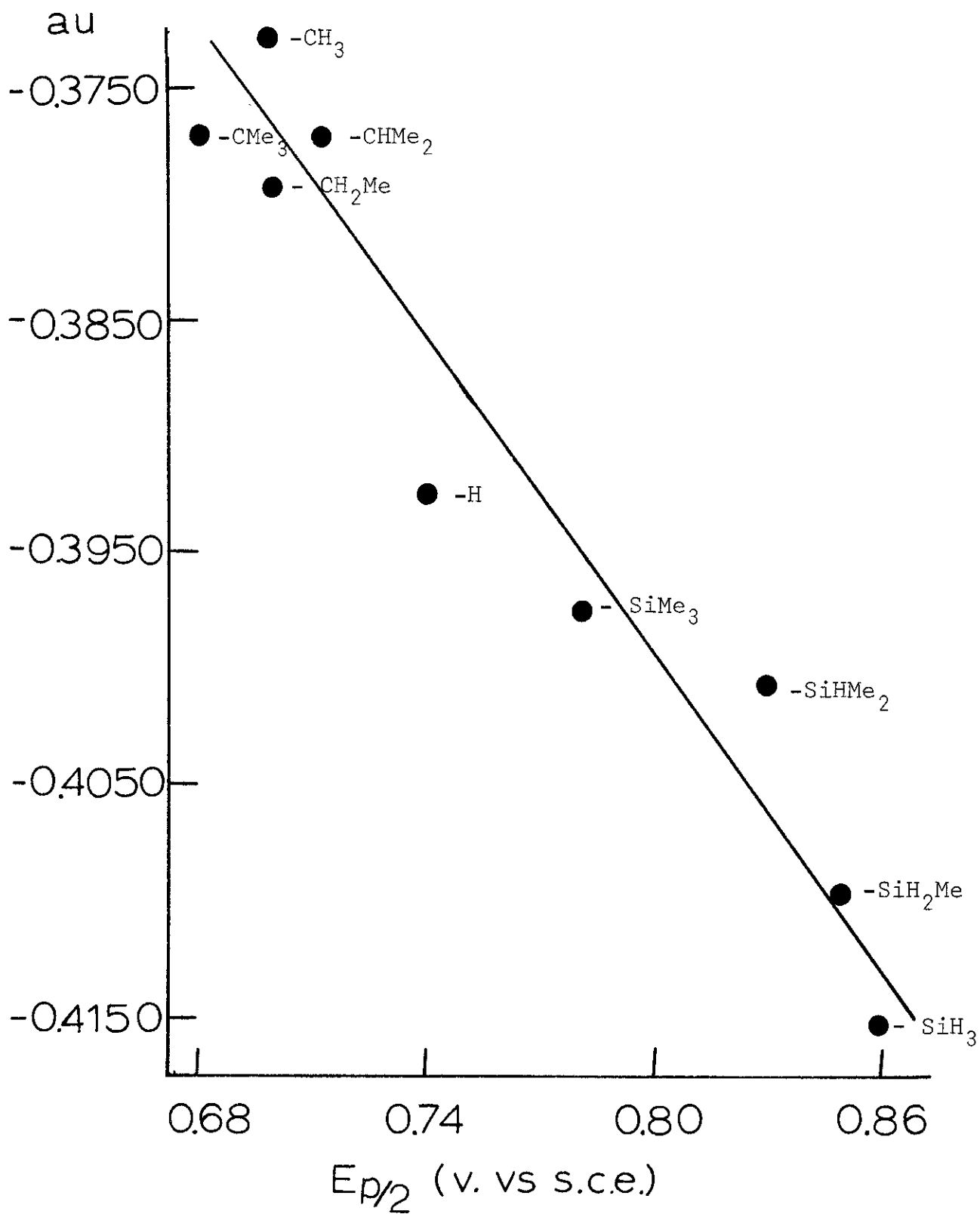


Fig. 2.1. Plot of the CNDO/2 calculated highest filled MO energies vs. half-peak oxidation potentials for Group IV substituted N,N-dimethylanilines.

increases. Jones (12) has pointed out that as the contribution of the nitrogen lone pair orbital to the π system in ring substituted anilines increases, the base strength decreases, and the highest filled MO is destabilized. Larger nitrogen contribution is observed for silicon compounds than for carbon compounds, as expected from the higher ionization energies obtained for silicon compounds. Increasing the nitrogen coefficient from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline is consistent with increasing the ionization energy in the same way. The coefficients indicate that the major interaction between silicon and this orbital is of the d-p π type and that p-p π interactions do not contribute significantly to the stabilization of the highest filled MO. It is also apparent that the d orbital coefficient increases from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline. This is probably due to the -I effect of the silyl hydrogen (20,21,22).

In order to assess the total effect of Group IV substitution in these systems, the total charge perturbations and bond orders for the orbitals of interest were examined. Table 2.4 lists the formal charges, Δq (3), and the total electron densities for the substituent's p and d orbitals. These have been separated into σ and π components. More positive Δq_{π} of the nitrogen is observed for silicon compounds than for carbon compounds, indicating the greater involvement of the nitrogen lone-pair orbital in lower-lying occupied molecules orbitals

TABLE 2.4

CNDO/2 NET ATOMIC CHARGES FOR PARA GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	Δq^a	Atoms							Substituent orbitals' density						
		N	1	2	3	4	M	M-H ^b	M-Me ^b	P	d				
-H	Tot	-0.152	0.155	-0.062	0.034	-0.031	-0.002	-0.004							
	σ	-0.319	0.091	0.028	-0.001	0.032									
	π	0.167	0.064	-0.090	0.035	-0.063									
-CH ₃	Tot	-0.153	0.146	-0.057	0.019	0.003	-0.139								2.719
	σ	-0.319	0.096	0.020	0.009	0.026	-0.137								1.856
	π	0.167	0.050	-0.077	0.010	-0.029	0.137								0.863
-CH ₂ Me	Tot	-0.153	0.145	-0.056	0.015	0.004	0.018	-0.009	-0.006						2.997
	σ	-0.318	0.097	0.021	0.008	0.034	0.017								1.998
	π	0.165	0.048	-0.077	0.007	-0.030	0.001								0.999
-CHMe ₂	Tot	-0.153	0.144	-0.054	0.012	0.003	0.040	-0.017	-0.007						3.006
	σ	-0.327	0.088	0.021	0.010	0.029	0.051								1.995
	π	0.174	0.056	-0.075	0.002	-0.026	-0.011								1.011
-CMe ₃	Tot	-0.153	0.145	-0.054	0.010	0.000	0.053	-0.017	-0.007						3.019
	σ	-0.318	0.098	0.022	0.005	0.031	0.054								2.018
	π	0.165	0.047	-0.076	0.005	-0.031	-0.001								1.001
-SiH ₃	Tot	-0.147	0.187	-0.084	0.108	-0.162	0.412	-0.156							1.818
	σ	-0.334	0.072	0.027	0.005	-0.116	0.251								1.193
	π	0.187	0.115	-0.111	0.103	-0.048	0.161								0.625
-SiH ₂ Me	Tot	-0.148	0.183	-0.083	0.102	-0.155	0.306	-0.153	-0.214						1.800
	σ	-0.332	0.076	0.026	0.006	-0.117	0.143								1.188
	π	0.184	0.107	-0.109	0.096	-0.038	0.163								0.709
-SiHMe ₂	Tot	-0.149	0.178	-0.082	0.097	-0.145	0.215	-0.150	-0.204						0.612
	σ	-0.330	0.078	0.026	0.006	-0.116	0.053								1.781
	π	0.181	0.100	-0.108	0.091	-0.029	0.162								1.191
-SiMe ₃	Tot	-0.149	0.178	-0.082	0.093	-0.140	0.136	-0.191							0.590
	σ	-0.329	0.080	0.025	0.006	-0.113	-0.016								1.762
	π	0.180	0.098	-0.107	0.087	-0.027	0.152								1.165
															0.597

^aExcess total charge density on the atom indicated.^bAverage Δq .

in silicon compounds. A general tendency for electron density to be shifted toward the silicon and of the silyl compound is observed. This electron density accumulates at the silicon methyl carbons or silyl-hydrogens. The +I inductive effect of the silyl group shows up as increased σ electron density at carbon atom 4. Along with this there is a decrease of π density at the same carbon (12).

CNDO/2 bond orders and bond densities for interaction between the Group IV element and its ring carbon for these series of compounds are listed in Table 2.5. An examination of the off-diagonal terms of the CNDO/2 density matrices for these series of compounds shows the relative importance of d- $p\pi$ bonding and p- $p\pi$ hyperconjugation for the ground state. The total interaction of d orbitals with the system is significantly larger than the $p\pi$ interaction for the silicon compounds. The total hyperconjugative $p\pi$ interaction in the ground state is generally greater for silicon compounds than for the carbon analogs. The $p\pi$ interaction increases for both carbon and silicon compounds as the number of hydrogens in the substituent increases. Increasing total bond order from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline, as well as from p-tert-butyl- to p-methyl-N,N-dimethylaniline, is consistent with the increasing trend of ionization potentials observed.

TABLE 2.5

CNDO/2 BOND DENSITIES^a AND BOND ORDERS^b FOR THE INTERACTION BETWEEN THE GROUP IV ELEMENT AND ITS RING CARBON FOR PARA SUBSTITUTED N,N-DIMETHYLANILINES

Substituent orbitals	MH ₃			MH ₂ Me			Substituent								
	C	Si	Si	C	Si	Si	C	C	MMe ₂	Si	C	C	MMe ₃	Si	
s	0.674	0.684	0.684	0.704	0.677	0.677	0.692	0.676	0.678	0.679					
pσ	1.349	1.166	1.166	1.288	1.143	1.143	1.277	1.123	1.260	1.100					
dσ		0.776	0.776		0.810	0.810		0.833		0.832					
pπ	0.250	0.237	0.237	0.191	0.223	0.223	0.178	0.214	0.176	0.209					
dπ		0.365	0.365		0.353	0.353		0.339		0.340					
σBO	1.012	1.313	1.313	0.996	1.314	1.314	0.985	1.316	0.969	1.306					
πBO	0.125	0.301	0.301	0.096	0.288	0.288	0.089	0.277	0.088	0.275					
Total BO	1.137	1.614	1.614	1.092	1.602	1.602	1.074	1.593	1.057	1.581					

^aTotal bonding density minus antibonding density for the orbital indicated.

^bBond density/2.

The solution ultraviolet spectra of Group IV substituted N,N-dimethylanilines show three major bands in the near-ultraviolet region as shown in Figure 2.2, the spectrum of o-dimethylsilyl-N,N-dimethylaniline. In order of increasing energy the transitions observable in solution spectra are the LE_{α} band, a localized excitation to antisymmetric π^* orbital; the CT_s band, a band corresponding to charge transfer from nitrogen to the symmetric π^* orbital; and the CT_a band, a charge transfer transition to the antisymmetric π^* orbital (11). The wavelengths and relative intensities of the bands for acetonitrile solutions of the para series of the compounds are listed in Table 2.6. All of the bands are shifted slightly to the red (longer wavelengths) for both alkyl and silyl substituted N,N-dimethylanilines (Table 2.6). This is consistent with the destabilization of the ground states observed for alkyl substituted compounds relative to the ground state of N,N-dimethylaniline. However, the larger red shift for silyl compounds is only consistent with a greater stabilization for their excited states compared to the carbon compounds. The larger excited state stabilizations for silicon compounds might be expected because of the better energy match between silicon orbitals and the π^* orbitals of the ring (4).

It can be seen that the LE_{α} and the CT_a bands are less sensitive to substituent effects. This is what would be expected on the basis of the simple molecular orbital

TABLE 2.6

ELECTRONIC TRANSITIONS FOR PARA GROUP IV SUBSTITUTED
N,N-DIMETHYLANILINES IN ACETONITRILE SOLUTION

Substi- tuent	LE _α		Transition CT _s		CT _a	
	λ _{max} , Å ^o	ε _{max} × 10 ⁻³	λ _{max} , Å ^o	ε _{max} × 10 ⁻⁴	λ _{max} , Å ^o	ε _{max} × 10 ⁻⁴
-H	2998	2.78	2517	1.62	2007	2.17
-CH ₃	3064	2.03	2543	1.37	2032	1.92
-CH ₂ Me	3046	1.89	2550	1.37	2028	1.85
-CHMe ₂	3039	1.77	2538	1.39	2032	1.86
-CMe ₃ ^a	3016	2.24	2533	1.99	2019	2.89
-SiH ₃	3058	2.34	2692	1.88	2032	1.63
-SiH ₂ Me	3052	2.11	2681	1.93	2026	1.66
-SiHMe ₂	3045	2.36	2651	1.73	2026	1.77
-SiMe ₃	2975	3.63	2658	2.51	2031	2.29

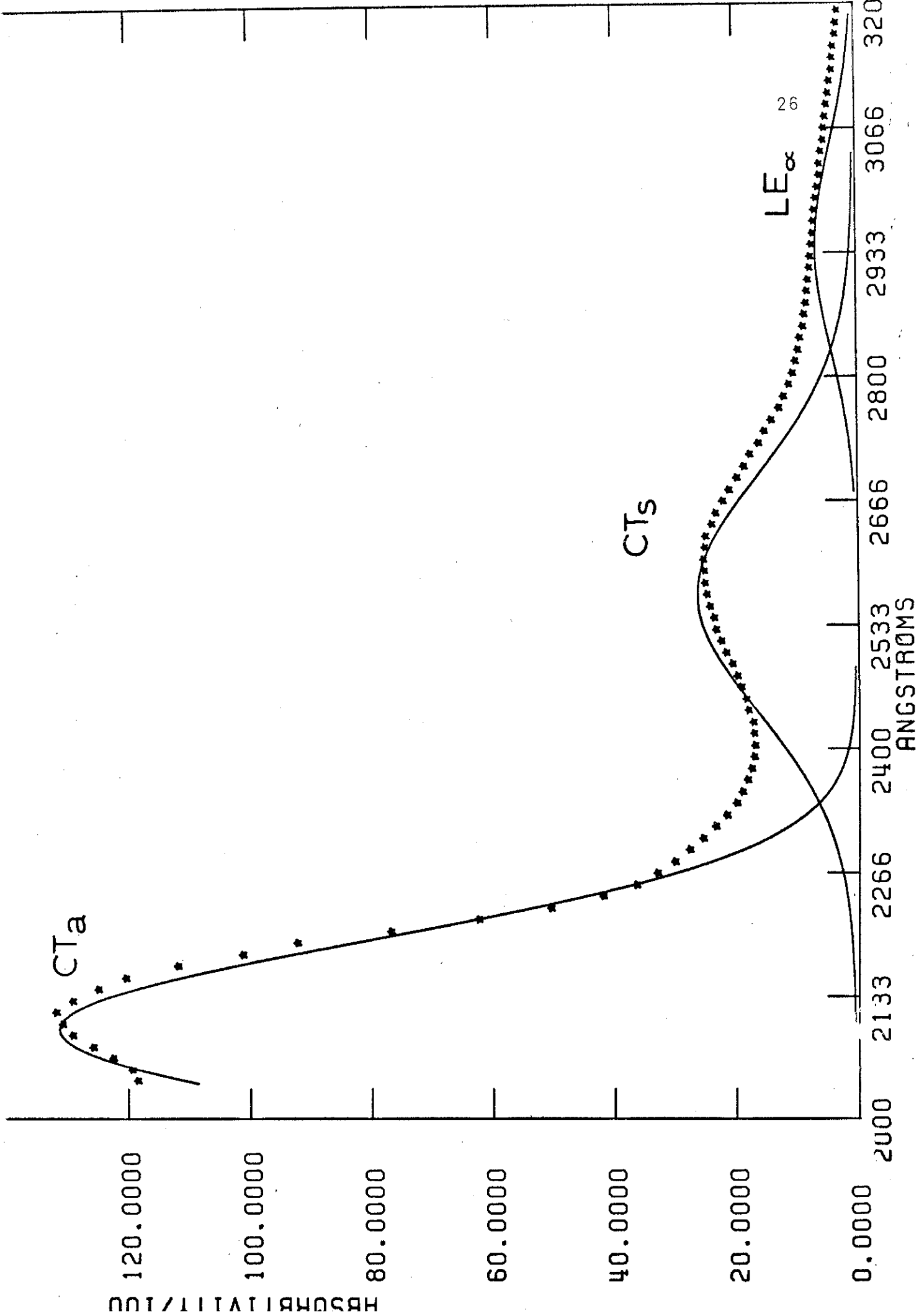
^aRef. 11.

Fig. 2.2

Ultraviolet spectrum of *o*-dimethylsilyl-N,N-dimethyl-
aniline in acetonitrile.

Concentration; 1.23×10^{-4} M.

*****, experimental; ———, computer fit band.



consideration of the antisymmetric π^* orbital with a node bisecting the 1 and 4 positions. The CTs band changes little from the parent to alkyl compounds, but shifts to the red for the silyl compounds. The band intensity also increases from alkyl to silyl compounds, suggesting that silyl groups are better charge delocalizing groups than alkyl groups. In the series of silicon compounds the CTs band is shifted to red from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline, and the intensity of the band generally increases. This is consistent with the increasing ionization energies observed for the ground states, as the methyl groups on silicon are replaced by hydrogen.

It is possible to compare the relative energies of the lower-lying excited states by constructing relative energy level diagrams from ultraviolet spectra and the energies of the ground states (11). Table 2.7 gives the excited-state energies, calculated from ultraviolet spectra, and the ground-state energies for the para series of compounds. Figure 2.3 is a plot of these data, which also shows the perturbation of the ground state (G) and the three excited states (LE_α , CTs, and CTa).

Generally, all of the states are destabilized by alkyl substitution and stabilized by silyl substitution, and these effects are larger for the excited states than for the ground state. It can be seen that the CTs state is the most sensitive to substituent effects.

TABLE 2.7

RELATIVE GROUND AND EXCITED STATE ENERGIES^a FOR PARA
GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	G	State LE _α	CT _s	CT _a
-H ^b	7.62	3.49	2.70	1.45
-CH ₃	7.50 ^c	3.45	2.62	1.40
-CH ₂ Me	7.50	3.42	2.64	1.39
-CHMe ₂	7.53	3.45	2.65	1.43
-CMe ₃ ^b	7.44	3.33	2.55	1.31
-SiH ₃	7.98	3.93	3.37	1.88
-SiH ₂ Me	7.95	3.89	3.33	1.83
-SiHMe ₂	7.89	3.82	3.21	1.76
-SiMe ₃ ^b	7.74	3.57	3.08	1.63

^aIn eV (-1).

^bRef. 21.

^cRef. 11.

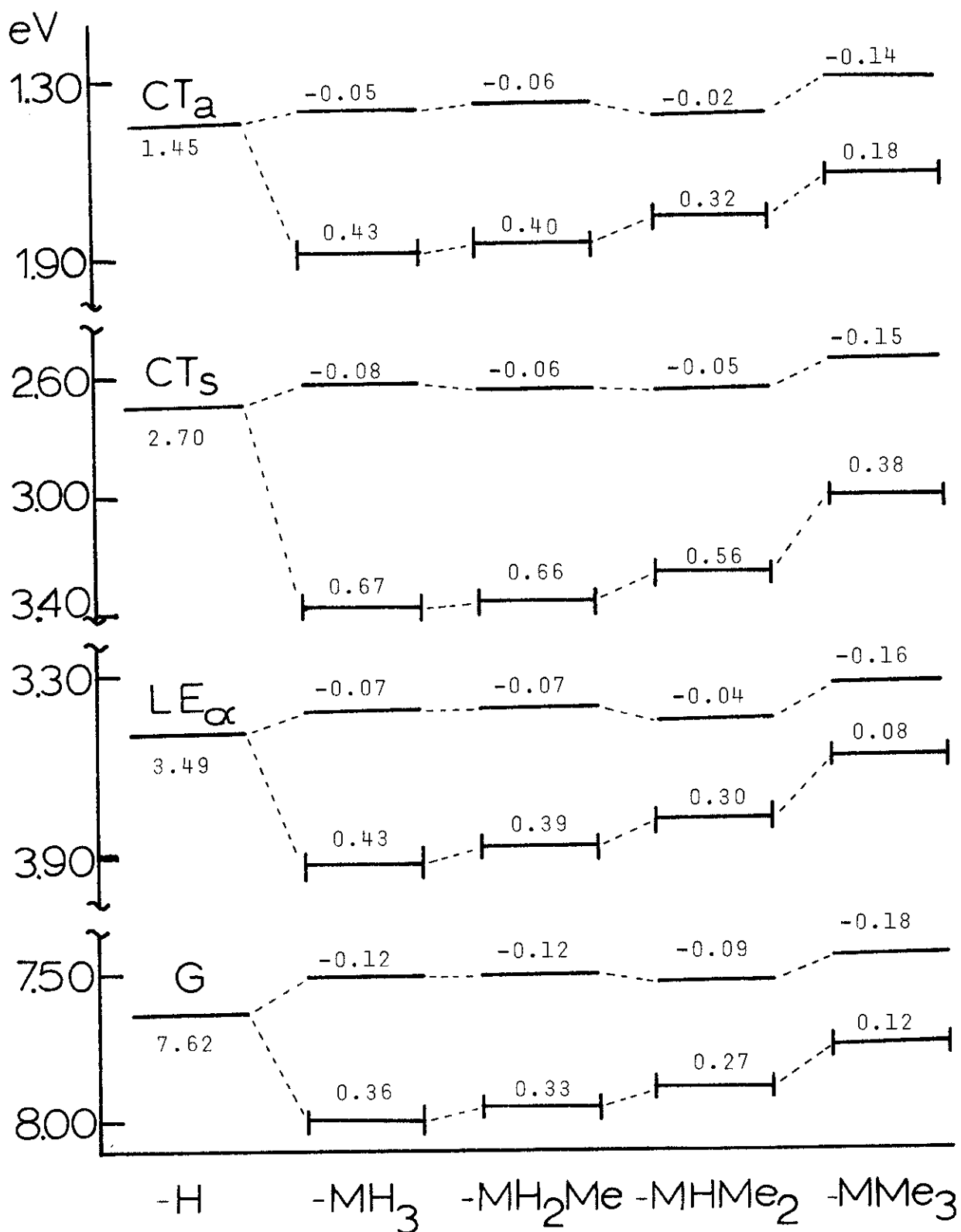


Fig. 2.3. Relative experimental energies for the ground and excited states of *para* Group IV substituted *N,N*-dimethylanilines, —, M = C; —|—, M = Si.

On the basis of CNDO/2 calculations for the ground states of the para Group IV substituted N,N-dimethylanilines, silyl groups are stronger electron-releasing groups than alkyl groups. In the absence of π electronic effects one would expect the σ inductive destabilization of the levels for the silyl compounds to be larger than for the alkyl compounds. It is clearly observed in Figure 2.1 that just the opposite is the case.

It is interesting that all of the excited states for the silicon compounds are destabilized as the number of methyl groups on silicon increases. This effect is the largest in the CTs bands. The trimethylsilyl group is the least charge-accepting group among the silyl groups. This is consistent with the -I effect of silyl hydrogens (35) and with the ordering of ground states for the silicon compounds. It has also been reported that increasing the number of hydrogens on silicon reduces the +I effect of the silicon and increases -R effect of the silyl substituent of phenylsilanes (28).

All of the energy levels of N,N-dimethylaniline are destabilized by alkyl substitution at the para position and stabilized by silyl substitution at the same position. The stabilization observed for the ground states of the silyl compounds compared to the alkyl compounds is attributed to the p and d orbital interactions of the silicon, with the major perturbation being the d-p π interactions. The stabilization effect of silyl groups increases as the number of

hydrogens on the silicon increases. The effect is larger for the excited states than for the ground states.

Ortho Group IV Substituted N,N-dimethylanilines

The oxidation potentials for the ortho series of compounds listed in Table 2.8 were determined by cyclic voltammetry in acetonitrile solution, using tetrabutylammonium perchlorate as the supporting electrolyte. The ionization energies for the compounds were calculated from eq. 2.1, using the oxidation potentials which are included in the table.

In general, the ground state energies of the silicon compounds are lower than their carbon analogs. However, a crossover occurs with the ortho Me_3M ($\text{M} = \text{C}$ and Si) substituents and the ground-state energy of o-trimethylsilyl compound is slightly higher than o-tert-butyl compound. Ordering of ground states for the ortho series of compounds does not follow that for the para compounds. However, the ground-state energy generally decreases as the size of substituent increases. It appears that the ordering of the ground states for the ortho substituted N,N-dimethylanilines is predominantly a result of the steric interactions between the dimethylamino group and the ortho substituent.

It is well known that in ortho substituted N,N-dimethylanilines the substituent twists the dimethylamino group to

TABLE 2.8

HALF-PEAK OXIDATION POTENTIALS AND IONIZATION ENERGIES
FOR ORTHO GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	$E_{p/2}^a$ v vs. sce	Ionization energy ^b eV
-H	0.74 ^c	7.62 ^c
-CH ₃	0.86	7.98
-CH ₂ Me	0.85	7.94
-CHMe ₂	0.89	8.06
-CMe ₃	1.03	8.48
-SiH ₃	0.93	8.18
-SiH ₂ Me	0.92	8.15
-SiHMe ₂	0.91	8.12
-SiMe ₃	0.94	8.21

^aDetermined in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte.

^bCalculated from eq. 2.1.

^cRef. 21.

minimize the steric interaction between two substituents, which causes the lone pair of the nitrogen to be twisted out of conjugation with the ring π orbitals (20). It has been reported that the ring carbon-nitrogen bond length in ortho substituted N,N-dimethylanilines increases due to loss of the conjugation, as the size of substituents increases (23). Turner (26) has also reported that the degree of mixing of the nitrogen lone pair with the π orbitals decreases in ortho substituted N,N-dimethylanilines as the size of substituents increases, which results in lowering of the ground state of the molecule. The relative steric perturbations of substituents may be determined quantitatively by measuring the lone pair twist angles for the series of compounds.

The intensity of the CTs band in ortho substituted anilines is related to the lone pair twist angle, and the relationship of eq. 2.2 (11) has been widely used to calculate the twist angle,

$$\cos^2\theta = \epsilon/\epsilon^{\circ} \quad \text{eq. 2.2}$$

where ϵ is the molar extinction coefficient of the CTs band for the partially twisted compound and ϵ° is the corresponding value for the non-substituted compound.

The ultraviolet spectroscopic data for ortho Group IV substituted N,N-dimethylanilines in acetonitrile solution are listed in Table 2.9. The intensity of the CTs band rapidly

TABLE 2.9

ELECTRONIC TRANSITIONS FOR ORTHO GROUP IV SUBSTITUTED
N,N-DIMETHYLANILINES IN ACETONITRILE SOLUTION

Substi- tuent	LE _α		Transition CT _s		CT _a	
	λ _{max} , Å	ε _{max} × 10 ⁻²	λ _{max} , Å	ε _{max} × 10 ⁻³	λ _{max} , Å	ε _{max} × 10 ⁻⁴
-H	2998	27.76	2517	16.21	2007	2.17
-CH ₃	2834	9.37	2482	6.40	2056	1.51
-CH ₂ Me	2805	11.16	2484	5.69	2067	1.52
-CHMe ₂	2792	11.81	2478	4.69	2062	1.33
-CMe ₃	2544	2.95	2351	0.50	2059	1.23
-SiH ₃	3000	8.70	2573	3.53	2094	1.50
-SiH ₂ Me	2984	8.71	2566	3.54	2083	1.74
-SiHMe ₂	2940	6.51	2566	2.63	2098	1.31
-SiMe ₃	2841	3.81	2554	1.64	2090	1.24

decreases as the substituent size increases from o-methyl- to o-tert-butyl-, or o-silyl- to o-trimethylsilyl-N,N-dimethylaniline. The twist angles of the nitrogen lone pair for the series of compounds, calculated from eq. 2.2, using the molar extinction coefficients of the CTs band, are listed in Table 2.10. The twist angle increases for both the alkyl and silyl compounds, and the substituent size increases. A higher twist angle is observed for the silicon compounds than for the carbon compounds except for o-tert-butyl-N,N-dimethylaniline.

If the steric interaction between the dimethylamino group and the ortho substituent is the major perturbation to the ground-state energies, the change in the ionization energies of the components would be proportional to the change in the twist angles. Figure 2.4 shows the plot of ionization energies versus the twist angles. Indeed, a fairly good linear relationship between the two values is observed, indicating that the ground-state energy observed for the series of compounds is mainly a function of the steric interactions between the dimethylamino group and the substituent at the ortho position.

Considering that the ring carbon-silicon bond (1.84 \AA) is longer than the corresponding carbon-carbon bond (1.52 \AA), one would expect less steric interactions for silicon compounds than for carbon compounds. However, higher twist angles are

TABLE 2.10

INTERMOLECULAR CHARGE TRANSFER BANDS AND TWIST ANGLES
OF THE NITROGEN LONE PAIR FOR ORTHO GROUP IV
SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	λ_{\max} , \AA	$\epsilon_{\max}^{\text{CT}_s^a} \times 10^{-3}$	ϵ/ϵ^0	θ deg ^b	Ref ^c
-H	2517	16.21	(1)	(0)	(0)
-CH ₃	2482	6.40	0.395	50	50
-CH ₂ Me	2484	5.69	0.351	54	56
-CHMe ₂	2478	4.69	0.289	57	58
-CMe ₃	2351	0.50	0.031	80	78
-SiH ₃	2573	3.53	0.218	62	
-SiH ₂ Me	2566	3.54	0.218	62	
-SiHMe ₂	2566	2.63	0.146	68	
-SiMe ₃	2554	1.64	0.101	71	

^aMeasured in acetonitrile solution.

^bCalculated from $\text{Cos}^2\theta = \epsilon/\epsilon^0$.

^cRef. 20.

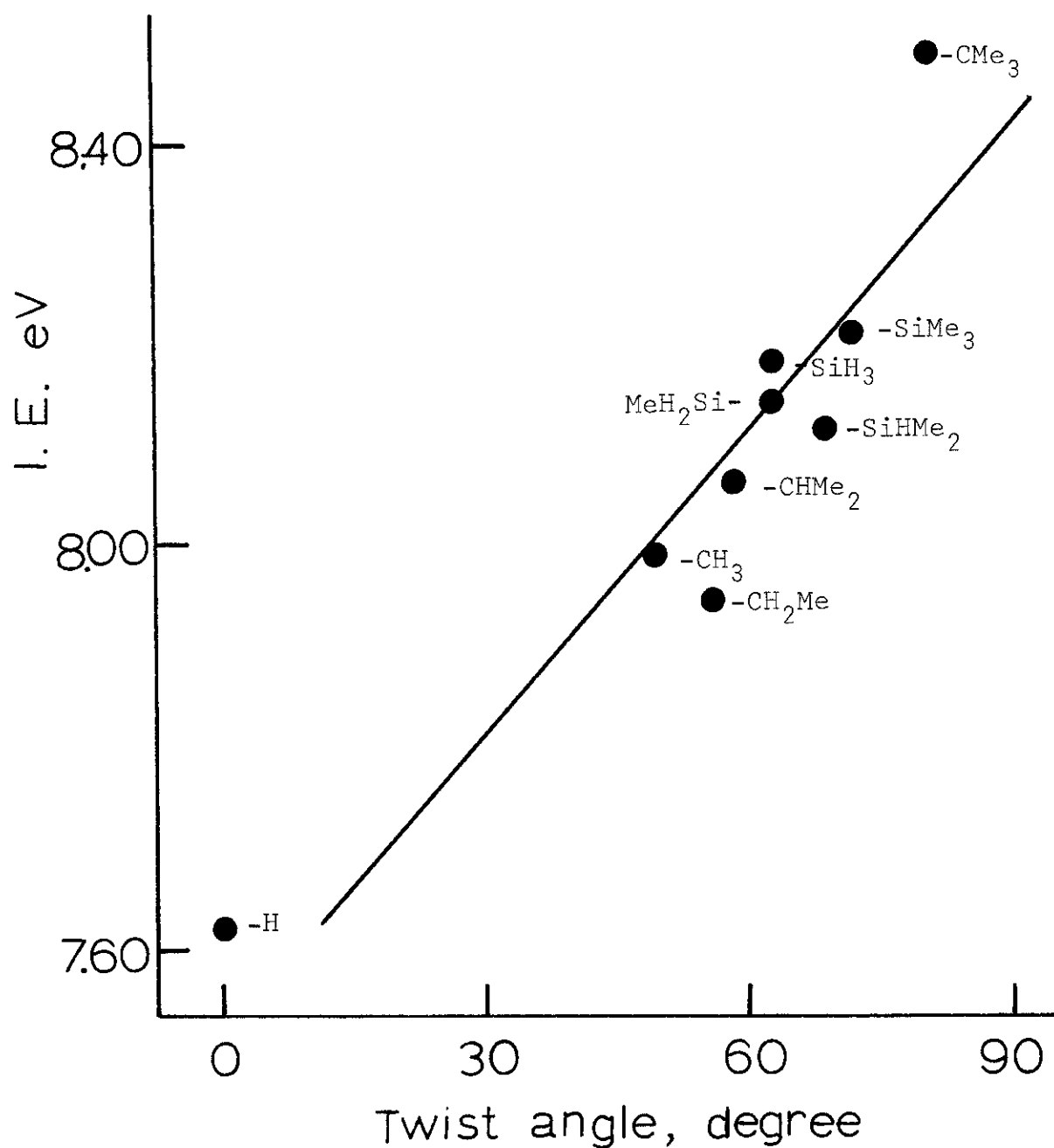


Fig. 2.4. Plot of the ionization energies vs. the nitrogen lone pair twist angles for Group IV substituted N,N-dimethylanilines.

observed for silicon compounds than for carbon compounds except for o-tert-butyl-N,N-dimethylaniline. The change in the twist angles is greater going from o-methyl- to o-tert-butyl-N,N-dimethylaniline, 30° , than going from o-silyl- to o-trimethylsilyl-N,N-dimethylaniline, 9° , indicating that the orientation of the nitrogen lone pair is not greatly affected by changing the substituent size in silicon compounds. Eaborn (15) has reported that the steric effect in protodesilylation reactions of ortho substituted phenyl trimethylsilanes—including o-trimethylsilyl-N,N-dimethylaniline—is very small. Both results suggest that through-space interactions between the nitrogen lone pair and the silyl substituents exist in the ortho silyl substituted N,N-dimethylanilines.

The CNDO/2 calculations for the ortho Group IV substituted N,N-dimethylanilines have been performed. For these compounds the nitrogen was assumed to be tetrahedrally hybridized, with the lone pair rotated from the plane perpendicular to the aromatic ring, towards the ortho substituent. The angles in Table 2.10 were used for the lone pair twist angles. However, the CNDO/2 calculated highest filled MO energies for the compounds do not correlate with the oxidation potentials, indicating these calculations are not reliable. It is interesting to note that the highest filled MO's are not either pure π or σ orbitals but an admixture of both. A higher

degree of mixing is observed for silicon compounds than for carbon compounds.

The low-lying excited-state energies for the ortho series of compounds have been calculated from the ultraviolet spectra and the ground state energies, which are listed in Table 2.11. Figure 2.5 shows the plot of the data with the perturbations for G, LE_{α} , CTs, and CTa states compared to the parent compounds. All of the states are stabilized by alkyl or silyl substitution. Generally the excited states for silicon compounds are lower than those for carbon compounds. The ordering of CTs and CTa states is similar to that of the ground state, indicating that the major perturbation to these states is the steric interactions between the dimethylamino group and the ortho substituent. However, the ordering of LE_{α} state is different from those of the other states, and the change in energies is not sensitive to the substituent size. This suggests that the LE_{α} state is least sensitive to the steric interactions.

In the ortho series of compounds the rotational angle of the nitrogen lone pair is greater for silicon compounds than for carbon compounds. The plot of ionization energies versus the relational angles for the compounds gives a straight line, indicating a dependence of the ground-state energies on the nitrogen lone pair angles. The energies of both ground and excited states for the silicon compounds are generally

TABLE 2.11

RELATIVE GROUND AND EXCITED STATE ENERGIES^a FOR ORTHO
GROUP IV SUBSTITUTED N,N-DIMETHYLANILINES

Substituent	G	State LE _α	CT _S	CT _a
-H ^b	7.62	3.49	2.70	1.45
-CH ₃	7.98	3.61	2.99	1.95
-CH ₂ Me	7.94	3.52	2.95	1.94
-CHMe ₂	8.06	3.62	3.06	2.05
-CMe ₃	8.48	3.61	3.26	2.46
-SiH ₃	8.18	4.05	3.36	2.26
-SiH ₂ Me	8.15	4.00	3.32	2.20
-SiHMe ₂	8.12	3.90	3.29	2.21
-SiMe ₃	8.21	3.85	3.36	2.28

^aIn eV (-1).

^bRef. 11.

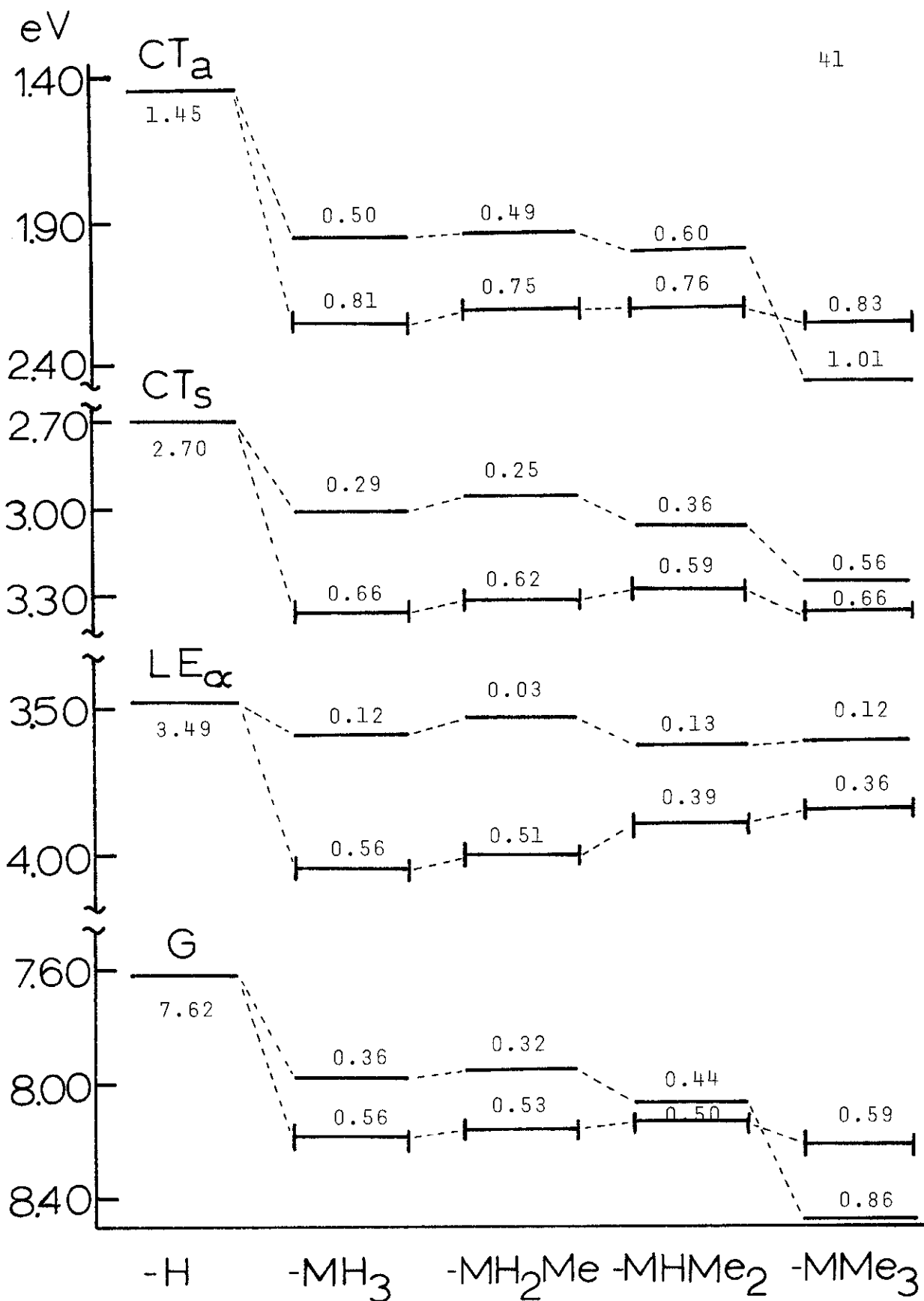


Fig. 2.5. Relative experimental energies for the ground and excited states of *ortho* Group IV substituted *N,N*-dimethylanilines, —, M = C; - - -, M = Si.

lower than those for carbon compounds. The steric interactions between the dimethylamino group and the ortho substituents are the major perturbation for both ground state and excited states in the ortho series of compounds.

Experimental

Reagents.--The solvents used for the organometallic reactions were distilled from lithium aluminum hydride prior to use and all such reactions were carried out under an atmosphere of dry nitrogen or argon. Acetonitrile was purified using a modification of the method given by Mann (30), in which the final purification step was distillation of the solvent from phosphorus pentoxide. Tetrabutylammonium perchlorate (Matheson, Coleman and Bell, polarographic grade) was used without further purification. All anilines were purified by gpc collection, using a 20' x 3/8" stainless steel column of 30% SE-30 on 45/60 mesh Chromasorb-W at about 200° with a helium flow of about 150 ml/min, for characterization and prior to the measurements made in this study.

General method for methylation of anilines (16).--To a solution of the appropriate aniline in an equal volume of water was added three equivalents of dimethylsulfate in the following manner. One equivalent of dimethylsulfate was added dropwise with stirring and kept stirring until homogeneous. The solution was then neutralized with 25% sodium hydroxide

solution with cooling in an ice bath. The second equivalent was added and neutralized as before, except that a slight excess of the base was used. Finally, the third equivalent was added to the solution. The solution was made strongly basic with the sodium hydroxide solution and allowed to stand until clear. The organic layer was separated, combined with the ether washings of the aqueous layer, and dried over anhydrous magnesium sulfate. The products were obtained by distillation of the resulting solutions.

General method for o-lithio-N,N-dimethylanilines (25).--

To a solution of the appropriate N,N-dimethylaniline in an equal volume of tetramethylethylenediamine was added one equivalent of p-butyllithium in hexane (12.5%, Apache Chemical). The mixture was stirred under an inert atmosphere of dry nitrogen or argon with reflux if necessary until the precipitation of the yellow o-lithio-compound was observed. The derivatizing reagent dissolved in dry tetrahydrofuran was added to the reaction mixture in normal derivatization. Inverse derivatization consisted of dissolving the o-lithio-compound in dry tetrahydrofuran and adding the solution dropwise to a solution of the derivatizing reagent in dry tetrahydrofuran. After stirring overnight the mixture was hydrolyzed with water, the organic layer separated, combined with ether washings of the aqueous layer, and dried over anhydrous magnesium sulfate.

The products were obtained by distillation of the resulting solutions.

General method for p-lithio-N,N-dimethylaniline (22).--

To a solution of p-bromo-N,N-dimethylaniline (10.0 g) in an appropriate amount of dry benzene (10 ml) was added one equivalent of n-butyllithium in hexane (12.5%, Apache Chemical). The mixture was stirred under an inert atmosphere of dry nitrogen or argon for about four hours. After dissolving the p-lithio-compound in dry tetrahydrofuran inverse derivatization was then carried out by adding the solution dropwise to a solution of the derivatizing reagent in dry tetrahydrofuran. The precipitates were filtered under nitrogen and the products were prepared by the lithium aluminum hydride reduction of the solutions.

N,N-dimethyl-p-toluidine was obtained commercially (Aldrich).

p-Ethyl-N,N-dimethylaniline was prepared in 67% yield by methylation of p-ethylaniline (Aldrich) using the general method described above; bp, 92°C/10 mm (Lit (10), 104°C/18 mm).

p-Isopropyl-N,N-dimethylaniline was synthesized by methylation of p-isopropylaniline prepared from cumene (Eastman) using the procedure of Hansch and Helmkamp (17); bp, 88-89°C/10 mm (Lit (17), 111-112°C/16 mm): nmr (CCl₄ with TMS as the internal standard): -1.15, doublets (6H), CH(CH₃)₂; -2.74, septets (1H), CH; -2.76, singlet (6H), N(CH₃)₂; -6.40, doublets

(2H), ortho protons; -6.80, doublets (2H), meta protons, $J = 8\text{hz}$.

Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.49; N, 8.58.
Found: C, 80.88; H, 10.40; N, 8.44; mass spectrum, parent (M^+), 163.

p-Silyl-N,N-dimethylaniline was prepared by the lithium aluminum hydride reduction of p-trichlorosilyl-N,N-dimethylaniline, prepared by inverse derivatization of p-lithio-N,N-dimethylaniline with tetrachlorosilane (PCR) in dry tetrahydrofuran. 20% overall yield, bp, $82^\circ\text{C}/3\text{ mm}$ (Lit (29), $81^\circ/5\text{ mm}$), mp, 48°C (Lit (29), $45-50^\circ\text{C}$): nmr (CCl_4 with TMS as the internal standard): -3.00, singlet (3H), SiH_3 ; -4.26, singlet (6H), $\text{N}(\text{CH}_3)_2$; -6.68, doublets (2H), ortho protons; -7.42, doublets (2H), meta protons, $J = 8\text{hz}$.

Anal. Calcd for $C_8H_{13}\text{NSi}$: C, 63.51; H, 8.66; N, 9.26.
Found: C, 63.30; H, 8.66; N, 9.18; mass spectrum, parent (M^+) 151.

p-Methylsilyl-N,N-dimethylaniline was synthesized in 42% overall yield by the lithium aluminum hydride reduction of p-methyldichlorosilyl-N,N-dimethylaniline, prepared by inverse derivatization of p-lithio-N,N-dimethylaniline with methyltrichlorosilane (Columbia); bp, $107^\circ\text{C}/10\text{ mm}$ (Lit (29), $110^\circ\text{C}/16\text{ mm}$): nmr (CCl_4 with TMS as the internal standard): -0.34, triplets (3H), SiCH_3 ; $J = 4\text{hz}$; -3.02, singlet (6H),

$N(CH_3)_2$; -4.38, quartets (2H), SiH_2 , $J = 4\text{hz}$; -6.68, doublets (2H), ortho protons, -7.39, doublets (2H), meta protons, $J = 8\text{hz}$.

Anal. Calcd for $C_9H_{15}NSi$: C, 65.39; H, 9.15; N, 8.48.
Found: C, 65.50; H, 9.10; N, 8.36; mass spectrum, parent (M^+) 165.

p-Dimethylsilyl-N,N-dimethylaniline was prepared by inverse derivatization of the p-lithio-N,N-dimethylaniline with dimethylchlorosilane (PCR) in dry tetrahydrofuran; 67% yield, bp, $120^\circ\text{C}/10\text{ mm}$ (Lit (29), $122^\circ\text{C}/14\text{ mm}$); nmr (CCl_4 with TMS as the internal standard): -0.27, doublets (6H), $Si(CH_3)_2$, $J = 4\text{hz}$; -2.95, singlet (6H), $N(CH_3)_2$; -4.46, heptets (1H), SiH , $J = 4\text{hz}$; -6.66, doublets (2H), ortho protons; -7.34, doublets (2H), meta protons, $J = 8\text{hz}$.

Anal. Calcd for $C_{10}H_{17}NSi$: C, 67.04 ; H, 9.32; N, 7.96.
Found: C, 66.66; H, 9.42; N, 7.85; mass spectrum, parent (M^+) 179.

N,N-dimethyl-o-toluidine was prepared by methylation of o-toluidine (Aldrich) using the general method described above; bp, $65^\circ\text{C}/10\text{ mm}$ (Lit (19), $76^\circ\text{C}/18\text{ mm}$).

o-Ethyl-N,N-dimethylaniline was prepared by methylation of o-ethylaniline (Aldrich) using the same procedure as above; bp, $85^\circ\text{C}/20\text{ mm}$ (Lit (7), $81.5\text{-}82^\circ\text{C}/14\text{ mm}$).

o-Isopropyl-N,N-dimethylaniline was synthesized in 57% yield by lithiation of o-ethyl-N,N-dimethylaniline using the

same procedure for o-lithio-N,N-dimethylaniline, followed by coupling with methyl iodide (Eastman) in dry tetrahydrofuran. (In this reaction 30% of the starting material was recovered) bp, 91°C/20 mm (Lit (39), 98°C/23 mm); nmr (CCl₄ with TMS as the internal standard): -1.20, doublets (6H), J = 7hz, C(CH₃)₂; -2.70, singlet (6H), N(CH₃)₂; -3.58, septets (1H), J = 7hz; CH; -7.05, multiplets (4H), aromatic protons.

Anal. Calcd for C₁₁H₁₇N: C, 80.93; H, 10.73; N, 7.91. Found: C, 80.70; H, 10.58; N, 8.85; mass spectrum, parent (M⁺) 163.

o-Tert-butyl-N,N-dimethylaniline was prepared from tert-butylbenzene (Eastman) using the method of Brown and Nelson (8); bp, 91-92°C/10 mm (Lit (8), 106.5°C/10 mm).

Anal. Calcd for C₁₂H₁₉N: C, 81.36; H, 10.73; N, 7.91. Found: C, 81.44; H, 10.83; N, 8.02; mass spectrum, parent (M⁺) 177.

o-Silyl-N,N-dimethylaniline was synthesized in 37% overall yield by the lithium aluminum hydride reduction of o-trichlorosilyl-N,N-dimethylaniline, prepared by inverse derivatization of o-lithio-N,N-dimethylaniline with tetrachlorosilane (PCR) in dry tetrahydrofuran; bp, 62°C/10 mm; nmr (CCl₄ with TMS as the internal standard): -4.14, singlet (3H), SiH₃; -2.66, singlet (6H), N(CH₃)₂; -7.16, multiplet (4H), aromatic protons.

Anal. Calcd for $C_8H_{13}NSi$: C, 63.51; H, 8.66; N, 9.26.
 Found: C, 63.74; H, 8.96; N, 9.46; mass spectrum, parent
 (M^+) 151.

o-Methylsilyl-N,N-dimethylaniline was synthesized in 36% overall yield by the lithium aluminum hydride reduction of o-methyldichlorosilyl-N,N-dimethylaniline, prepared by inverse derivatization of the o-lithio-N,N-dimethylaniline with methyldichlorosilane (Columbia) in dry tetrahydrofuran; bp, $68^\circ C/10$ mm; nmr (CCl_4 with TMS as the internal standard): -0.34, triplets (3H), $J = 4$ hz, $SiCH_3$; -2.61, singlet (6H), $N(CH_3)_2$; -4.24, quartets (2H), $J = 4$ hz, SiH_2 ; -7.08, multiplet (4H), aromatic protons.

Anal. Calcd for $C_9H_{15}NSi$: C, 65.39; H, 9.15; N, 8.47.
 Found: C, 65.09; H, 9.40; N, 8.47; mass spectrum, parent
 (M^+) 165.

o-Dimethylsilyl-N,N-dimethylaniline was prepared in 68% yield by inverse derivatization of o-lithio-N,N-dimethylaniline with dimethylchlorosilane (PCR). bp, $77^\circ C/10$ mm; nmr (CCl_4 with TMS as the internal standard): -0.27, doublets (6H), $J = 4$ hz, $Si(CH_3)_2$; -2.70, singlet (6H), $N(CH_3)_2$; -4.48, septets (1H), $J = 4$ hz, SiH ; -7.18, multiplet (4H), aromatic protons.

Anal. Calcd for $C_{10}H_{17}NSi$: C, 66.97; H, 9.56; N, 7.81
 Found: C, 67.04; H, 9.32; N, 7.96; mass spectrum, parent
 (M^+) 179.

o-Trimethylsilyl-N,N-dimethylaniline was prepared in 54% yield inverse derivatization of o-lithio-N,N-dimethylaniline with trimethylchlorosilane (Aldrich). bp, $91^{\circ}/20$ mm (Lit (43), $104^{\circ}/20$ mm); nmr (CCl_4 with TMS as the internal standard): -0.26, singlet (9H), $\text{Si}(\text{CH}_3)_3$; -2.64, singlet (6H), $\text{N}(\text{CH}_3)_2$; -7.20, multiplet (4H), aromatic protons.

Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{NSi}$: C, 68.31; H, 9.82; N, 7.26. Found: C, 68.52; H, 9.88; N, 6.96; mass spectrum, parent (M^+) 193.

Oxidation potentials were determined by cyclic voltammetry using a standard three electrode cell consisting of a platinum bottom working electrode (Beckman, 39273), a saturated calomel reference electrode, and a platinum coil as the counter electrode. The potential sweep was provided by a Chemtrix 300 polarographic amplifier with the type 205 polarographic time base plug in units. A Keithley 600A electrometer was used to calibrate the starting potentials and the measurements were recorded using a Tektronix 564 storage oscilloscope equipped with a polaroid camera.

In a typical run a solution 10^{-4} M in sample and 0.1 M in tetrabutylammonium perchlorate was maintained under an atmosphere of dry argon throughout the measurement. A rate of 0.100 V/sec was employed scanning a 1.00 V range. The average deviation of $E_{p/2}$ values measured in separate runs was ± 0.01 V.

Ultraviolet spectra were taken with a Cary 14 spectrophotometer using quartz cells with a 10 mm path length. The

temperature was unregulated ambient, which was generally around 23°C. Samples for the measurement of extinction coefficients were prepared by standard dilution methods. The spectra whose bands are significantly overlapped have been analyzed by using the non-linear least square fit computer program, MROCOS, obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830.

Proton nmr spectra were recorded with a Jeolco PS-100 spectrometer. Mass spectra were obtained with a Perkin Elmer RMU-6E instrument. Elemental analyses were performed by C. F. Geiger Microanalytical Laboratories, Ontario, California. All boiling points and melting points were uncorrected.

The CNDO/2 program employed was that of Pople (34), and was obtained from the Quantum Chemistry Exchange Program (34). The bond lengths and bond angles used in the CNDO/2 calculations are given in Table 2.12. All of the co-ordinates for the CNDO/2 calculations were obtained by using a computer program which calculated the XYZ atom co-ordinates from the data in Table 2.12. The molecular conformations employed were those determined to have the least steric strain on the basis of inspection of models.

TABLE 2.12

STANDARD BOND ANGLES AND BOND DISTANCES
FOR CNDO/2 CALCULATIONS

Bond	Length in Å ^o	Angle	Source
C-H _{amine}	1.060		a
N-C _{amine}	1.470		a
C-N _{ring}	1.370		a
C-C _{ring}	1.392		a
C-H _{ring}	1.110		a
C-C _{ring}	1.520		a
C-H _{methyl}	1.090		a
C-Si _{ring}	1.840		b
Si-C _{trimethylsilyl}	1.865		b
Si-H	1.480		c
C _{ring} -Si-H _{silyl}		111 ^o	c
C _{ring} -Si-H _{methylsilyl}		109.4 ^o	c
C _{ring} -Si-H _{dimethylsilyl}		108 ^o	c

^a"Tables of Interatomic Distances and Configurations in Molecules and Ions", Special Publications 11, The Chemical Society, Burlington House, London, 1958, p. 140, 172-73, 199-201.

^b"Handbook of Chemistry and Physics", Chemical Rubber Co., Cleveland, Ohio, 1966, p. F-126.

^cRef. 31.

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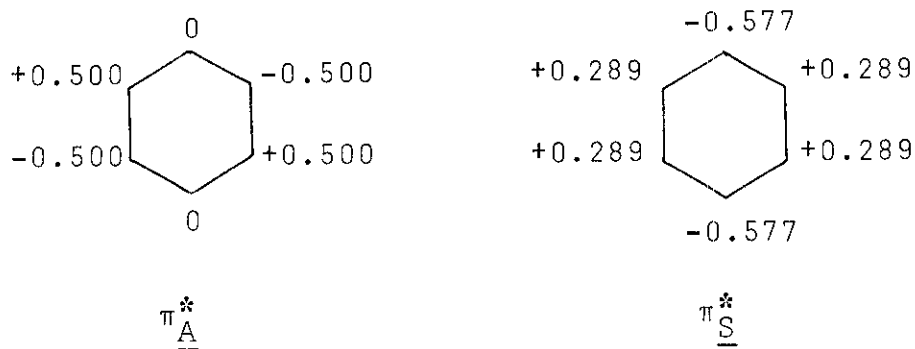
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CHAPTER III

THE RADICAL ANIONS OF TRIMETHYLSILYL SUBSTITUTED N,N-DIMETHYLANILINES

The technique of electron spin resonance (esr) spectroscopy has been widely applied to the investigation of substituent effects on mono-substituted benzene derivatives (1, 5) and multiply substituted benzenes (4, 21). Substitution at the benzene nucleus removes the degeneracy of the lowest-lying π^* (e_{2u}) orbitals of benzene giving rise to radical anions of substituted benzenes in which the unpaired electron is found in a predominantly antisymmetric (A) or symmetric (S) state (1).



Electron-donating substituents such as alkyl substituents cause only small perturbations of the benzene π^* orbitals, slightly raising the energy of the S state and giving radical anions whose esr spectra may be interpreted in terms of interactions between the S and A states (2, 13). Electron

withdrawing substituents, on the other hand, stabilize the S state and give radical anions typified by large hyperfine splitting (hfs) for the proton para to the substituent and smaller coupling constants for the ortho and meta protons (4). In a recent study Sipe and West found that in the anion radicals of trimethylsilyl- or trimethylgermyl- alkylbenzenes the organometal substituent dominates the ordering of the MO energy levels by accepting electron density more effectively than the alkyl substituents release it (21). This result is consistent with the small perturbations of the aromatic systems produced by alkyl substituents (2, 13), and naturally raises the question as to what the dominating influence will be when a strongly perturbing substituent such as the dimethylamino group is pitted against the trimethylsilyl group. To answer this question we have investigated the esr spectra of the radical anions of ortho, meta, and para-trimethylsilyl-N,N-dimethylaniline.

The strong electron-donating effect of the dimethylamino group would be expected to significantly raise the energy of the symmetric π^* orbital and give rise to radical anions in which the A state was the predominant contributor. However, this same electron donation decreases the electron affinity of the compound. For this reason the radical anions of aniline, N-alkylanilines or ring alkylated anilines have not, to our knowledge, been reported. The introduction of an electron

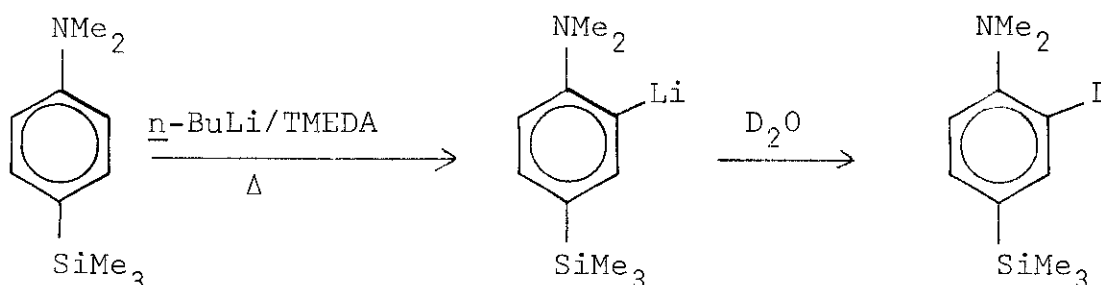
withdrawing ring substituent sufficiently increases the electron affinity of anilines to permit reduction. The esr spectra of several nitroanilines have been reported (7). The hfs for these radicals indicate that the unpaired electron is largely localized in the nitro group. Gerson and co-workers have shown that the reduction of anilines may be achieved when the electron donating effect of nitrogen is diminished through trimethylsilyl substitution at nitrogen (9). In both N,N-bis(trimethylsilyl)aniline and N,N,N',N'-tetrakis(trimethylsilyl)-p-phenylenediamine radical anion the unpaired electron is found to occupy the antisymmetric π^* orbital, as would be predicted by the simple MO considerations given above (9).

In the previous chapter we demonstrated that the trimethylsilyl group is electron withdrawing in both ground states and excited states of Group IV substituted N,N-dimethylanilines. A greater -R effect was observed in the excited states because of the better energy match between the silicon orbitals and the antibonding orbitals of the aromatic system. Indeed, the trimethylsilyl ring substituent sufficiently enhances the electron affinity of N,N-dimethylaniline to permit reduction to the radical anion. The radical anions of trimethylsilyl substituted N,N-dimethylanilines may be conveniently prepared by metal reduction at low temperatures in mixed ether solvents.

In this chapter, the esr spectra of the radical anions of o-, m-, and p-trimethylsilyl-N,N-dimethylaniline, the first examples of N,N-dialkylaniline radical anions which do not have strongly electron withdrawing ring substituents, and the assignment of coupling constants will be reported. The CNDO/2 descriptions of the radical anions will also be discussed.

Results

4-Trimethylsilyl-N,N-dimethylaniline.--The esr spectrum of 4-trimethylsilyl-N,N-dimethylaniline radical anion is shown in Figure 3.1. The spectrum consists of a triplet of triplets due to coupling of the unpaired electron with two sets of equivalent ring protons, with hfs of 3.25 and 4.55 G. An expanded spectrum permits the measurement of a smaller splitting of 0.15 G arising from the trimethylsilyl protons. No coupling of the unpaired electron with the protons or nitrogen of the dimethylamino group, or with potassium was resolved. On the basis of the esr spectrum of the 2-d-4-trimethylsilyl-N,N-dimethylaniline anion, the 3.25 G hfs is assigned to the 2,6-protons, ortho to the dimethylamino group, and the 4.55 G hfs to the 3,5-protons.



Scheme 3.1

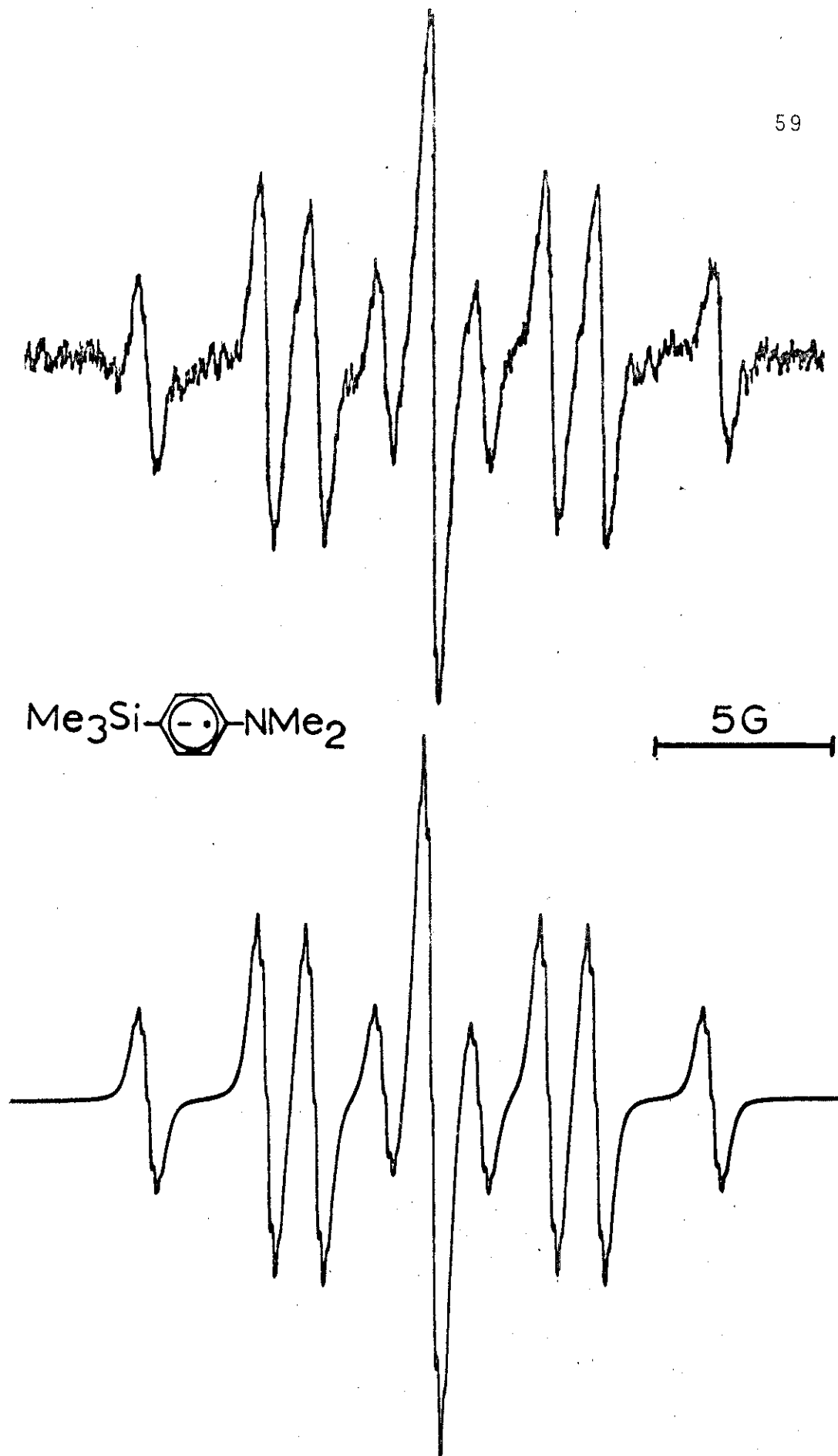


Fig. 3.1. ESR spectrum of the radical anion of 4-trimethylsilyl-N,N-dimethylaniline: upper, experimental; lower, computer simulated using Lorentzian line shapes and a line width of 0.15 G.

The lithiation of N,N-dimethylaniline using n-butyllithium in tetramethylethylenediamine (TMEDA) has been shown to give o-lithio-N,N-dimethylaniline (17). While the metallation of N,N-dimethylaniline does not require heat, the lithiation of 4-trimethylsilyl-N,N-dimethylaniline, Scheme 3.1, requires reflux for at least one half hour to give the yellow precipitate of the ortho-lithiated compound. This might be due to the reduced availability of the nitrogen lone-pair for complexation with the ortho-lithium in the silicon compound (14). When the radical anion of the deuterated compound was prepared the esr spectrum showed both deuterated and undeuterated compounds in the ratio of about 7:3. For 2-d-4-trimethylsilyl-N,N-dimethylaniline the 3.25 G hfs appeared as a doublet.

2-Trimethylsilyl-N,N-dimethylaniline.--The spectrum of 2-trimethylsilyl-N,N-dimethylaniline radical anion is shown in Figure 3.2. The spectrum consists of four doublet hfs of 8.48, 3.60, 1.72, and 0.50 G and a coupling with the trimethylsilyl protons of 0.26 G. The 8.48 G coupling is assigned to the 5-proton, para to the trimethylsilyl group, on the basis of the esr spectrum of 2-trimethylsilyl-5-methyl-N,N-dimethylaniline radical anion, Figure 3.3, which shows an hfs for the 5-methyl protons of 9.11 G. The small perturbations produced by methyl substitution (2, 13), and the fact that substitution of a methyl group for a hydrogen on an aromatic nucleus results in three equivalent methyl proton coupling constants which are

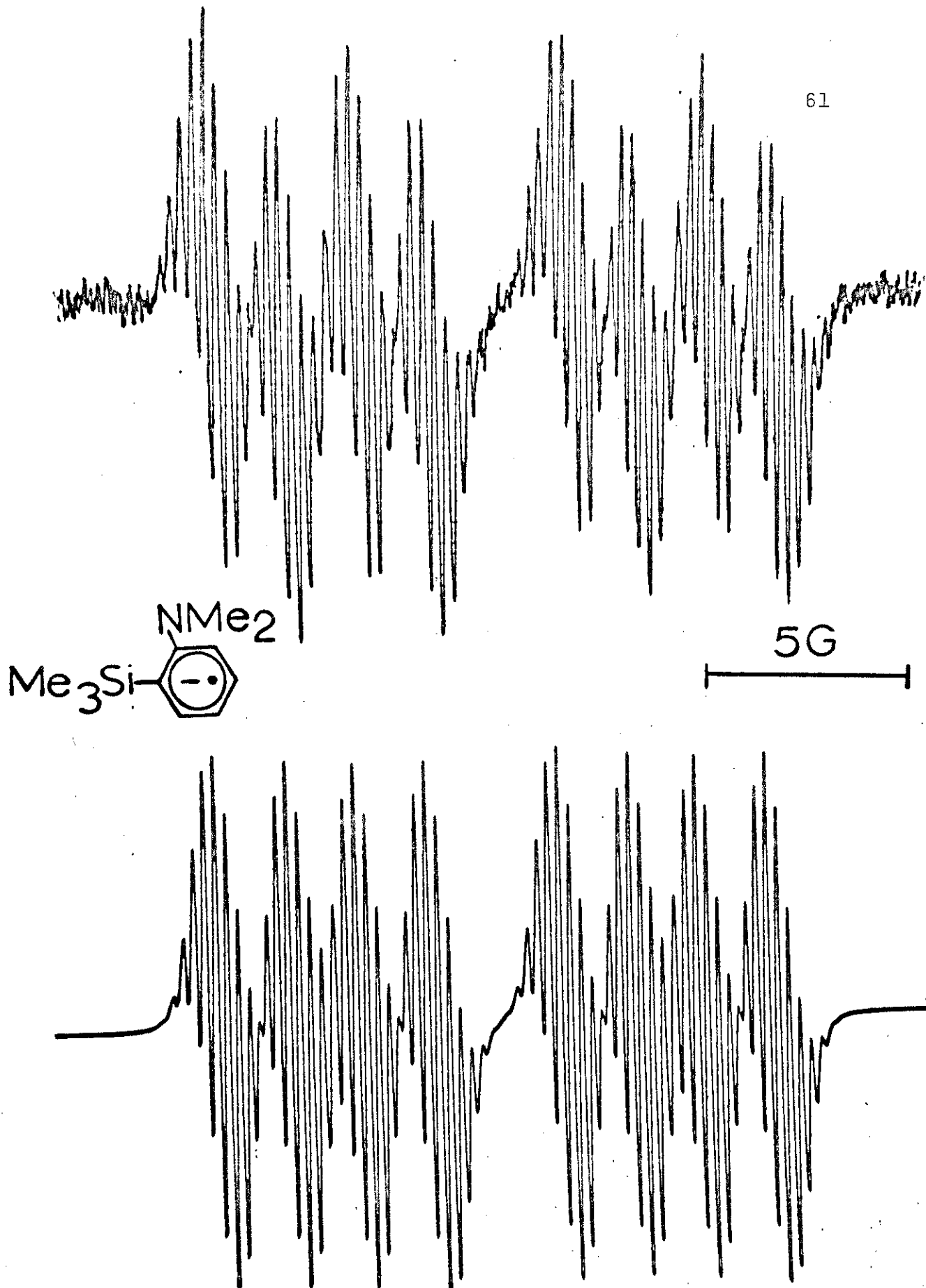


Fig. 3.2. ESR spectrum of the radical anion of 2-trimethylsilyl-N,N-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.13 G.

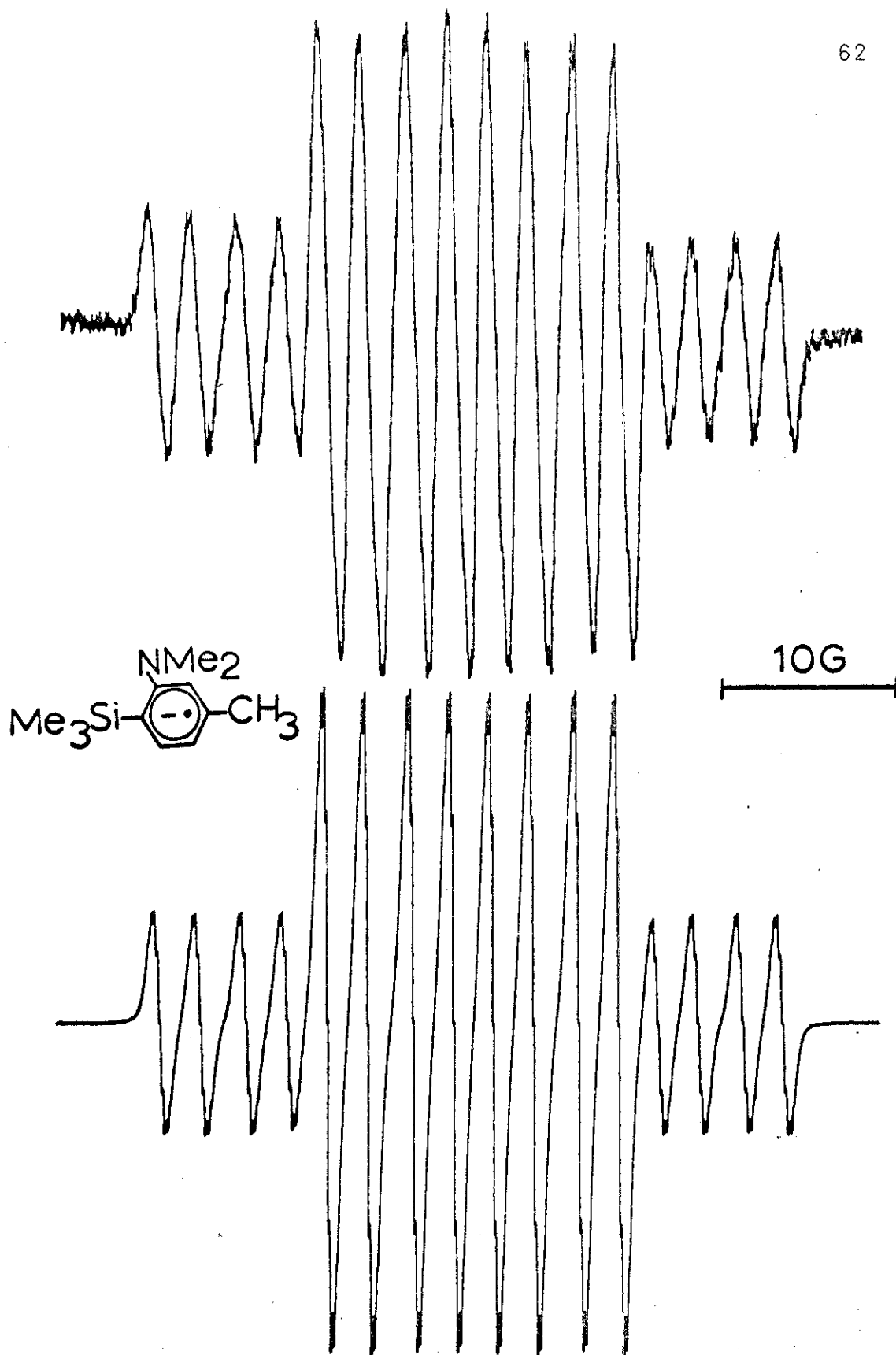
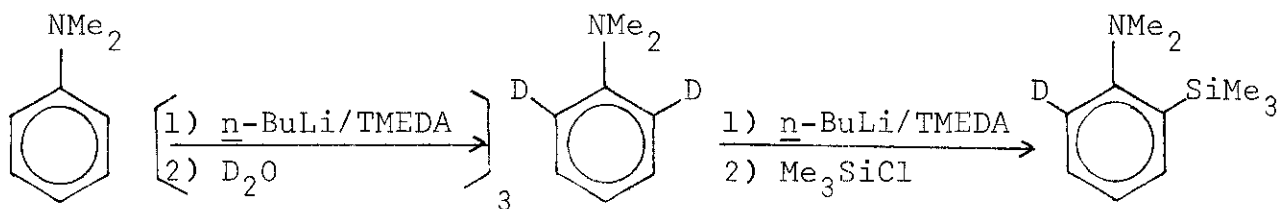


Fig. 3.3. ESR spectrum of the radical anion of 2-trimethylsilyl-5-methyl-N,N-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.18 G.

similar to that for the displaced hydrogen (18) substantiates this assignment.

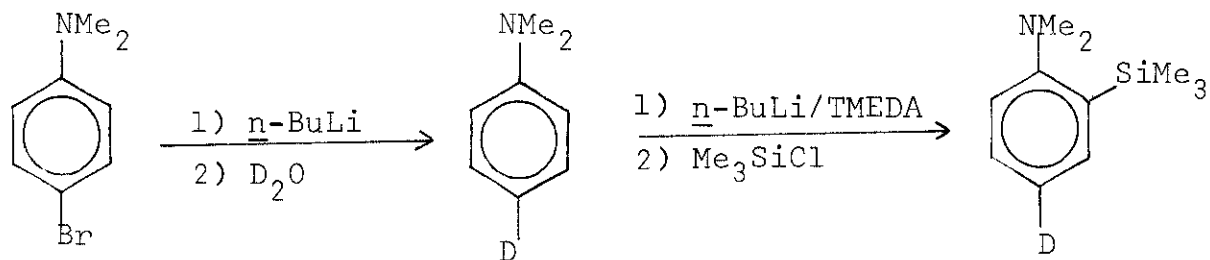
The 1.72 G hfs in 2-trimethylsilyl-N,N-dimethylaniline is assigned to the 6-proton because deuteration in the 6-position causes this splitting to disappear. Scheme 3.2 shows the synthesis of 6-d-2-trimethylsilyl-N,N-dimethylaniline. On a purely statistical basis,



Scheme 3.2

ignoring any isotope effect in the four consecutive ortho lithiations, one would expect the product to be 87.5% deuterium in the 6-position. On the basis of mass spectrum, nmr and the esr spectrum of the radical anion the compound was completely deuterated in the 6-position.

The esr spectrum of the radical anion of 4-d-2-trimethylsilyl-N,N-dimethylaniline, Scheme 3.3, was essentially the same as its undeuterated analog except for broadening of the lines because of the deuterium substitution and the absence of the 0.50 G hfs, assigning that coupling to the 4-proton in 2-trimethylsilyl-N,N-dimethylaniline. By a process of elimination the remaining 3.60 G coupling in the spectrum of

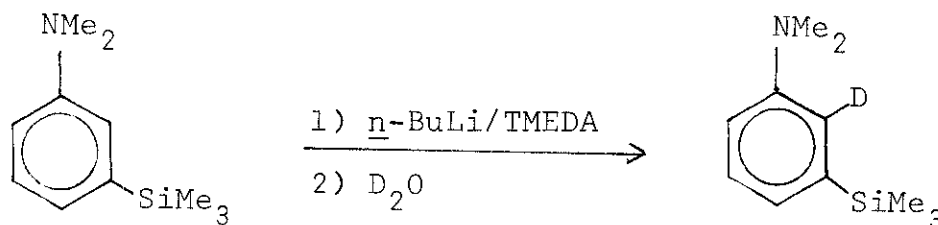


Scheme 3.3

2-trimethylsilyl-N,N-dimethylaniline anion must be assigned to the 3-proton.

3-Trimethylsilyl-N,N-dimethylaniline.--For 3-trimethylsilyl-N,N-dimethylaniline radical anion the esr spectrum shown in Figure 3.4 consists of four doublets of 7.35, 4.25, 2.67 and 0.76 G due to the ring protons and an hfs of 0.23 G by the trimethylsilyl protons. The largest coupling is assigned to the 6-proton on the basis of the esr spectrum of 3-trimethylsilyl-6-methyl-N,N-dimethylaniline, Figure 3.5, which has the largest coupling of 8.89 G associated with the protons of the 6-methyl group.

Scheme 3.4 illustrates the synthesis of 2-d-3-trimethylsilyl-N,N-dimethylaniline. The esr spectrum of the radical



Scheme 3.4

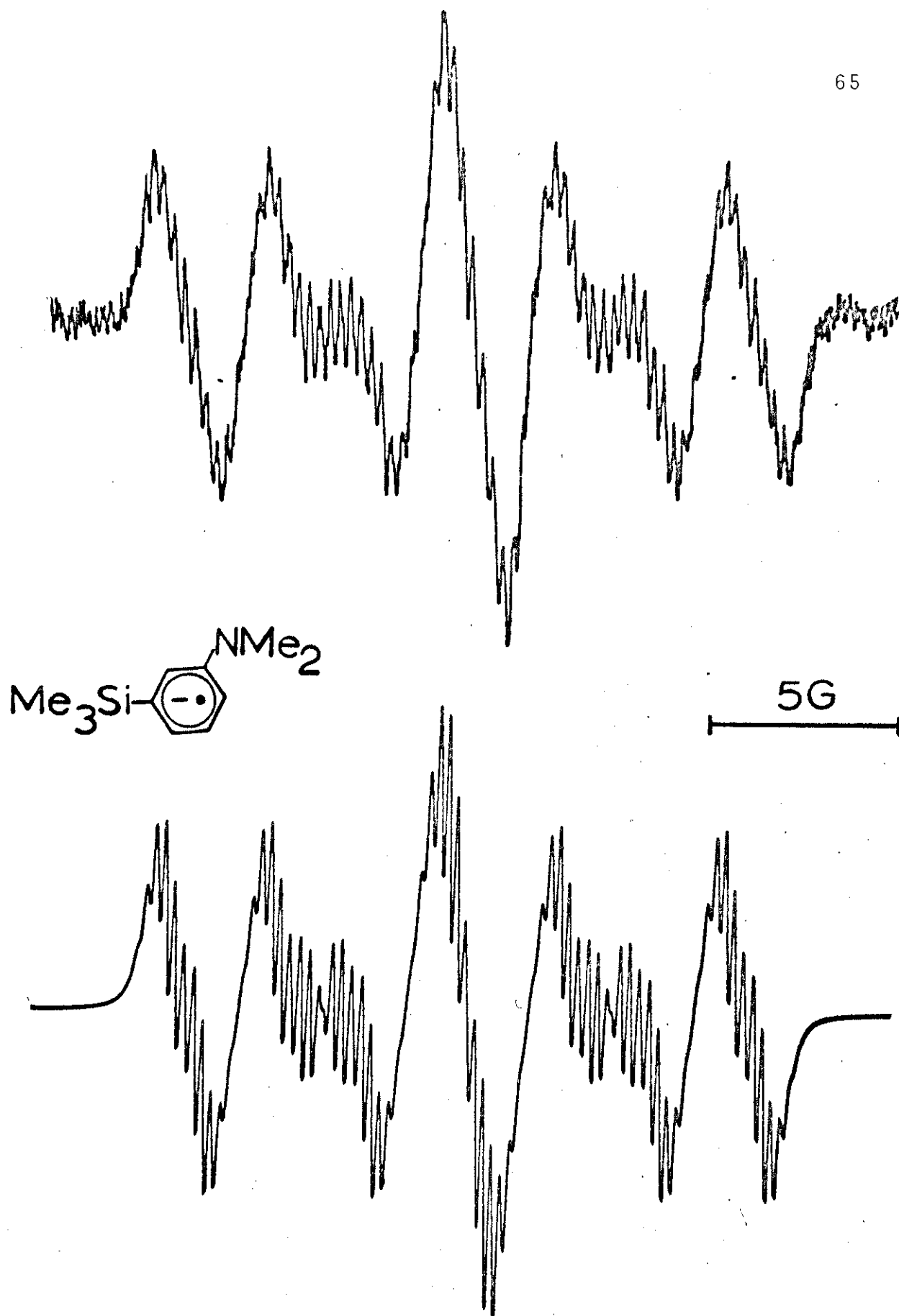


Fig. 3.4. ESR spectrum of the radical anion of 3-trimethylsilyl-N,N-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.17 G.

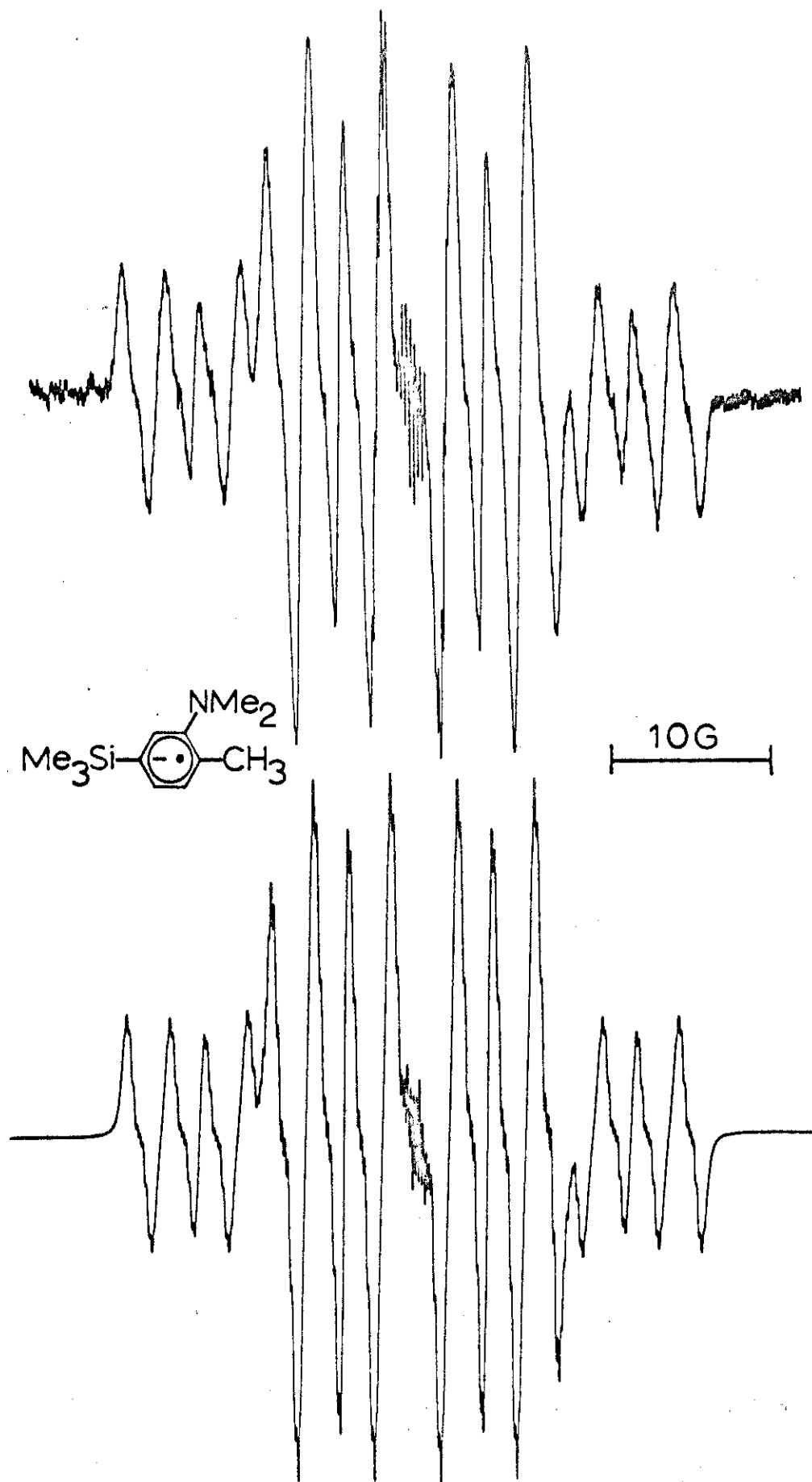
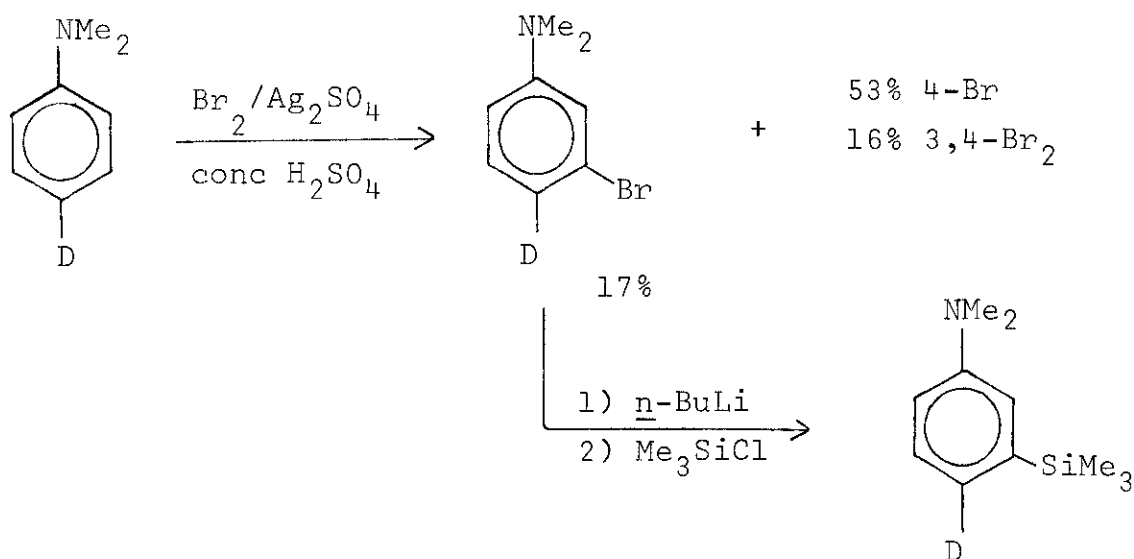


Fig. 3.5. ESR spectrum of the radical anion of 3-trimethylsilyl-6-methyl-N,N-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.21 G.

anion of the product is complicated by the presence of about 50% of unlabeled aniline. However, based on computer simulations of the spectrum, only the 4.25 G coupling is reduced in intensity, assigning that hfs to the 2-position. It is interesting to note that 3-trimethylsilyl-N,N-dimethylaniline was apparently lithiated only in the 2-position for no intensity diminishment in the lines assigned to the 6-proton was observed.

The assignment of the remaining coupling constants for 3-trimethylsilyl-N,N-dimethylaniline was achieved by the synthesis of 4-d-3-trimethylsilyl-N,N-dimethylaniline, Scheme 3.5. In contrast to what might be expected on the basis of



Scheme 3.5

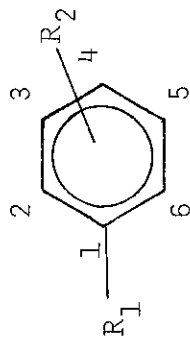
previous reports (10), the bromination of 4-d-N,N-dimethylaniline in concentrated sulfuric acid gave the para-brominated

compound as the major product. However, the smaller scale of the reaction, 2.5 G of N,N-dimethylaniline compared to 4.8 G of the literature scale, and slight excess bromine employed might result in the different product distributions. In the esr spectrum of the radical anion of 4-d-3-trimethylsilyl-N,N-dimethylaniline the 0.78 G coupling has disappeared, assigning that coupling to the 4-position and leaving the 2.67 G hfs to be assigned to the 5-proton in 3-trimethylsilyl-N,N-dimethylaniline.

The hyperfine coupling constants which have been assigned are collected in Table 3.1. In none of the radicals involved in this study were we able to resolve hfs due to the nitrogen or the dimethylamino protons. This result is somewhat surprising in light of the fact that the protons and nitrogen of the dimethylamino group have splittings of 0.71 and 1.13 G respectively in the radical anion of p-nitro-N,N-dimethylaniline (9). It might be suggested that in these radicals loss of the dimethylamino group resulted in the absence of these couplings. To check this point we isolated the products from a sample which gave the spectrum of 4-trimethylsilyl-N,N-dimethylaniline radical anion by careful hydrolysis of the sample with ethanol. Analysis of the mixture by glc showed only ethanol, THF, DME and 4-trimethylsilyl-N,N-dimethylaniline to be present. No trimethylsilyl benzene, an anticipated product if cleavage of the dimethylamino group had occurred, was observed.

TABLE 3.1

HYPERFINE COUPLING CONSTANTS FOR TRIMETHYLSILYL SUBSTITUTED AROMATIC RADICAL ANIONS



Substituents R_1	R_2	Hyperfine coupling constants ^a						Conditions ^b (Ref)
		2	3	4	5	6	$SiMe_3$	
Me_3Si	H	2.66	1.06	8.18	1.06	2.66	0.26	(21)
$(Me_3Si)_2N$	H	5.1	5.7	0.5 ^c	5.7	5.1	0.1 ^c	(9)
Me_2N	2- Me_3Si		3.60	0.50	8.48	1.72	0.26	A, -50 C
Me_2N	3- Me_3Si	4.25		0.78	2.67	7.35	0.23	B, -50 C
Me_2N	4- Me_3Si	3.25	4.55		4.55	3.25	0.15	A, -90 C
Me_2N	2- Me_3Si -5-Me		4.72	0.42	9.11 ^d	2.23	0.18	A, -90 C ^e
Me_2N	3- Me_3Si -6-Me	4.75	0.74	2.67	2.67	8.89 ^d	0.20	B, -90 C ^e

^aIn gauss, \pm 0.03 G for this work.^bA = 2:1 tetrahydrofuran/dimethoxyethane; B = 2:1 2-methyl-tetrahydrofuran/dimethoxyethane.^cEstimated.^dMethyl protons.^eAssigned by analogy to 2-, and 3-trimethylsilyl-N,N-dimethylaniline anions respectively.

Qualitatively, the order of stability of the radical anions, based on the conditions required for their production and the length of time that the radical persisted in the esr experiment is 2-trimethylsilyl- \approx 3-trimethylsilyl- > 2-trimethylsilyl-5-methyl- \approx 3-trimethyl-6-methyl- > 4-trimethylsilyl-N,N-dimethylaniline.

Discussion

The hyperfine coupling constants which have been assigned are listed in Table 3.1. Also included for the purpose of comparison are the reported hfs for trimethylsilylbenzene radical anion (21) and for N,N-bis(trimethylsilyl)aniline radical anion (9). It is clear that the pattern of the hfs for both 2-, and 3-trimethylsilyl-N,N-dimethylaniline closely resembles that reported for trimethylsilylbenzene in which the unpaired electron is found in the symmetric π^* orbital. For these and the ring methyl compounds the highest spin density occurs at the position para to silicon. It is tempting in light of this result to suggest that the unpaired electron resides in an orbit which is "symmetric" with respect to the mirror plane defined by the point of silicon substitution on the aromatic ring. However another relationship is clear in the data in Table 3.1. For all of the anilines listed, the smallest spin density occurs at the position para to the amino group. However, this relationship would not have been so apparent if the coupling constants in these radicals had

been assigned on the basis of CNDO/2 calculations. These calculations incorrectly predict a larger π spin density at C-4 and a smaller spin density at C-5 for 3-trimethylsilyl-N,N-dimethylaniline (Table 3.2). Indeed, the smallest hfs for the trimethylsilyl protons is observed when the trimethylsilyl group is para to the amino group. Furthermore the hfs for the other positions are intermediate between what would be expected for a purely symmetric orbital (trimethylsilylbenzene) or for a purely antisymmetric orbital (N,N-bis(trimethylsilyl)aniline). Thus, in contrast to the alkylbenzenes where the magnitude of electron withdrawal and stabilization of the S orbital of benzene by the trimethylsilyl group is greater than the destabilization effect of the alkyl substituents (21), it appears that in the trimethylsilyl substituted anilines the donor effect of the dimethylamino group and the acceptor effect of the trimethylsilyl group are nearly evenly matched. While it is not strictly correct to discuss S or A molecular orbitals for any except the para substituted compound, the highest occupied molecular orbital in these radical anions may be regarded as one which is both antisymmetric with respect to the plane defined by the point of nitrogen substitution and symmetric with respect to the plane defined by the point of silicon substitution. Nevertheless, the large couplings observed for the positions para to silicon, and the small couplings for positions meta to silicon in

cases where the dimethylamino group would favor large spin densities indicate that the electron withdrawal by the trimethylsilyl group is the more important influence in the radical anions. These conclusions are supported by CNDO/2 calculations on the radical anions.

In the previous chapter we discussed CNDO/2 calculations for the ground states of para series of Group IV substituted N,N-dimethylanilines. They gave good agreement with experimentally determined ionization potentials. We extended the calculations to the radical anions of the trimethylsilyl-substituted anilines. Table 3.2 gives the calculated π spin densities for these species and for trimethylsilylbenzene radical anion. Figure 3.6 shows a plot of a McConnell type relation (19):

$$\underline{a}_i^H = \rho_{C_i} Q_{CH}^H$$

for the experimental ring proton hfs, \underline{a}_i^H , and the CNDO/2 π spin density for the appropriate ring carbon, ρ_{C_i} . For the purpose of this correlation the signs for the hyperfine couplings were assumed to be correctly predicted by the CNDO calculation combined with the McConnell relation. The linearity of the plot is reasonable and least squares fit of the data gives a value for Q_{CH}^H of -23.0 G for these radical anions. This result is comparable to Q_{CH}^H values observed for other aromatic radical anions (3).

TABLE 3.2

CNDO/2 π SPIN DENSITIES FOR TRIMETHYLSILYL SUBSTITUTED
N,N-DIMETHYLANILINE RADICAL ANIONS^a

Substituents R ₁ R ₂	π -Spin density								
	N	1	2	3	4	5	6	Si	d
H 4-SiMe ₃	-	0.313	-0.073	0.179	0.093	0.179	-0.073	0.113	0.207
Me ₂ N 4-SiMe ₃	0.038	0.318	-0.103	0.195	0.065	0.195	-0.103	0.119	0.206
Me ₂ N 3-SiMe ₃	-0.012	-0.073	0.213	0.103	0.132	-0.045	0.280	0.119	0.218
Me ₂ N 2-SiMe ₃	-0.002	0.177	0.086	0.196	-0.087	0.325	-0.072	0.104	0.197

^a α - β spin. Numbering as in Table 3.1.

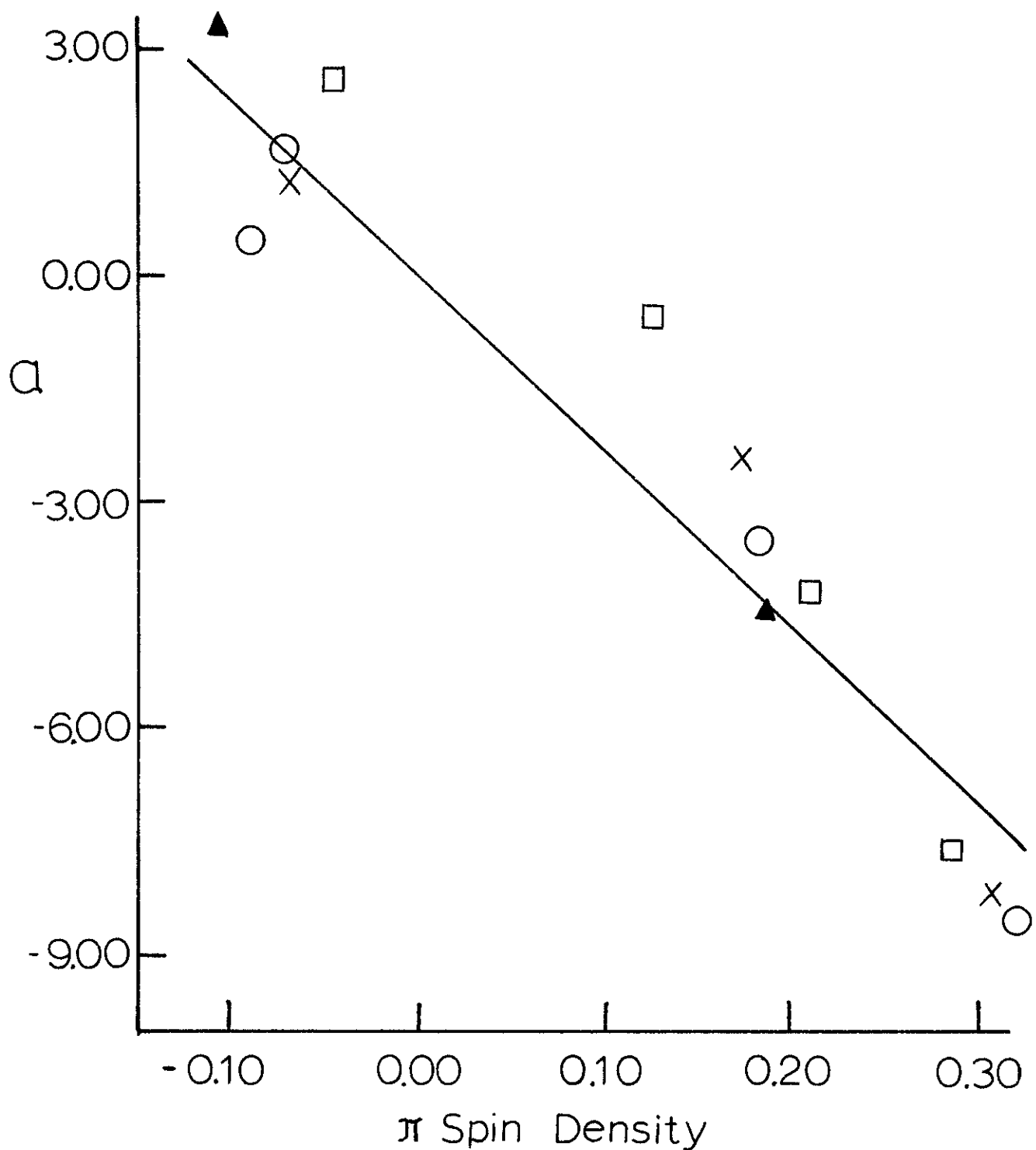
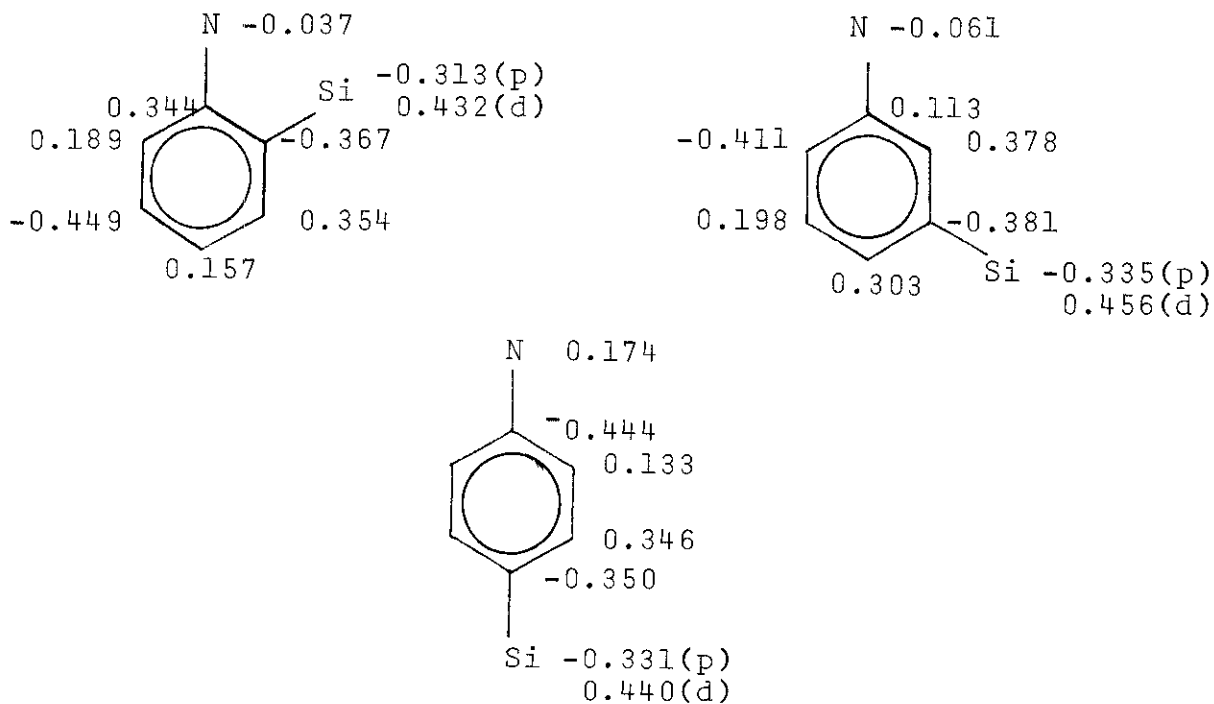


Fig. 3.6. Plot of the CND0/2 calculated π spin density against the esr hyperfine coupling constants for the radical anions of trimethylsilylbenzene, X; 4-trimethylsilyl-, ▲; 3-trimethylsilyl-, □; and 2-trimethylsilyl-*N,N*-dimethylaniline, ○.

The results given in Table 3.2 also suggest a reason for the very small couplings with the dimethylamino group in the aniline radical anions. For each of the radicals the lowest π spin density occurs at nitrogen. In the calculations the dimethylamino group was held for both 3-, and 4-trimethylsilyl-N,N-dimethylaniline, allowing maximum conjugation with the ring π system (see experimental section). One might reasonably expect that electronic repulsions in the anions would cause the dimethylamino group to be nearly tetrahedral and twisted out of conjugation. The effect, apparent for the 2-trimethylsilyl compound, is to even more drastically reduce the nitrogen π spin density. The values for the nitrogen spin density given in Table 3.2 may therefore be considered to be maximum values. While there are not sufficient data available to establish a value of Q_N^N for aniline radical anions it is well known that in heterocyclic nitrogen radicals the major contribution to the nitrogen hyperfine splitting comes from the spin density on nitrogen itself. The spin polarization effect from π spin densities on neighboring atoms in the heterocyclic systems is small (8, 11, 12, 22, 24). If the same considerations apply to aniline radical anions, then, in spite of large π spin densities at adjacent ring carbon atoms, one would not expect to observe resolvable couplings with the dimethylamino group in the esr spectra of aniline radical anions.

Consistent with the qualitative order of stability we observed for the aniline radical anions, the CNDO calculations predict 4-trimethylsilyl-N,N-dimethylaniline radical anion to be about 5 kcal/mole less stable than either 2-, or 3-trimethylsilyl-N,N-dimethylaniline radical anion, based on the total electronic energies obtained for the molecules.

Finally it is of interest to compare the highest filled molecular orbitals (MO) for the aniline radical anions. The CNDO coefficients for these highest filled MO's, in which only atomic orbitals of π symmetry contribute significantly, are given below.



In each case the orbital closely approximates a π^* orbital which is symmetric with respect to the plane perpendicular to the

ring and defined by the point of silicon substitution. The nitrogen's contribution to the orbital is small. Both the silicon $p\pi$ and $d\pi$ coefficients are significantly larger than those obtained for the highest filled MO in the ground states of these molecules; viz. $p\pi = 0.010$, $d\pi = 0.158$ for 4-trimethylsilyl-N,N-dimethylaniline; $p\pi = 0.012$, $d\pi = -0.051$ for 3-trimethylsilyl-N,N-dimethylaniline (6). In addition, while the magnitude of silicon's π interaction with the aromatic system was dependent on the ring's π density at the point of substitution for the ground states it is nearly independent of the point of substitution in the radical anions.

Thus, on the basis of the esr results and the CNDO/2 calculations, it appears that the trimethylsilyl group is the major perturbing influence in the radical anions of trimethylsilyl-substituted N,N-dimethylanilines. It not only increases the electron affinity of the anilines sufficiently to permit reduction but also plays the dominant role in determining the spin distribution in the radical anions. These effects are indicated to be due to significant $p-p\pi^*$ and $d-p\pi^*$ interactions between silicon and the aromatic ring by the CNDO/2 calculations.

Experimental

2-Trimethylsilyl-5-methyl-N,N-dimethylaniline.--Normal derivatization of ortho-lithiated N,N-dimethyl-m-toluidine with trimethylchlorosilane prepared by the general method

as described in Chapter II with stirring under argon for 3 hrs gave 1.5 g (48.7% yield) of 2-trimethylsilyl-5-methyl-N,N-dimethylaniline (None of the other possible product from this reaction, 2-trimethylsilyl-3-methyl-N,N-dimethylaniline, was observed in the reaction mixture.); bp, 102°/10 mm; nmr (CCl₄ with TMS as the internal standard): -0.22, singlet (9H), Si(CH₃)₃; -2.30, singlet (3H), 5-CH₃; -2.60, singlet (6H), N(CH₃)₂; -7.06, doublets (1H), H₄; -7.18, singlet (1H), H₆; -7.46, doublet (1H), H₃, J₃₄ = 8 hz.

Anal. Calcd for C₁₂H₂₁NSi: C, 69.49; H, 10.26; N, 6.71; mass 207. Found: C, 69.25; H, 10.20; N, 7.05; mass spectrum, parent (M⁺) 207.

3-Trimethylsilyl-5-methyl-N,N-dimethylaniline.--Bromination of N,N-dimethyl-o-toluidine (Aldrich) by the procedure of Gorvin (10) gave a 33% yield of 3-bromo-5-methyl-N,N-methylaniline; bp 115 ~ 118°/10 mm; nmr (CCl₄ with TMS as the internal standard): -2.21, singlet (3H), 6-CH₃; -2.65, singlet (6H), N(CH₃)₂, -6.96, doublets (1H), H₅; -7.00, doublet of doublets (1H), H₄; -7.07, doublets (1H), H₂, J_{2,4} = 1.5 hz, J_{4,5} = 4 hz, mass spec. found (M⁺), 213 and 215 with about equal intensity. Derivatization in the normal manner with trimethylchlorosilane of 3-lithio-6-methyl-N,N-dimethylaniline, prepared by lithium-halogen exchange (15), gave a 61% yield of 3-trimethylsilyl-6-methyl-N,N-dimethylaniline; bp 114-115°/10 mm; nmr (CCl₄ with TMS as the internal standard):

-0.23, singlet (9H), $\text{Si}(\text{CH}_3)_3$; -2.31, singlet (3H), 6- CH_3 ;
 -2.72, singlet (6H), $\text{N}(\text{CH}_3)_2$; -7.09, singlet (2H), H_4 and
 H_5 ; -7.16, singlet (1H), H_2 .

Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{NSi}$: C, 69.49; H, 10.26, mass
 207. Found: C, 69.25; H, 9.90; mass spectrum parent (M^+)
 207.

2-d-4-Trimethylsilyl-N,N-dimethylaniline.--Normal deri-
 vatization with D_2O of 2-lithio-4-trimethylsilyl-N,N-di-
 methylaniline, prepared by ortho lithiation of 4-trimethyl-
 silyl-N,N-dimethylaniline (14) with stirring for 2 hrs and
 refluxing for an additional hour, followed by the normal
 work-up gave an 81% yield of product; bp $127^\circ/10$ mm (lit (14),
 bp $101^\circ/1.3$ mm); nmr (CCl_4 with TMS as the internal standard):
 -6.64, doublets, ortho protons; and -7.38, multiplet, meta
 protons, $J_{45} = 8$ hz, $J_{35} = 3$ hz with an intensity ratio of
 about 1.2:2 indicating about 80% ortho deuteration; mass
 spec. ratio of the 193/194 peaks showed > 80% deuteration.

4-d-2-Trimethylsilyl-N,N-dimethylaniline.--Derivatization
 with D_2O of 4-lithio-N,N-dimethylaniline, prepared by lithium-
 halogen exchange with 4-bromo-N,N-dimethylaniline (15), gave
 2.5 g (82% yield) of 4-d-N,N-dimethylaniline; bp $76^\circ/10$ mm;
 mass spec. ratio of the 121/122 parent peaks indicated 87%
 deuteration. nmr (CCl_4 with TMS as the internal standard):
 -2.90, singlet (6H), $\text{N}(\text{CH}_3)_2$, -6.68, doublets (~2H), ortho

protons; -7.20, doublets (~2H), meta protons. The product was ortho lithiated and coupled with trimethylchlorosilane as described above to give 2.2 g (58% yield) of 4-d-2-trimethylsilyl-N,N-dimethylaniline; bp 81°/10 mm.

6-d-2-Trimethylsilyl-N,N-dimethylaniline.--The ortho lithiation procedure described above followed by hydrolysis with D₂O was carried out with N,N-dimethylaniline (Aldrich) to give 6.1 g (87% yield) of 2-d-N,N-dimethylaniline; bp 76°/10 mm. The ortho lithiation of the deuterated material was repeated two more times to give 3.4 g (48% yield) of 2,6-d₂-N,N-dimethylaniline; bp 76°/10 mm. 6-d-2-Trimethylsilyl-N,N-dimethylaniline was then prepared from the deuterated compound using the procedure described above to give a 55% yield; bp 81°/10 mm. The mass spec. parent = 194, and nmr, (CCl₄ with TMS as the internal standard): -7.26, multiplet (~3H), ring protons, indicate that the compound was essentially completely deuterated in the 6-position.

2-d-3-Trimethylsilyl-N,N-dimethylaniline.--The ortho lithiation procedure of 3-trimethylsilyl-N,N-dimethylaniline followed by hydrolysis with D₂O gave 76% protons; bp 110°/10 mm. Based on the nmr (CCl₄ with TMS as the internal standard): -7.07, multiplet (~3.67 H), aromatic protons, and the mass spec., ratio of the 193/194 parent peaks compared with the same ratio for the undeuterated compound, the compound was approximately 35% deuterated. The esr spectrum

showed that deuteration had only occurred in the 2-position as the intensity of the splitting due to the 6-proton was not affected.

4-d-3-Trimethylsilyl-N,N-dimethylaniline.--The bromination of 2.5 g 4-d-N,N-dimethylaniline using the procedure of Gorvin (10) gave 1.3 g (32% yield) of monobrominated product. Lithium-halogen exchange (15) with 1.0 g of this product followed by coupling with trimethylchlorosilane gave 0.6 g (58% yield) of silylated material which was shown by glc analysis to be 25% 4-d-3-trimethylsilyl-N,N-dimethylaniline and 75% 4-trimethylsilyl-N,N-dimethylaniline. The deuterated compound was purified by glc for the esr experiments. By mass spec. it was ~73% deuterated.

Esr Spectra of the Radical Anions.--The esr solvents, tetrahydrofuran, 2-methyltetrahydrofuran and dimethoxyethane were distilled from lithium aluminum hydride or sodium under an atmosphere of dry nitrogen and then vacuum transferred to storage bulbs containing sodium/potassium alloy and anthracene on the vacuum line. The solvents were repeatedly degassed until the dark blue color of anthracene radical anion appeared. When a sample was prepared the appropriate amounts of solvents to give the indicated volume composition were transferred into the sample cell using standard high-vacuum techniques. Otherwise the samples were prepared using the

usual techniques (13, 16), using triply sublimed potassium metal as the reducing agent.

Theoretical Calculations.--The CNDO/2 program employed was described in Chapter II. The bond angles and bond lengths were not varied for the anions. For both 3-, and 4-trimethylsilyl-N,N-dimethylaniline radical anions the dimethylamino group was treated as planar with the C-N-C angle of 120° in the plane of the aromatic ring. These values are reasonably close to the recently reported electron diffraction data for N,N-dimethylaniline where the C-N-C intervalence angle at nitrogen is 116° (23). For 2-trimethylsilyl-N,N-dimethylaniline the nitrogen was assumed to be tetrahedrally hybridized with the lone pair rotated 73° from the plane perpendicular to the aromatic ring, towards the trimethylsilyl group. This configuration is based on the rotational angle for the lone pair which we have determined spectroscopically for the ground state (see Chapter II). The trimethylsilyl group was also taken as tetrahedral and was oriented with one of the methyl groups in the plane of the aromatic ring and directed away from the dimethylamino group.

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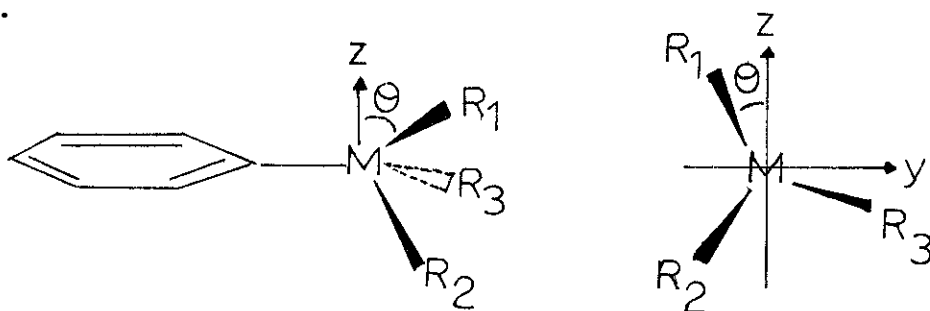
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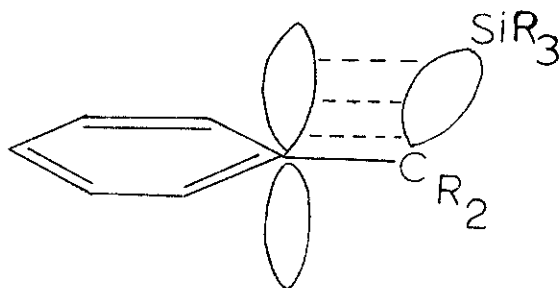
CHAPTER IV

THE RADICAL ANIONS OF PARA SILYL SUBSTITUTED N,N-DIMETHYLANILINES

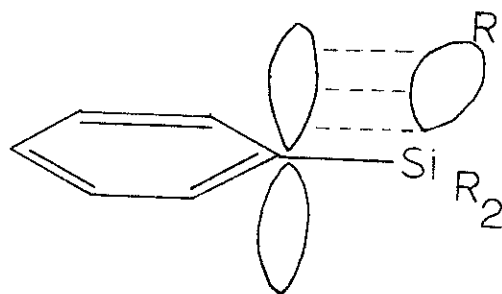
Since Traylor (22) proposed a hyperconjugative σ - π interaction between the relatively high energy organometallic σ bond and the aromatic π system, the importance of σ - π interactions in organosilicon compounds has been well established both experimentally (1,28,29,41,44) and theoretically (30,31,40). Recently both Pitt (31) and Schweig (33) have presented detailed analyses of hyperconjugation and its role in Group IV chemistry. In these papers, the relative roles of hyperconjugation, p-d π bonding, and inductive effects in determining trends in ionization and reduction potentials, electrophilic reactivity, electronic spectra, and charge distributions were considered. The σ - π hyperconjugative interaction is expected to be inversely proportional to the energy separation between the σ and π orbitals involved, and also dependent on the dihedral angle, (θ), between the σ orbital involved and the π orbital.



All of the previous work dealt with the systems having the silicon at positions β to the aromatic π system (IV-1), where the σ electron density of the substituent is primarily associated with the benzylic position, and where the participating σ energies are probably higher than that of the highest filled MO of benzene (29). The σ - π interactions for the systems having silicon substituents at positions β to the aromatic π system (IV-2) have not previously been studied in detail.



IV-1



IV-2

Jones has demonstrated that the use of esr in conjunction with CNDO/2 calculations can be usefully applied to the investigation of the bonding interactions between aromatic π systems and Group IV substituents. On the bases of these studies both d- $p\pi$ and hyperconjugative p- $p\pi$ interactions were indicated to contribute to the ground state stabilization of the silicon compound with respect to the carbon analog, with d- $p\pi$ interaction being more important, based on CNDO/2 calculations (14).

In the previous chapter it has been demonstrated that the trimethylsilyl group is the major perturbing influence and plays the dominant role in determining the spin distribution in the radical anions of trimethylsilyl substituted N,N-dimethylanilines. These effects are indicated to be due to significant p- $p\pi^*$ and d- $p\pi^*$ interactions by the CNDO/2 calculations. The silicon $d\pi$ and $p\pi$ coefficients for the highest filled MO in the radical anions are significantly larger than those obtained for the ground states, suggesting that the interactions between the silicon orbitals and π^* orbitals are more significant than their interactions with the π orbitals. This might be expected because of the better energy match between the silicon orbitals and π^* orbitals (11). The magnitude of the silicon $p\pi$ coefficient is comparable to the $d\pi$ coefficient, showing that the p- $p\pi^*$ inter-

action is as important as the d-p π^* interaction in the radical anions.

It is known that the silicon-hydrogen bond ($\text{>Si}^{\delta+}\text{-H}^{\delta-}$) is more polar than the silicon-carbon bond (5,18,26,34,35). The replacement of methyl groups on silicon by hydrogens would be expected to raise the silicon σ orbital energy and lower the σ^* orbital energy, which would increase the p-p π^* interaction (31). We have therefore investigated p-trimethylsilyl-, p-dimethylsilyl-, p-methylsilyl-, and p-silyl-N,N-dimethylaniline radical anion to examine how the replacement of methyl groups on silicon by hydrogens affects the bonding interactions in these para silyl substituted N,N-dimethylanilines.

There have been several reports of esr spectra of aromatic radical anions containing silicon-hydrogen bonds (17,23,24,25,39,37). However, the hyperfine splittings due to the silyl hydrogens were assigned widely differing values (0.81 G (16), 6.0 G (26)), because the investigators were observing paramagnetic species resulting from further reactions of the parent radical anions (39). Possible mechanisms involved in these reactions have been discussed by O'Brien et al., who generated the parent radical anions of phenylsilanes electrolytically and compared these with the radicals produced by potassium reduction. Electrolytic

reduction was a milder method and produced only the parent radical anions, while potassium reduction gave secondary or tertiary spectra due to further reactions (39).

The primary spectra of radical anions of para silyl substituted N,N-dimethylanilines generated electrolytically or by potassium reduction are reported and discussed in the first part of this chapter. The preliminary interpretations of the secondary or tertiary spectra resulting from the further reactions are reported in the second part.

Results and Discussion

Primary Radicals

In Figure 4.1 is shown the spectrum of the radical anion of p-silyl-N,N-dimethylaniline generated electrolytically using tetrabutylammonium perchlorate as the supporting electrolyte in THF solution at -92°C . This spectrum cannot be obtained by potassium reduction due to rapid further reactions. The spectrum consists of a large quartet of 5.35 G due to three hydrogens on silicon and smaller triplet couplings of 3.94 G and 1.59 G due to two sets of two equivalent ring protons. The 3.94 G coupling is assigned to protons meta and the 1.59 G coupling protons ortho to the dimethylamino group, respectively, by analogy with the coupling constants of p-trimethylsilyl-N,N-dimethylaniline radical anion (Chapter III).

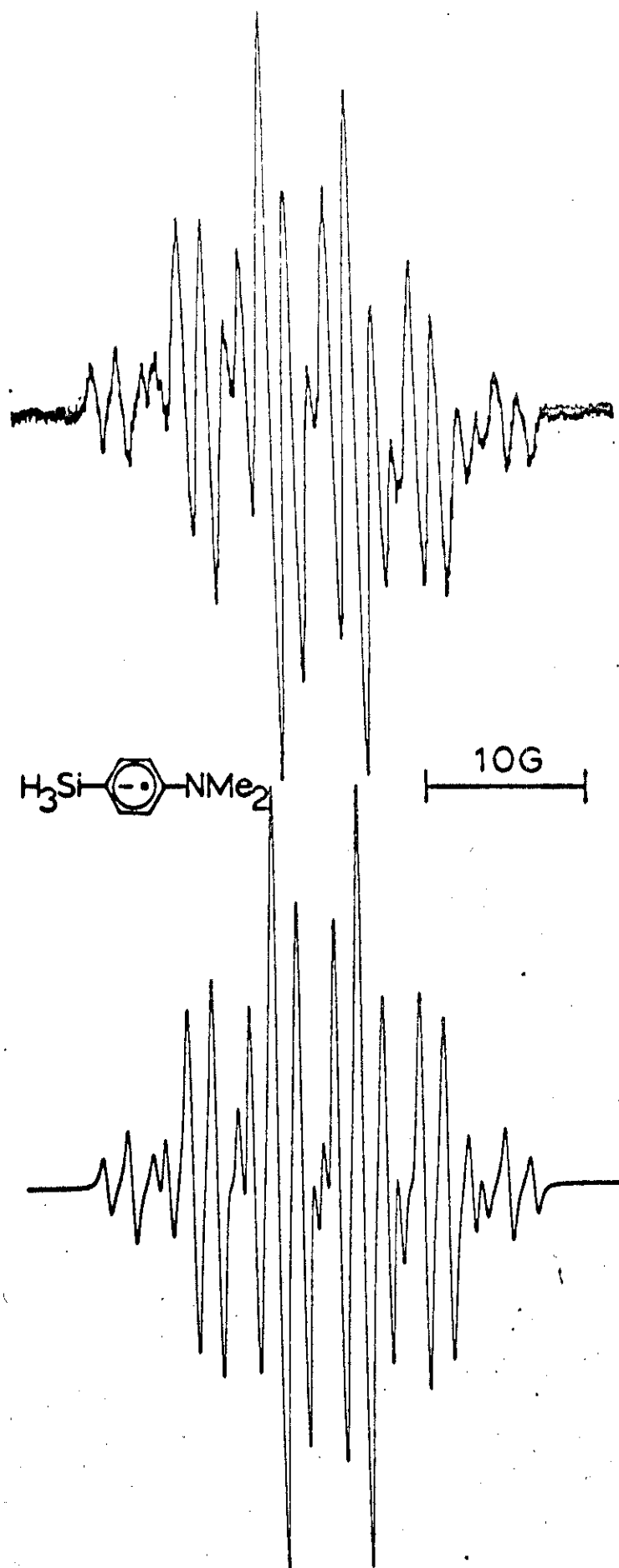


Fig. 4.1. ESR spectrum of the radical anion of p-silyl-N,N-dimethylaniline, generated electrolytically; upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.25 G.

No coupling constants due to the nitrogen or the protons of the dimethylamino group have been identified or resolved in p-silyl-N,N-dimethylaniline radical anion. However, the line width of 0.8 G is considerably larger than those for trimethylsilyl substituted N,N-dimethylanilines, viz. 0.15 G, Chapter III. This broadening might be attributed to the unresolved couplings of the nitrogen and protons of the dimethylamino group. The fit of the simulated spectrum, using a line width of 0.25 G, was improved by adding the couplings of 0.10 G and 0.05 G for the nitrogen and the methyl protons on nitrogen, respectively.

The spectrum of the p-methylsilyl-N,N-dimethylaniline radical anion generated electrolytically in THF using tetrabutylammonium perchlorate as the supporting electrolyte at -90°C is shown in Figure 4.2. The spectrum consists of three triplets, 4.02 G, 3.81 G, and 1.81 G, due to three sets of two equivalent protons. The smallest triplet coupling of 1.81 G is assigned to the hydrogens at positions ortho to the dimethylamino group. The couplings of 4.02 G and 3.81 G are assigned to the meta protons and to the protons on silicon, respectively. It is possible for the assignments of these two couplings to be reversed. Either of the possible assignments would be acceptable for the purpose of discussion in the present work. However, the trend of the couplings for meta protons to increase from p-silyl-

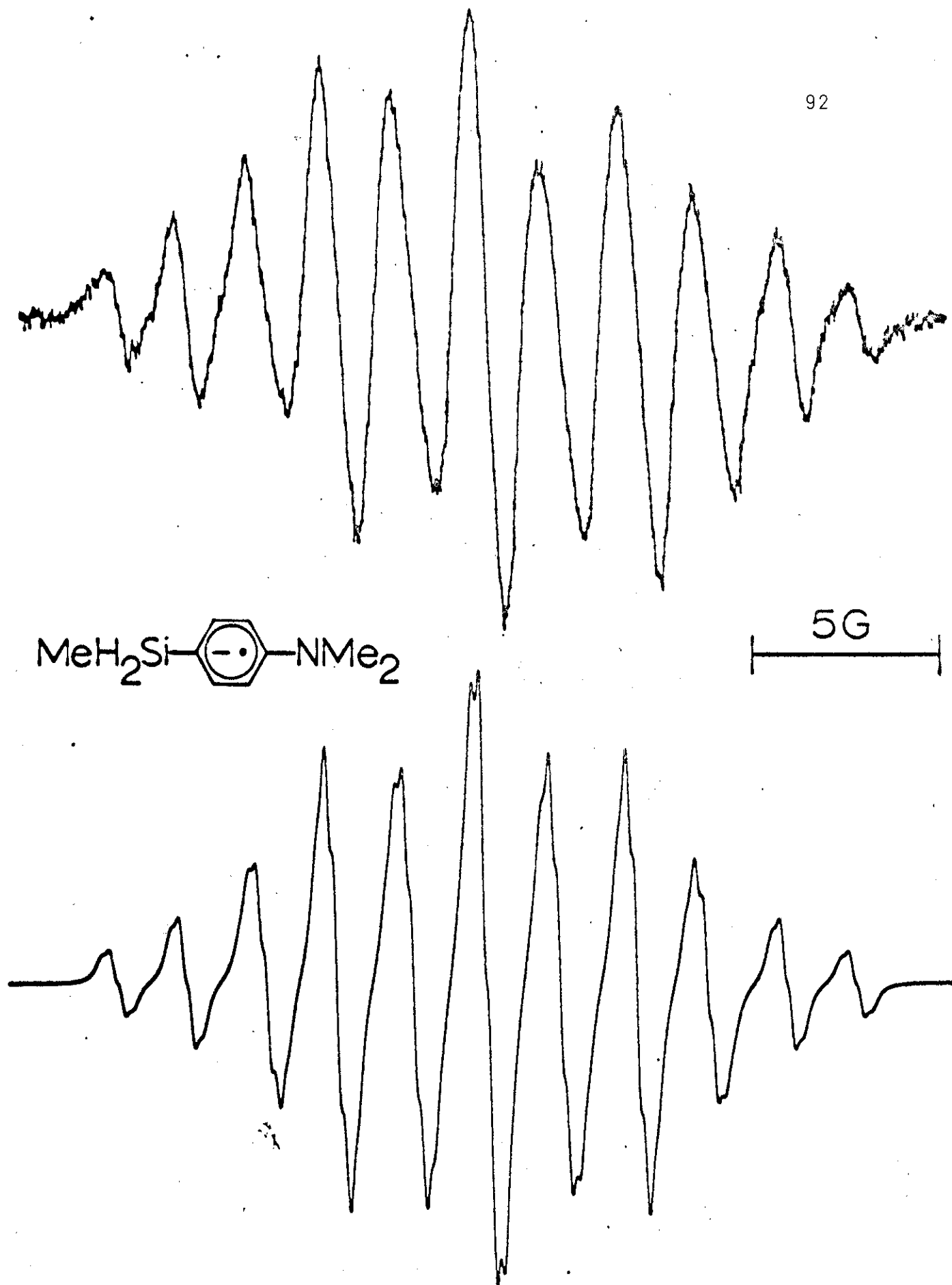


Fig. 4.2. ESR spectrum of the radical anion of p-methylsilyl-N,N-dimethylaniline, generated electrolytically: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.20 G.

to p-trimethylsilyl-N,N-dimethylaniline (see Table 4.1) supports the former assignments. Experimental couplings which could be assigned to the methyl protons on silicon and the nitrogen and protons of the dimethylamino group were not resolved. The fit of the simulated spectrum, using a line width of 0.20 G, was improved by adding a 0.20 G coupling for the methyl protons on silicon (see Figure 4.2). The simulation was further improved by adding other couplings of 0.05 G and 0.03 G for the nitrogen and dimethylamino protons, respectively.

Potassium reduction of p-dimethylsilyl-N,N-dimethylaniline in THF and DME solution at -90°C gave a greenish yellow solution which gave the esr spectrum shown in Figure 4.3. The spectrum shows a large triplet 4.07 G which is split into a doublet of 3.08 G and a triplet of 2.39 G. The doublet coupling of 3.08 G is obviously due to the only unique proton in the system, the hydrogen on silicon. The triplets of 4.07 G and 2.39 G are assigned to the hydrogens meta and ortho to the dimethylamino group, respectively. An expanded spectrum permits the measurement of a smaller splitting of 0.18 G arising from the methyl protons on silicon. Electrolytic reduction gives the same, although a much weaker, spectrum.

The hyperfine coupling constants for these three radical anions are collected in Table 4.1 along with the previously

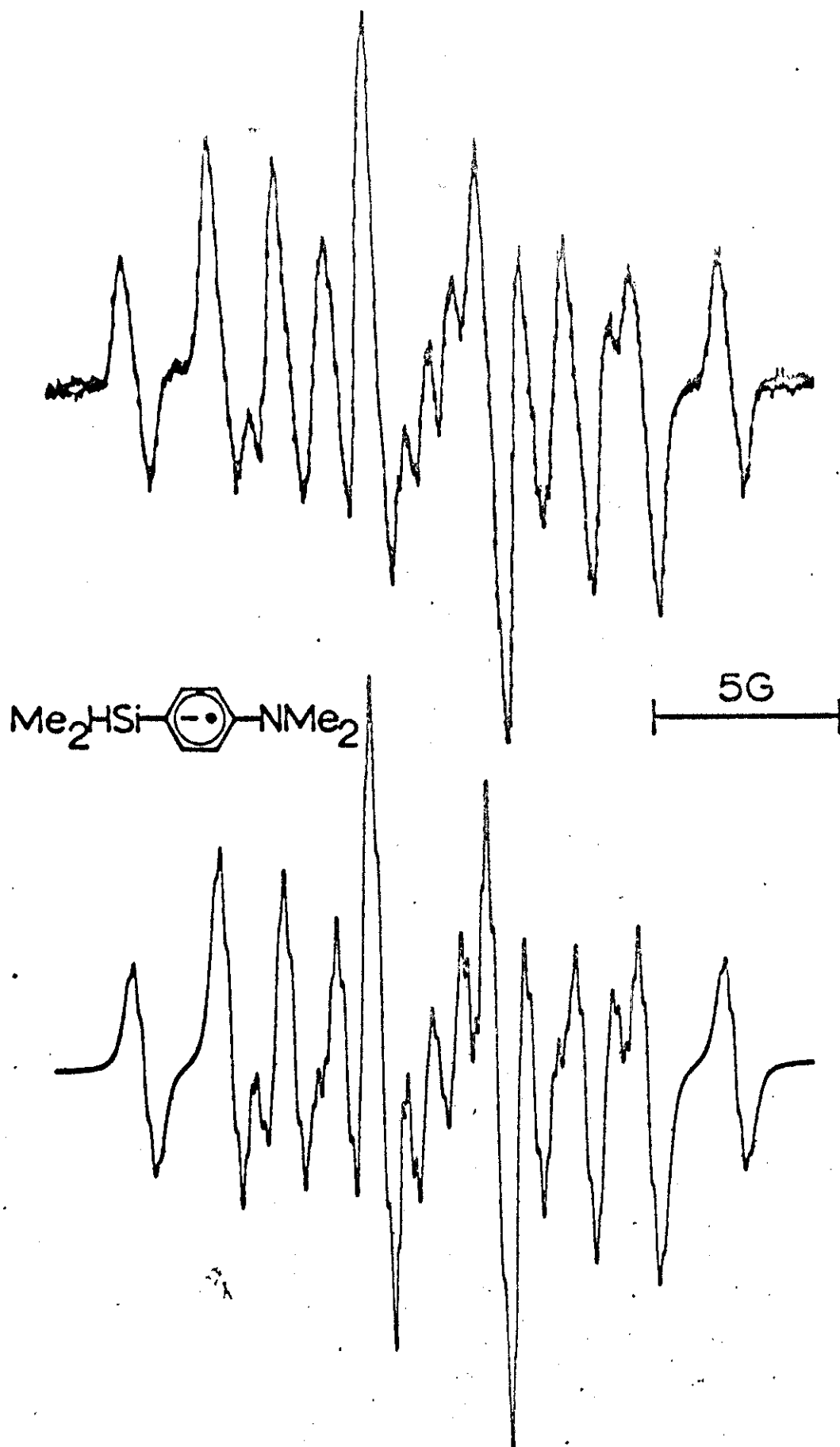


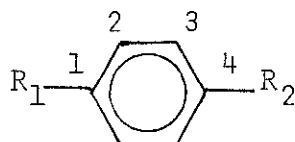
Fig. 4.3. ESR spectrum of the radical anion of p-dimethylsilyl-N,N-dimethylaniline, generated by potassium reduction: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.18 G.

reported constants for other radical anions for comparison. The couplings due to nitrogen or methyl protons on nitrogen in silylaniline radical anions are not resolved in any of the cases. Maximum possible values can be estimated and are included in the table. The line width increases from the p-dimethylsilyl- to the p-silyl-N,N-dimethylaniline radical anion. In spite of the possible counterion (K^+) interaction, a narrower line width is observed for p-dimethylsilyl-N,N-dimethylaniline. Line broadening in phenylsilane radical anions as the number of hydrogens on silicon increases has also been observed elsewhere and attributed to the silicon d-orbital involvement (39). A part of the reason for line broadening in these silylanilines might be due to unresolved couplings of nitrogen and dimethylamino protons, which must be less than 0.20 G. The small coupling with the dimethylamino group in trimethylsilyl substituted N,N-dimethylaniline radical anions could not be resolved and a possible reason for this has been suggested in the previous chapter.

As seen in Table 4.1, the ring proton coupling constants in silylanilines are considerably larger than those in phenylsilanes, indicating that the orbital in which the unpaired electron resides is neither pure π^* symmetric or π^* anti-symmetric but an admixture of the two. This is consistent with the fact that the coupling constants for silyl hydrogens in the silylanilines are considerably smaller than those in

TABLE 4.1

HYPERFINE COUPLING CONSTANTS^a OF SILYL
SUBSTITUTED AROMATIC RADICAL ANIONS;



Substituents		^a N- <u>Me</u>	^a N	^a H ₂	^a H ₃	^a Si-H	^a Si- <u>Me</u>
R ₁	R ₂						
NMe ₂	SiMe ₃			3.25	4.55		0.15
NMe ₂	SiHMe ₂			2.39	4.07	3.10	0.18
NMe ₂	SiH ₂ Me	0.03 ^e	0.05 ^e	1.78	4.02	3.81	0.20 ^e
NMe ₂	SiH ₃	0.05 ^e	0.10 ^e	1.59	3.94	5.35	
NMe ₂	NO ₂ ^b	0.71	1.13	1.10	3.33	12.00 ^c	
H	SiHMe ₂ ^d		8.15 ^f	0.86	2.72	7.20	0.11
H	SiH ₂ Me ^d		8.40 ^f	0.64	2.76	6.33	0.20 ^e
H	SiH ₃ ^d		8.46 ^f	0.52	3.08	8.04	

^aIn gauss

^bD. H. Geske *et al.*, *J. Amer. Chem. Soc.*, **86**, 987(1962).

^c^aNO₂

^dRef. 39.

^eEstimated.

^f^aH₁

phenylsilanes. Symmetric character increases from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline and approaches that of p-nitro-N,N-dimethylaniline. The strong electron donating effect of the dimethylamino group of these radical anions results in low spin densities at the 1,4-positions. The ring proton coupling constants in silylanilines decrease from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline. While the coupling constants for ortho protons decrease rapidly, the meta proton coupling constants decrease slowly. This may be attributed to through-space interaction between silicon and meta carbons (14). A concomitant increase in the coupling constants for both methyl protons and hydrogens on silicon indicates that the interaction of the silyl substituent with the π^* orbital of the radical increases as methyl groups on silicon are replaced by hydrogen. This is consistent with the results of ultraviolet studies for phenyl silanes (18,26). The size of the ring proton couplings for p-silyl-N,N-dimethylaniline shows that the electron withdrawal by the silyl group approaches that of the nitro group.

In order to gain a better understanding of the bonding interactions between the silyl substituents and the ring π system, CNDO calculations have been performed. In particular, it was anticipated that CNDO/2 calculations would help to determine the effect of replacing methyl groups on silicon by hydrogen and to differentiate among inductive, hyperconjugative, and d- $p\pi^*$ interactions.

In the calculations the dimethylamino group was held planar for the radical anions, allowing maximum conjugation with the ring π system as suggested elsewhere (14). A silicon-hydrogen bond was held coplanar with the ring plane as is indicated by the nmr studies of silyl substituted aromatic systems (27).

The total calculated electronic energy and the spin distributions in the ring were not affected significantly by rotation of the silyl substituent. For p-silyl-N,N-dimethylaniline the energy for the configuration with one hydrogen perpendicular to the ring was lower than that for the coplanar geometry by 0.083 kcal/mole (Appendix II). The silicon-hydrogen σ^* orbital energies decreased from p-dimethylsilyl- to p-silyl-N,N-dimethylaniline.

The highest occupied MO of p-silyl-N,N-dimethylaniline radical anion with a planar dimethylamino group was a σ type orbital involving mainly silicon, the hydrogens on silicon, and ring carbon-4 (see Figure 4.4). This is in contrast to the experimental hyperfine couplings for the radical anion which indicate the highest filled MO to be an orbital of π^* symmetry. If, in the CNDO calculation, the dimethylamino group was treated as tetrahedral or if the C-N bond was slightly lengthened (1.43 Å) the calculation correctly gave an orbital of π^* symmetry as the hfmo in the radical anion. It is conceivable that in these systems where the additional electron occupies a predominately aromatic π^* orbital, electron

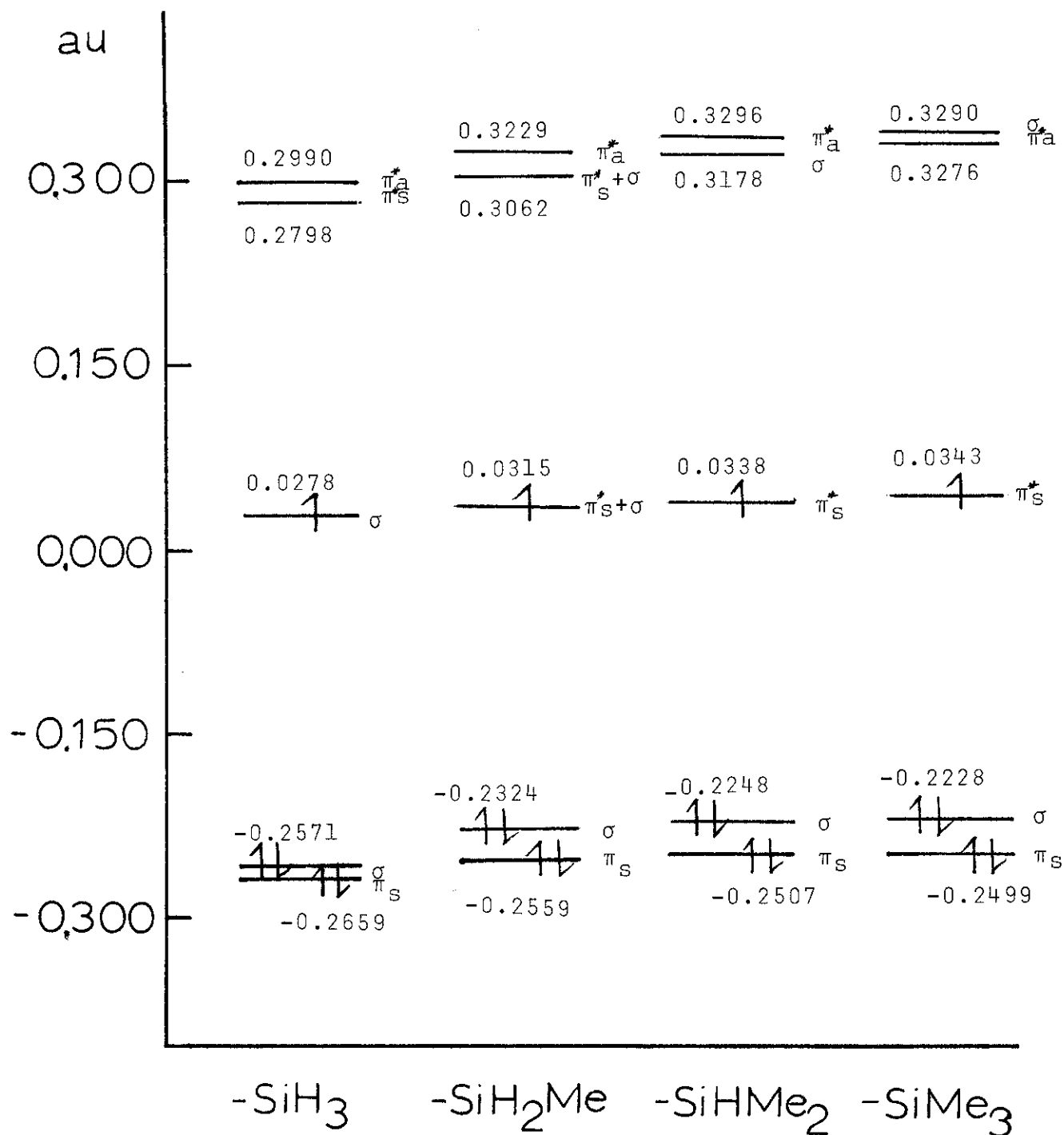
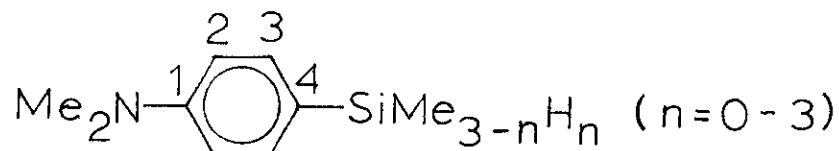


Figure 4.4. Several molecular orbitals below and above the highest filled MO and their energies for para silyl substituted N,N-dimethylaniline radical anions calculated by CNDO/2 approximation

repulsion between the unpaired electron and the nitrogen lone pair results in a twisting of the dimethylamino group out of conjugation (Chapter III). This is supported by the fact that the CNDO/2 calculations predict the tetrahedral conformation of the dimethylamino group in p-silyl-N,N-dimethylaniline radical anion to be about 29 kcal/mole more stable than the planar conformation, based on the total electronic energies obtained for the molecule. Slightly higher total energy was obtained for the geometry with the longer ring carbon-nitrogen bond. The total energy of this molecule also decreases in a small but significant way as the lone pair of nitrogen is twisted from perpendicular to coplanar with the ring plane. The results of optimizing the geometry are collected in Appendix II. The following discussion of the CNDO/2 results is based on the geometry:

The dimethylamino group was tetrahedral, the lone pair was twisted 30° from the ring plane, and a silyl hydrogen was perpendicular to the ring plane.

In Tables 4.2, 4.3, and 4.4, the numbering given below was used.



In the previous chapter it has been observed that the McConnell type plot of CNDO/2 π spin density versus the hyperfine

coupling constants for the trimethylsilyl substituted aromatic systems gives a good linearity with -23.0 G as the Q value. The CNDO/2-calculated π spin densities for para silyl substituted N,N-dimethylaniline radical anions are given in Table 4.2 along with the spin densities calculated from the McConnell-type equation using experimental hyperfine coupling constants and -23.0 G for Q. A fairly good agreement can be seen between the two spin densities.

Table 4.3 gives the energy and the atomic orbital coefficients for the highest filled MO in para silyl substituted N,N-dimethylaniline radical anions. The highest filled MO energy decreases from p-trimethylsilyl- to p-silyl-N,N-dimethylaniline as the interaction between the substituent and the orbital increases. This decreasing energy is consistent with the ordering of energy levels for both the ground and excited states observed in Chapter II. The orbital is clearly a π^* symmetric orbital with respect to the plane that bisects the 1,4-positions and is perpendicular to the ring plane. In every case the MO has a node between the nitrogen and the ring. The coefficients for ring carbon-2 and -6 decrease rapidly but change little for the 3 and 5 carbons, correlating well with the pattern of the hyperfine coupling constants for the ring protons. The magnitudes of the silicon p and d orbital coefficients are comparable with each other and the $p\pi$ coefficient increases from p-trimethylsilyl- to p-silyl-N,N-

TABLE 4.2

 II SPIN DENSITIES FOR PARA SILYL SUBSTITUTED
 N,N-DIMETHYLANILINE RADICAL ANIONS

Substi- tuent		Atoms					
		1	2	3	4	p	d
-SiMe ₃	Calc. ^a	0.3316	-0.0842	0.1802	0.0866	0.1052	0.1952
	Exp. ^b	-	-0.1413	0.1978	-	-	-
-SiHMe ₂	Calc. ^a	0.3309	-0.0882	0.1861	0.0767	0.1050	0.2072
	Exp. ^b	-	-0.1039	0.1769	-	-	-
-SiH ₂ Me	Calc. ^a	0.3026	-0.0893	0.1847	0.0492	0.1429	0.1956
	Exp. ^b	-	-0.0774	0.1748	-	-	-
-SiH ₃	Calc. ^a	0.3130	-0.0936	0.1901	0.0521	0.1623	0.1843
	Exp. ^b	-	-0.0691	0.1713	-	-	-

^aCNDO/2 spin density obtained from the difference between the α and β spin density.

^bCalculated from the equation, $a = \rho Q$, using the experimental hyperfine coupling constants for a and the value of -23.0 G for Q .

TABLE 4.3

CNDO/2 π COEFFICIENTS AND THE ENERGY FOR THE HIGHEST FILLED
 MOLECULAR ORBITAL OF PARA SILYL SUBSTITUTED
 N,N-DIMETHYLANILINE RADICAL ANIONS^a

Substi- tuent	Energy ^b	Atoms						
		N	1	2	3	4	$\overbrace{\text{Si}}^{\text{p}} \text{---} \text{d}$	
-SiMe ₃	0.0275	0.058	-0.459	0.161	0.341	-0.367	-0.314	0.429
-SiHMe ₂	0.0231	0.059	-0.459	0.156	0.346	-0.357	-0.325	0.443
-SiH ₂ Me	0.0219	0.058	-0.437	0.137	0.341	-0.327	-0.387	0.432
-SiH ₃	0.0157	0.060	-0.444	0.140	0.346	-0.332	-0.401	0.419

^aInasmuch as this is a π^* symmetric orbital for all the molecules, these are coefficients of the atomic orbitals of π symmetry.

^bIn atomic units.

dimethylaniline, while the $d\pi$ coefficient changes little. This suggests that the $p-p\pi^*$ interaction is as important as the $d-p\pi^*$ interaction in these radicals.

In Table 4.4, the formal charges, Δq (12), and the total electronic densities for silicon p and d orbitals are listed. A general tendency for electron density to be shifted toward the silicon end of the radical anions can be observed. This electron density accumulates at the methyl carbons and hydrogens on silicon. An increase of σ electron density at its point of attachment along with an increase of positive charge on silicon suggests that the +I inductive effect of the silyl group increases from the trimethylsilyl to the silyl group. However, there is a decrease of π density at the same carbon. Generally hydrogens on silicon accept electrons better than methyl groups on silicon, which is consistent with the dipole moment results for the ground states of alkylsilanes (35). Although the replacement of methyl groups on silicon by hydrogen reduces the electron density on silicon which would make the $d-p\pi^*$ interaction favorable, the d orbital involvement in both σ and π bonds decreases from the trimethylsilyl to the silyl group. These increasing +I inductive effects and decreasing d orbital density are not consistent with the esr results, which showed increasing spin delocalization into the silyl group as protons replaced methyl groups. However, the calculated p orbital density generally increases in the correct order.

TABLE 4.4

 CNDO/2 NET ATOMIC CHARGES FOR THE RADICAL ANIONS OF
 PARA SILYL SUBSTITUTED N,N-DIMETHYLANILINES

Substi- tuent	Δq^a	Atoms							Silicon	
		N	1	2	3	4	Si	Si-H ^b	Si-Me ^b	Orbitals' density p
-SiMe ₃	Tot	-0.143	0.014	-0.048	0.013	-0.145	-0.043	-0.174	1.797	1.400
	σ	-0.974	0.186	0.015	0.064	-0.048	0.068		1.139	0.957
	π	0.831	-0.172	-0.063	-0.051	-0.097	-0.111		0.668	0.443
-SiHMe ₂	Tot	-0.144	0.017	-0.048	0.015	-0.148	-0.010	-0.199	1.833	1.272
	σ	-0.975	0.184	0.015	0.064	-0.056	0.126		1.120	0.849
	π	0.831	-0.167	-0.063	-0.049	-0.092	-0.136		0.713	0.423
-SiH ₂ Me	Tot	-0.145	0.027	-0.047	0.017	-0.144	0.064	-0.203	1.864	1.113
	σ	-0.973	0.174	0.013	0.064	-0.081	0.225		1.106	0.710
	π	0.828	-0.147	-0.060	-0.047	-0.063	-0.161		0.758	0.403
-SiH ₃	Tot	-0.144	0.027	-0.047	0.019	-0.153	0.253	-0.207	1.814	0.944
	σ	-0.972	0.176	0.012	0.066	-0.079	0.408		1.049	0.554
	π	0.828	-0.149	-0.059	-0.047	-0.074	-0.155		0.765	0.390

^aExcess total charge density on the atom indicated.^bAverage Δq .

In Table 4.5 the off-diagonal terms of the CNDO/2 density matrices for the radical anions were examined to differentiate the relative importance of d-p π^* and hyperconjugative p-p π^* interactions. The d σ and d π bond densities decrease from the trimethylsilyl to the silyl group, while both p σ and p π densities increase. The σ bond order decreases in the same order, but the π bond order increases. These results suggest that the increasing interaction between silicon and the π^* orbitals going from trimethylsilyl to silyl should not be ascribed to p-d π^* interaction. The increasing p σ and p π densities are consistent with the esr results. Thus, on the basis of the esr results and the CNDO/2 calculations, it appears that the interaction of silicon with the π^* orbitals in para substituted N,N-dimethylaniline radical anions increases as the number of hydrogens on silicon increases. While both p-p π^* and d-p π^* interactions are involved, only the variation of the silicon p orbital parameters in the calculations follow the experimentally observed trends. These results strongly suggest that p-p π^* or hyperconjugative interaction is much more significant than d-p π^* effects in the excited states of unsaturated organosilicon molecules.

Bock has recently reported that CNDO/2 calculations, including 3d orbitals for silicon in the basis set, overemphasize d-p π back-bonding and that 3d silicon orbitals need

TABLE 4.5

CNDO/2 BOND DENSITIES^a AND BOND ORDERS^b FOR THE INTERACTION BETWEEN THE SILICON AND ITS RING CARBON FOR THE RADICAL ANIONS OF PARA SILYL SUBSTITUTED N,N-DIMETHYLANILINES

Substituent orbitals	Substituent			
	-SiMe ₃	-SiHMe ₂	-SiH ₂ Me	-SiH ₃
s	0.708	0.701	0.688	0.698
pσ	1.115	1.126	1.137	1.159
dσ	0.828	0.812	0.797	0.771
pπ	0.345	0.353	0.372	0.389
dπ	0.507	0.519	0.493	0.492
σBO	1.326	1.319	1.312	1.314
πBO	0.426	0.436	0.433	0.441
Total BO	1.752	1.755	1.745	1.755

^aTotal bonding density minus antibonding density for the orbital indicated.

^bBond density/2.

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 (16).

Secondary and Tertiary Spectra

After taking the primary spectrum of p-dimethylsilyl-N,N-dimethylaniline radical anion (see Figure 4.3) the solution was brought into contact with a potassium mirror at -78°C . Spectra of II and III shown in Figure 4.5 were recorded depending upon the length of contact time. Species II appeared after 15 ~ 20 hrs and species III 1 ~ 2 days after spectrum II was obtained. The patterns were produced somewhat more rapidly by frequently taking the cell out of the dry ice and acetone bath for a few seconds. 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 couplings for the silyl hydrogen of either $\text{Me}_2\text{HSi}-\text{C}_6\text{H}_4-\text{SiHMe}_2$ or $\text{pHMe}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiHMe}_2$ (Table 4.6). The quintet coupling of 1.85 G in spectrum II is similar to the coupling for the ring protons of benzene radical anion substituted at the 1,4-positions with organo silyl substituents (2,17,23,36,39) and is typical of such systems (39). The coupling constants of species II suggest

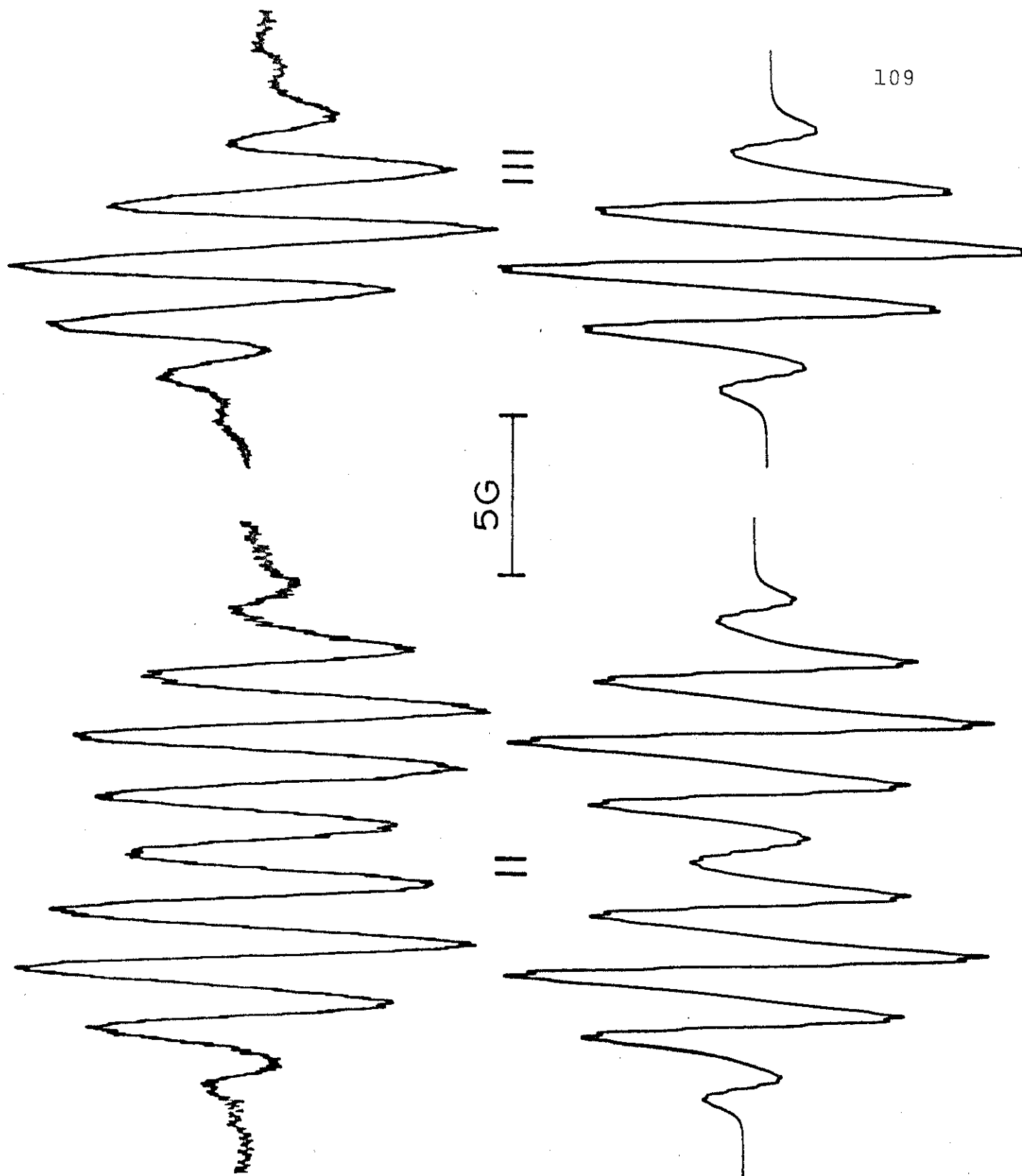
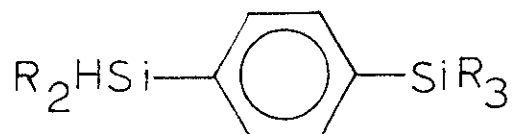


Fig. 4.5. ESR spectra of radical anions formed from the further reactions of p-dimethylsilyl-N,N-dimethylaniline: II, secondary spectrum; III, tertiary spectrum; upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.17 G.

that it is a 1,4-bis-(disilyl)-benzene system with one silyl hydrogen, IV-3.



IV-3

Considering that species II is formed in the reduction of p-dimethylsilyl-N,N-dimethylaniline and considering the mechanism proposed by O'Brien (39), species II may be tentatively identified as the radical anion of the 4-dimethylsilyl-(p-dimethylaminophenyl)dimethylsilyl benzene radical anion, $\text{Me}_2\text{HSi}-\text{C}_6\text{H}_4-\text{SiMe}_2-\text{C}_6\text{H}_4-\text{NMe}_2$. The couplings for methyl protons on silicon were not resolved but the fit of the simulated spectrum was improved by adding a coupling of 0.16 G for them.

Spectrum III consists of a quintet (1.78 G) with about the same couplings as the quintet of spectrum II (1.85 G). The extra peaks at both ends probably are due to remaining species II. There is no silyl hydrogen coupling. The absence of silyl hydrogen coupling in spectrum III suggests that silicon-hydrogen bond cleavage occurs during the reaction of species II to form III. Species III is tentatively identified as 4-trimethylsilyl-(p-dimethylaminophenyl)dimethylsilyl benzene radical anion, $\text{Me}_3\text{Si}-\text{C}_6\text{H}_4-\text{SiMe}_2-\text{C}_6\text{H}_4-\text{NMe}_2$. The

coupling with methyl protons on silicon was not resolved but the fit of the simulated spectrum was improved by adding a coupling of 0.16 G for the methyl protons.

Potassium reduction of p-methylsilyl-N,N-dimethylaniline did not give the primary spectrum shown in Figure 4.2. However, it gave a yellow solution within 5 minutes of reduction which gave the spectrum shown in Figure 4.6. The spectrum consists of a triplet of quintets. The triplet 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. The structure tentatively assigned to this species is 4-dimethylsilyl-(p-dimethylaminophenyl)methylsilyl benzene radical anion, $\text{MeH}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiHMe}-\text{C}_6\text{H}_4-\text{NMe}_2$.

Potassium reduction of p-silyl-N,N-dimethylaniline gave a yellow solution which had the spectrum shown in Figure 4.7. This spectrum apparently results from further reactions. The spectrum consists of a quintet of quintets. The quintet of 6.05 G is due to four silyl hydrogens and the quintet coupling of 1.70 G due to four ring protons of a 1,4-bis(disilyl)benzene ring. This species V is tentatively identified as 4-methyl-(p-dimethylaminophenyl)silyl benzene radical anion, $\text{MeH}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiH}_2-\text{C}_6\text{H}_4-\text{NMe}_2$.

The spectral characteristics of these intermediates radical anions produced by further reactions are collected in Table 4.6 along with the couplings of previously reported

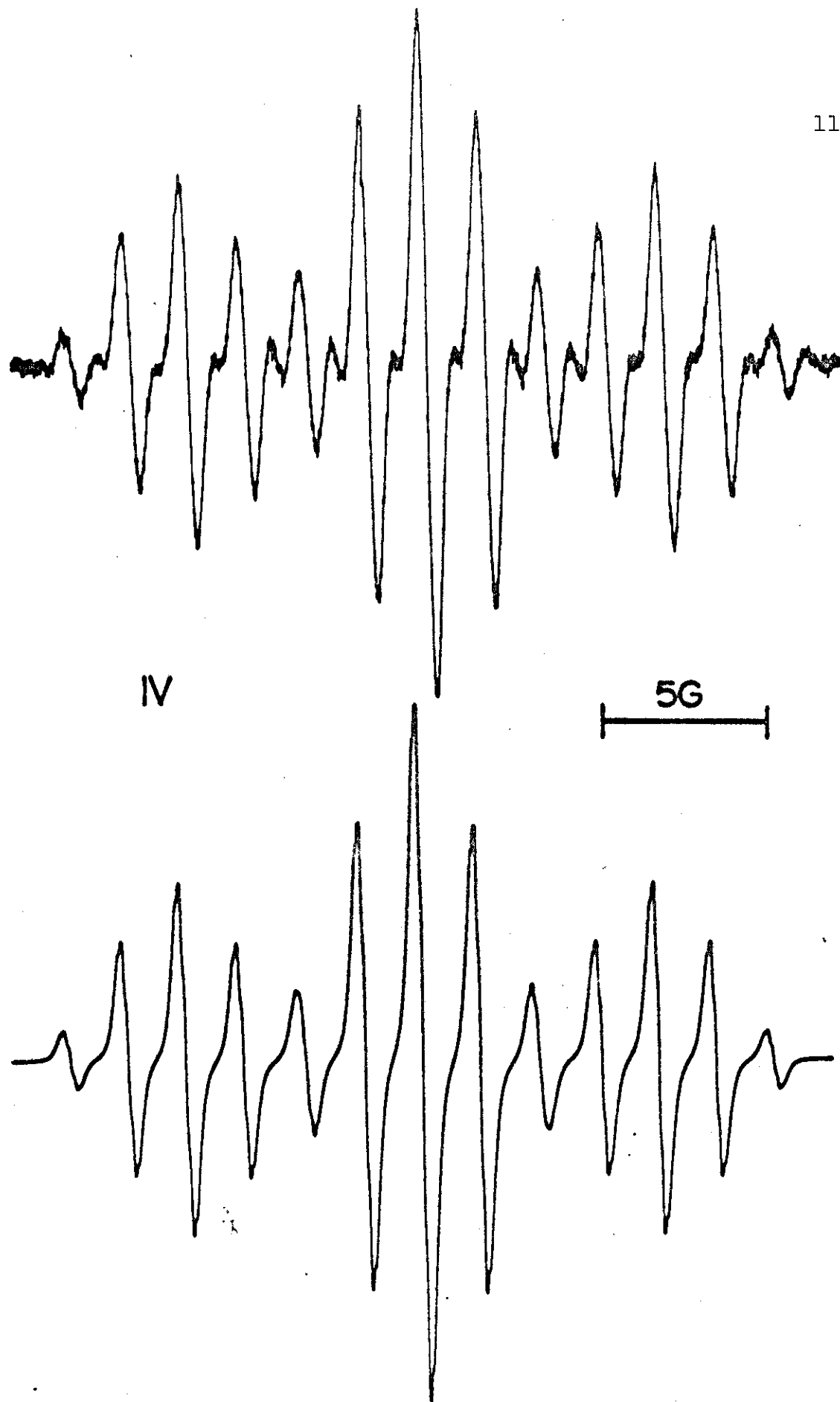


Fig. 4.6. ESR spectrum of the radical anion formed from the further reactions of *p*-methylsilyl-*N,N*-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.15 G.

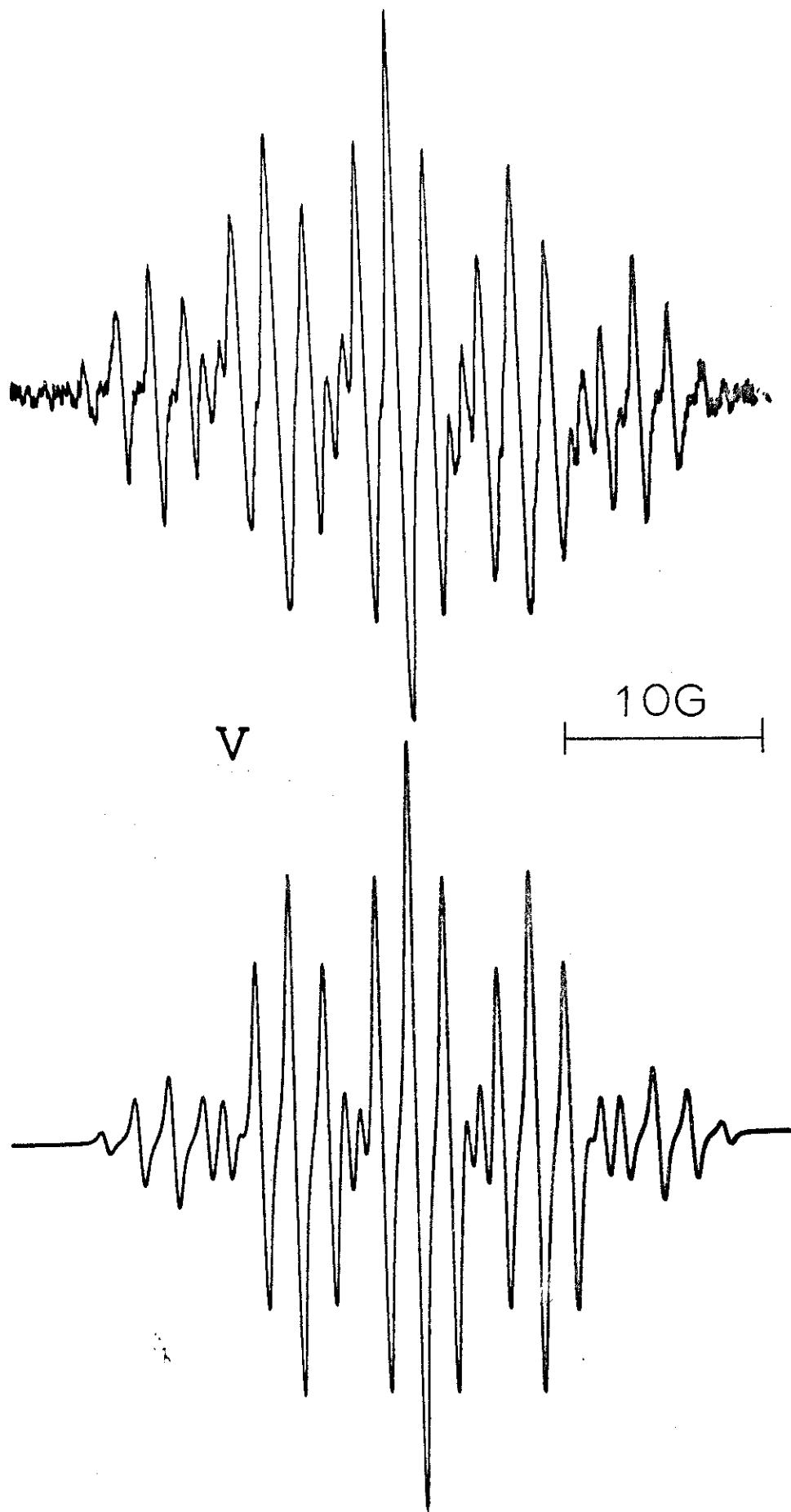
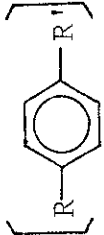


Fig. 4.7. ESR spectrum of the radical anion formed from the further reactions of *p*-silyl-*N,N*-dimethylaniline: upper, experimental; lower, computer-simulated using Lorentzian line shapes and a line width of 0.25 G.

TABLE 4.6

RADICAL ANIONS PRODUCED BY FURTHER REACTIONS OF PARA SILYLANILINES WITH POTASSIUM

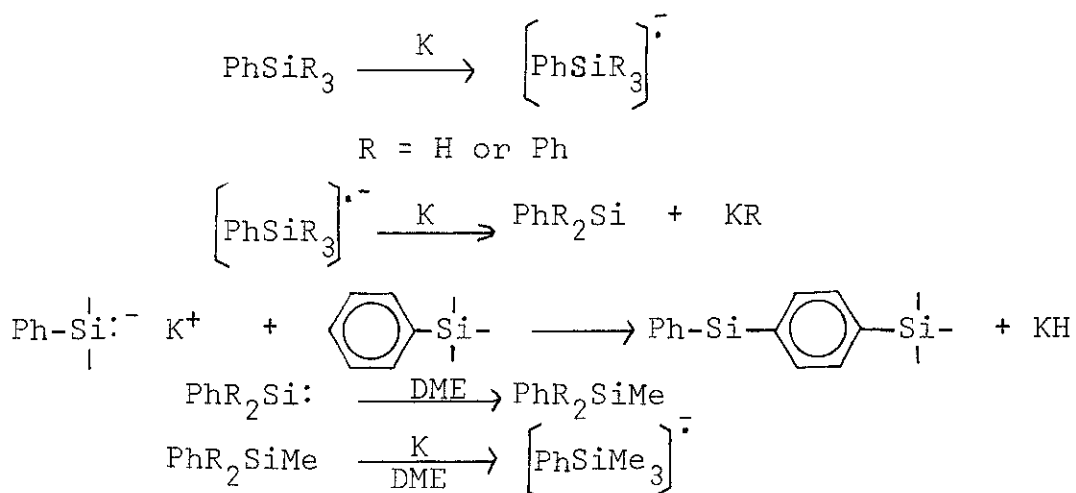
Starting compounds	Radical anions R	 R'	Coupling constants ^a			Pattern
			^a Si-H	^a aryl	^a Si-CH ₃	
P-SiH ₃ -C ₆ H ₄ -NMe ₂	MeH ₂ Si-	-SiH ₂ -C ₆ H ₄ -NMe ₂	6.05	1.70	0.15 ^d	V
P-MeH ₂ Si-C ₆ H ₄ -NMe ₂	Me ₂ HSi-	-SiHMe-C ₆ H ₄ -NMe ₂	7.21	1.75	0.14 ^d	IV
P-Me ₂ HSi-C ₆ H ₄ -NMe ₂	Me ₂ HSi-	-SiMe ₂ -C ₆ H ₄ -NMe ₂	7.05	1.85	0.16 ^d	II
	Me ₃ Si-	-SiMe ₂ -C ₆ H ₄ -NMe ₂		1.78	0.16 ^d	III
Me ₂ HSi-C ₆ H ₅ ^b	Me ₂ HSi-	-SiHMe-C ₆ H ₅	7.02	1.80		
	Me ₂ HSi-	-SiMe ₂ -C ₆ H ₅	6.28	1.88		
Me ₂ HSi-C ₆ H ₄ -SiHMe ₂ ^b	Me ₂ HSi-	-SiHMe ₂	7.28	1.78		
Me ₃ Si-C ₆ H ₄ -SiMe ₃ ^c	Me ₃ Si-	-SiMe ₃	1.78	0.27		

^aCoupling in Gauss.^bRef. 39.^cRef. 36.^dEstimated.

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1,4-bis(disilyl)benzene radical anions. The unpaired electron is presumably localized on the ring substituted at the 1 and 4 positions with two silyl groups in all the species because the other rings have strongly electron donating dimethylamino groups which reduce their electron affinity. It has also been reported that the unpaired electron is localized on only one ring in the radical anion of bis(4-biphenyl)dimethylsilane (13).

The proposed pathways for the formation of the secondary species are as follows: (a) potassium reduces the primary radical anion to the dianion and then the dianion loses a hydride from silicon, (b) the silyl anion produced undergoes para coupling with the unreacted phenylsilane to form a 1,4-bis(disilyl)benzene moiety, (c) the phenylsilyl anion reacts with DME and abstracts a methyl group.



Because the same type of 1,4-bis(disilyl)benzene radical anions are formed from further reactions of both phenylsilanes and

para silyl substituted N,N-dimethylanilines. A similar mechanism may be applied to explain the reactions observed here.

The possible mechanisms for the further reactions of silylanilines have been summarized in scheme 4.1. The species II and III in the potassium reduction of *p*-dimethylsilyl-N,N-dimethylaniline are not formed directly from the parent radical anion or species II, respectively, but require contact with the potassium mirror. This suggests that reduction to the dianion (IV-4) occurs before any cleavage reaction. The existence of the intermediate (IV-4) is consistent with the fact that the unpaired electron resides in π^* symmetric type orbital of trimethylsilyl substituted N,N-dimethylaniline radical anions (Chapter III) and the fact that the Birch reduction of trimethylsilyl substituted aromatic systems goes smoothly to their 1,4-dihydro derivatives. Birch reductions of ring substituted N,N-dimethylanilines have also been reported (6).

There are three possible modes of cleavage for the intermediate (IV-4), (a) ring carbon-nitrogen bond cleavage, (b) ring carbon-silicon cleavage, (c) silicon-hydrogen cleavage. The reductive cleavage of a carbon-nitrogen bond has been reported in other systems (4,12,19,20,21,22). The dimethylamino group, however, is not cleaved in the Birch reduction of ring substituted N,N-dimethylanilines (6). We have also

demonstrated that the ring carbon-nitrogen bond is not cleaved upon potassium reduction of p-trimethylsilyl-N,N-dimethylaniline (Chapter III).

Benkeser and Foster (7,8) have reported the cleavage of the silicon-phenyl bond in the reactions of aromatic organosilanes with alkali metals. If this were the case, the silyl anion formed should undergo nucleophilic attack on ring carbon-1 and displace dimethylamide to produce a 1,4-bis(disilyl)benzene moiety. This is most unlikely in these electron rich aromatic systems.

Finally, the silicon-hydrogen bond cleavage may be formed in this system because the anion formed can be stabilized by the phenyl group attached to silicon (15). Resonance stabilization of benzylic anions is well known and para-coupling of the benzylic anions with electrophiles have previously been observed in other systems (9,42). The nucleophilic displacement of silyl hydrogens by anions appears to be quite general (7,8).

Some brownish yellow precipitates which appeared after the potassium reaction in the esr cell were presumed to be either KH or KNMe_2 . The precipitates did not disappear after a long period of time at room temperature, but disappeared when the sample tube was opened and the solution was exposed to the atmosphere. The abstraction of a methyl group from DME by silyl anions has been reported (38,43) and discussed

elsewhere (39). The abstraction reaction of a methyl group by silyl anions appears to be less favorable than coupling with the unreacted silylaniline. The reason for the absence of subsequent para-coupling reactions probably is the limited concentration of the silylaniline.

The observation of silicon-hydrogen bond cleavage is consistent with the fact that the silicon-hydrogen orbitals largely contribute to the hyperconjugative p-p π^* interaction suggested by CNDO/2 calculations in the silyl aniline radical anions, as was discussed in part 1 of this chapter.

Experimental

Metallic reductions were carried out in vacuo by allowing 10^{-3} M solutions of the appropriate silyl anilines dissolved in THF, DME, or 2-methyl-THF at -78°C to react with a potassium mirror previously cooled in liquid nitrogen. ESR spectra were recorded with the resulting solutions of radical anions contained in side-arm sample tubes out of contact with the metallic mirror.

Electrolytic reductions were performed using a sample cell containing two platinum electrodes. Anion radicals were generated directly in the ESR cell cavity using a simple Heathkit ID-32 dc power source. The variable dc voltage source was increased until an ESR spectrum appeared. No reference electrode was employed. Polarographic grade tetrabutylammonium perchlorate (10^{-2} M) was used as the supporting electrolyte.

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CHAPTER V

SUMMARY

The ground states and lower-lying excited states for a series of ortho and para $\text{Me}_n\text{H}_{3-n}\text{M}$ ($\text{M} = \text{C}$ or Si , $n = 0-3$) substituted N,N-dimethylanilines have been examined for the bonding interactions between the substituents and the ring π system.

In the para series of compounds the ionization potentials, determined by cyclic voltammetry, are higher for the silicon compounds than for their carbon analogs. The ionization potential decreases as the number of methyl groups on the substituent increases in both the silicon and carbon series, but the effect is much larger for the silicon compounds. Based on correlations between the ultraviolet spectra and the ground-state energies, the excited states of the silicon compounds exhibit larger stabilizations than the ground states. Further evidence for the strong interaction between the silyl substituents and the excited states is the fact that the radical anions of the silyl substituted N,N-dimethylanilines may be generated by electrolytic or metal reduction. The same techniques fail to produce any radicals for the carbon compounds. The silyl substituted radicals represent the first examples of aniline radical anions which do not bear strongly electron-

withdrawing ring substituents.

The hyperfine coupling constants (hfcc) for the anion radicals, unambiguously assigned by labelling experiments, indicate that the lowest-lying antibonding orbital is predominantly a π^* orbital symmetric with respect to the plane defined by the point of silicon substitution on the ring. The electron-donating effect of the dimethylamino group is greatly diminished in the radical anions, evidently due to repulsion between the nitrogen lone pair and the additional electron. The ring proton hfcc of the para substituted silyl-aniline radical anions decreases with increasing number of hydrogens on silicon. A concomitant increase in the hfcc for the silyl hydrogens indicates that the interaction of the silyl substituent with the π^* orbital of the radical increases as methyl groups on silicon are replaced by hydrogen.

When potassium is used as the reducing agent, the radical anions undergo further reactions involving loss of hydride from the silicon to eventually produce new paramagnetic species. Coupled with CNDO/2 calculations, the results provide the first experimental evidence for the importance of $p_{Si}-\pi^*$ as opposed to $d_{Si}-\pi^*$ interaction in the excited states of unsaturated organosilicon molecules.

For the ortho substituted N,N-dimethylanilines the rotational angle of the dimethylamino group has been determined spectroscopically. In general, the angle is greater for the

silicon compounds than for their carbon analogs. However, a linear correlation between the ionization potentials and the rotational angles suggests that the ground state energy of the molecules is predominantly a function of the extent of lone pair conjugation with the ring. No evidence for a through-space interaction between the nitrogen lone pair and the vacant silicon d orbitals was found.

Overall, the study indicates that d orbital involvement in the interactions of organosilicon substituents with unsaturated systems is much less significant than is generally held. The importance of $p_{Si}-\pi$ and $p_{Si}-\pi^*$ hyperconjugative interactions between silicon σ^* orbitals and π system in producing the effects of silicon substitution on unsaturated systems has become more apparent.

APPENDIX

APPENDIX 1

CNDO/2 RESULTS OF GEOMETRY VARIATIONS FOR PARA SILYL SUBSTITUTED N,N-DIMETHYLANILINES

Substi- tuent	Si-H bond angle ^a	Total electronic energy ^b	HFMO energy ^b	N	Coefficients of HFMO Atoms			
					C _O	C _m	P	Si d ^c
-SiH ₃	0°	-345.9179638	-0.4156	0.663	-0.347	0.070	0.029	-0.182
	90°	-345.9161323	-0.4156	0.238	-0.321	0.070	0.027	-0.182
-SiH ₂ Me	0°	-397.2022052	-0.4070	0.663	-0.350	0.084	0.017	-0.170
-SiHMe ₂	0°	-453.7991433	-0.4008	0.643	-0.319	0.096	0.014	-0.158
	30°	-453.9449361	-0.4012	0.659	-0.317	0.094	0.010	-0.162
	60°	-454.2195666	-0.4028	0.658	-0.320	0.090	0.011	-0.172
	90°	-454.3497825	-0.4036	0.651	-0.320	0.087	0.010	-0.179

^aMeasured from the ring plane.

^bIn atomic unit.

^cIn the set-up of the overlap integrals the orientation of this dπ orbital is such that a negative coefficient indicates positive overlap.

APPENDIX 2

CNDO/2 RESULTS OF GEOMETRY VARIATION FOR PARA SILYL SUBSTITUTED N,N-DIMETHYLANILINES

Substi- tuent	Conformations		Total electronic energy ^c	N	1	2	II Spin density ^e			P	Si	d
	-NMe ₂ ^a	Si-H ^b					3	4	4			
-SiMe ₃	Td, 30°	90°	-519.5787557	-0.0049	0.3316	-0.0842	0.1802	0.0866	0.1052	0.1952	0.1952	
	Coplanar	90°	-515.8953359	0.0380	0.3184	-0.1028	0.1955	0.0646	0.1187	0.2058	0.2058	
-SiHMe ₂	Td, 30°	90°	-457.6632231	-0.0047	0.3309	-0.0882	0.1861	0.0767	0.1050	0.2072	0.2072	
	Coplanar	0°	-453.7329829	0.0364	0.3012	-0.1022	0.1918	0.0513	0.1468	0.1878	0.1878	
	Coplanar	90°	-454.2871219	0.0379	0.3133	-0.1058	0.1998	0.0522	0.1209	0.2158	0.2158	
-SiH ₂ Me	Td, 30°	90°	-400.4742101	-0.0039	0.3026	-0.0893	0.1847	0.0492	0.1429	0.1956	0.1956	
	Coplanar	0°	-397.1418941	0.0303	0.2357	-0.0909	0.1727	0.0007	0.2017	0.1660	0.1660	
	Coplanar	90°	-397.4144345	0.0202	0.1479	-0.0652	0.1206	0.0242	0.1627	0.1073	0.1073	
-SiH ₃	Td, 30°	90°	-348.8229905	-0.0040	0.3130	-0.0936	0.1901	0.0521	0.1623	0.1846	0.1846	
	Coplanar	0°	-345.8546896	-0.0004	-0.0022	0.0014	-0.0028	0.0020	-0.1020	0.0079	0.0079	
	Coplanar ^d	90°	-345.8548218	0.0008	0.0060	-0.0030	0.0051	-0.0017	-0.0834	0.0040	0.0040	
	Td, 90°	90°	-344.9593728	0.0228	0.2900	-0.1028	0.1962	0.0297	0.1762	0.1787	0.1787	
	Td, 60°	d	-344.0474075	-0.0008	0.3274	-0.0948	0.1954	-0.0682	0.1434	0.1795	0.1795	
	Td, 30°	d	-344.6519439	0.0134	0.3229	-0.1032	0.2013	0.0581	0.1507	0.1810	0.1810	
Td, 0°	d	-343.7548924	-0.0038	0.3280	-0.0905	0.1924	0.0726	0.1410	0.1790	0.1790		
Td, 90°	d	-349.5056890	0.0068	0.2285	-0.0835	0.1627	-0.0022	0.2028	0.1546	0.1546		

^aThe angle between the lone pair and the ring plane.

^bThe angle between the Si-H bond and the ring plane.

^cIn atomic unit.

^d116° for <CNC, 1.43 Å° for the C_{ring}-N bond, while 1.37 Å° was used for all other cases.

^eThe same numbering used as in Table 4.3.

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