

Experimental Section

The calorimeter and its operations have been previously described.^{4,8} Most of the compounds were commercially available. Liquid were dried over molecular sieves (Linde 4A) and distilled. Solids were recrystallized and vacuum dried over P₂O₅. Those acid chlorides not available were prepared from the corresponding acid with SOCl₂. All diketones were commercially available except for 2,6-dimethyl-3,5-heptanedione²³ and 3,6-octanedione²⁴ which were prepared using standard techniques. Those diesters not commercially available were prepared from the corresponding diacid chloride and the appropriate alcohol.

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References and Notes

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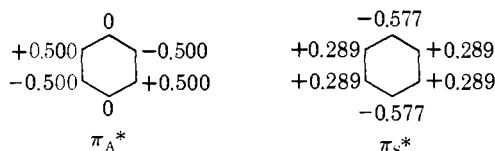
Bonding Studies in Group 4 Substituted Anilines. VI. Assignment of Coupling Constants and CNDO/2 Description of the Radical Anions of *o*-, *m*-, and *p*-Trimethylsilyl-*N,N*-dimethylaniline¹

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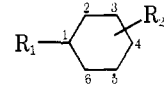
Abstract: The radical anions of *o*-, *m*-, and *p*-trimethylsilyl-*N,N*-dimethylaniline, generated by reduction with potassium in mixed ether solvents at low temperatures, have been studied by ESR spectroscopy. By metallation and lithium-halogen exchange reactions, appropriate deuterated and methylated analogs have been prepared, which permit unambiguous experimental assignment of all the hyperfine coupling constants for the radical anions. In every case, the highest spin density is shown to occur at the ring position para to the trimethylsilyl substituent. The coupling constants are consistent with a mixing of the symmetric and antisymmetric π^* orbitals of benzene and are correlated with the π spin densities obtained from CNDO/2 calculations. In spite of the strongly electron-donating dimethylamino group, the trimethylsilyl group is the major influence on the spin distributions in the radical anions. Based on the CNDO/2 results, the effect is apparently due to large interactions of both the silicon p and d orbitals with the aromatic π^* system.

The technique of electron spin resonance (ESR) spectroscopy has been widely applied to the investigation of substituent effects in monosubstituted benzene derivatives² and multiply substituted aromatics.^{3,4} 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.^{2a} Electron-donating substituents such as alkyl substitu-



ents 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.⁵ 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.³ In a recent study, Sipe and West found that, in the anion radicals of trimethylsilyl- or trimethylgermylalkylbenzenes, the organometal substituent dominates the ordering of the MO energy levels by accepting electron density more effectively than the alkyl substituents release it.⁴ This result is consistent with the small perturbations of the aromatic systems produced by alkyl substituents⁵ and naturally raises the question as to what the dominating influence will be

Table I. Hyperfine Splittings for Trimethylsilyl-Substituted Aromatic Radical Anions



R ₁	R ₂	Hyperfine Splittings, G ^a						Conditions ^b (Ref)
		2	3	4	5	6	SiMe ₃	
Me ₃ Si	H	2.66	1.06	8.18	1.06	2.66	0.26	(4)
(Me ₃ Si) ₂ N	H	5.1	5.7	≤0.5 ^c	5.7	5.1	≤0.1 ^c	(7)
Me ₂ N	2-Me ₃ Si		3.60	0.50	8.48	1.72	0.26	A, -50°C
Me ₂ N	3-Me ₃ Si	4.25		0.78	2.67	7.35	0.23	B, -50°C
Me ₂ N	4-Me ₃ Si	3.25	4.55		4.55	3.25	0.15	A, -90°C
Me ₂ N	2-Me ₃ Si-5-Me		4.72	0.42	9.11 ^d	2.23	0.18	A, -90°C ^e
Me ₂ N	3-Me ₃ Si-6-Me	4.75		0.74	2.67	8.89 ^d	0.20	B, -90°C ^e

^a ±0.03G for this work. ^b A = 2:1 tetrahydrofuran–dimethoxyethane; B = 2:1 2-methyltetrahydrofuran–dimethoxyethane. ^c Estimated. ^d Methyl protons. ^e The other hfs for these compounds are assigned by analogy to the hfs of 2-trimethylsilyl- and 3-trimethylsilyl-*N,N*-dimethylaniline anions, respectively.

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 *o*-, *m*-, and *p*-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.⁶ The hfs for these radicals indicate that the unpaired electron is largely localized in the nitro group. Gerson and coworkers have shown that the reduction of anilines may be achieved when the electron-donating effect of nitrogen is diminished through trimethylsilyl substitution at nitrogen.⁷ 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,⁷ as would be predicted by the simple MO considerations given above.

In our previous work, we demonstrated that the trimethylsilyl group is electron withdrawing in the ground states of para-substituted *N,N*-dimethylanilines.^{8,9} A greater -R effect might be expected in the excited states because of the better energy match between the silicon σ^* or d orbitals and the antibonding levels of the aromatic system. We have observed some evidence for this effect in the ultraviolet spectra of these anilines.¹⁰ Indeed the trimethylsilyl ring substituent sufficiently enhances the electron affinity of *N,N*-dimethylaniline to permit reduction to the radical anion.¹ We now report the detailed investigation of the ESR spectra of these radical anions, the unambiguous assignment of the hyperfine splittings, and the CNDO/2 analysis of the interactions in these species.

Results

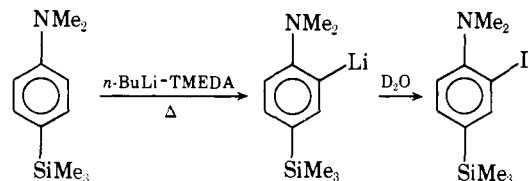
The radical anions of trimethylsilyl-substituted *N,N*-dimethylanilines may be conveniently prepared by metal reduction at low temperatures in mixed ether solvents. Qualitatively, the stability of these anions, based on the conditions required for their production and the length of time that the radical persisted in the ESR experiment is: 2-trimethylsilyl- \approx 3-trimethylsilyl- > 2-trimethylsilyl-5-methyl- \approx 3-trimethylsilyl-6-methyl- > 4-trimethylsilyl-*N,N*-dimethylaniline. The hyperfine splittings for these radical

anions are given in Table I. All of the hfs reported have been unambiguously assigned by the following experiments.

4-Trimethylsilyl-*N,N*-dimethylaniline. The ESR spectrum of 4-trimethylsilyl-*N,N*-dimethylaniline radical anion 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 and a splitting due to the trimethylsilyl protons of 0.15 G.¹ 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.

The lithiation of *N,N*-dimethylaniline using *n*-butyllithium in tetramethylethylenediamine (TMEDA) has been shown to give *o*-lithio-*N,N*-dimethylaniline.¹¹ While the metallation of *N,N*-dimethylaniline does not require heat, the lithiation of 4-trimethylsilyl-*N,N*-dimethylaniline (Scheme I) requires reflux for at least one-half hour to give the yellow precipitate of the ortho-lithiated compound. This

Scheme I



might be due to the reduced availability of the nitrogen lone-pair for complexation with the *o*-lithium in the silicon compound.⁹ 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 anion 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.¹ 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 1) which shows an hfs for the 5-methyl protons of 9.11 G. The small perturbations produced by methyl substitution⁵ 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 similar to that for the displaced hydrogen¹² substantiate 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 II shows

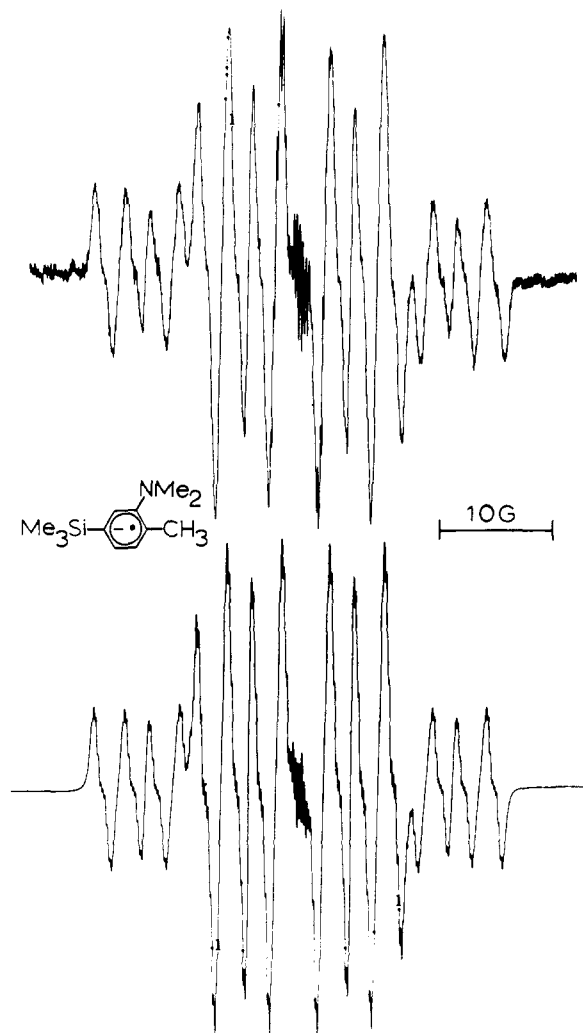
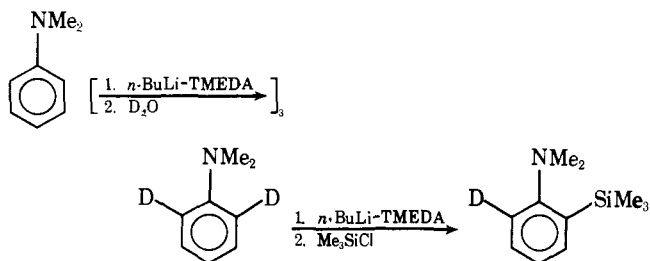


Figure 1. ESR spectrum of the radical anion of 2-trimethylsilyl-5-methyl-*N,N*-dimethylaniline: (upper) experimental; (lower) computer simulated.

Scheme II



the synthesis of 6-*d*-2-trimethylsilyl-*N,N*-dimethylaniline. On a purely statistical basis, 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 spectra, NMR, and the ESR spectrum of the radical anion, the compound was completely deuterated in the 6-position.

The ESR spectrum of the radical anions of 4-*d*-2-trimethylsilyl-*N,N*-dimethylaniline (Scheme III) was essen-

Scheme III

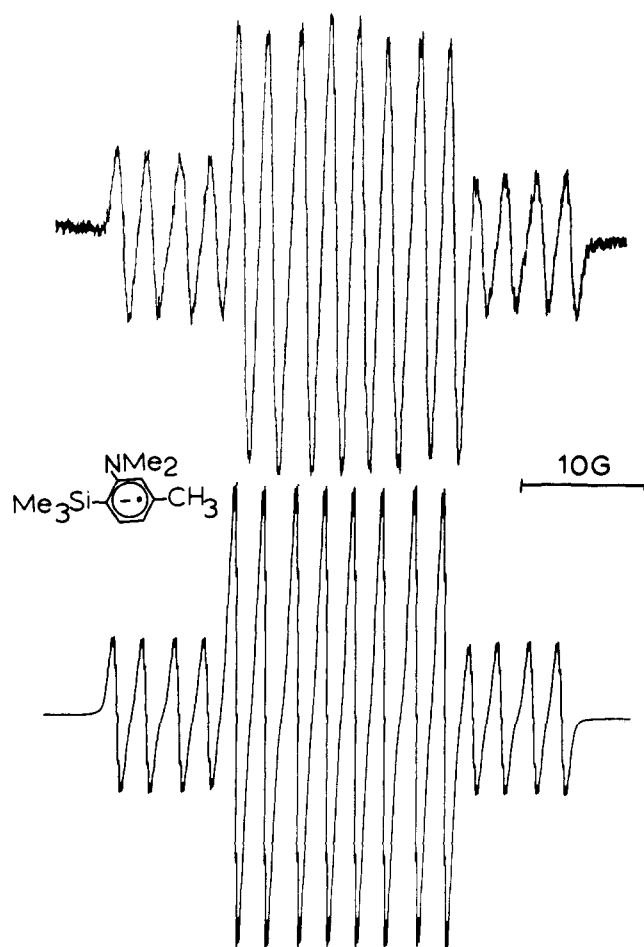
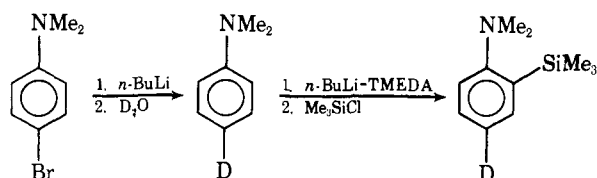


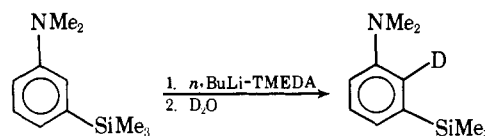
Figure 2. ESR spectrum of the radical anion of 3-trimethylsilyl-6-methyl-*N,N*-dimethylaniline: (upper) experimental; (lower) computer simulated.

tial 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 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 consists of four doublets of 7.35, 4.25, 2.67, and 0.78 G due to the ring protons and an hfs of 0.23 G by the trimethylsilyl protons.¹ 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 2) which has the largest coupling of 8.89 G associated with the protons of the 6-methyl group.

Scheme IV illustrates the synthesis of 2-*d*-3-trimethylsilyl-*N,N*-dimethylaniline. The ESR spectrum of the radical

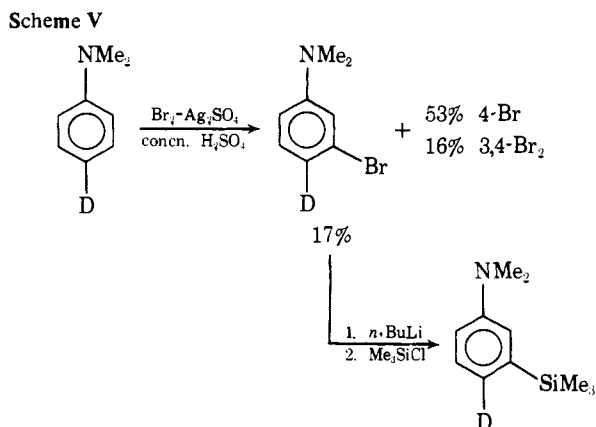
Scheme IV



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 V). In contrast to what might be expected on the



basis of previous reports,¹³ the bromination of 4-*d*-*N,N*-dimethylaniline in concentrated sulfuric acid gave the para-brominated compound as the major product.

In the ESR spectrum of the radical anion of 4-*d*-3-trimethylsilyl-*N,N*-dimethylaniline, the 0.78 G coupling had 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 I. 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 give splittings of 0.71 and 1.13 G, respectively, in the radical anion of *p*-nitro-*N,N*-dimethylaniline.⁶ It might be suggested that, in our 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 trimethylsilylbenzene, an anticipated product if cleavage of the dimethylamino group had occurred, was observed.¹

Discussion

The hyperfine coupling constants which have been assigned are listed in Table I. Also included for the purpose of comparison are the reported hfs for trimethylsilylbenzene radical anion⁴ and for *N,N*-bis(trimethylsilyl)aniline radical anion.⁷ 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 orbital 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 I. For all of the anilines listed, the smallest spin density occurs at the position para to the amino

group.¹⁴ 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,⁴ 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 densities¹⁶ 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.

We have previously performed CNDO/2 calculations for the ground states and radical cations of some group 4 substituted anilines. These gave good agreement with experimentally determined coupling constants and ionization potentials.⁸ Recently our CNDO/2 calculated charge densities have been shown to correlate well with changes in ¹³C chemical shifts.¹⁷ We have now extended the calculations to the radical anions of the trimethylsilyl-substituted anilines. Table II gives the calculated π spin densities for these species and for trimethylsilylbenzene radical anion. Figure 3 shows a plot of a McConnell type relation¹⁸

$$a_i^H = \rho_{Ci} Q_{CH}^H$$

for the experimental ring proton hfs, a_i^H , and the CNDO/2 π spin density for the appropriate ring carbon, ρ_{Ci} . 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.¹⁹

The results given in Table II 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.²⁰ 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.²¹ 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/mol less stable than either 2- or 3-

Table II. CNDO/2 π Spin Densities for Trimethylsilyl-Substituted *N,N*-Dimethylaniline Radical Anions^a

R ₁	R ₂	π spin density						Si		
		N	1	2	3	4	5	6	p π	d π
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 $\alpha - \beta$ spin. Numbering as in Table I.

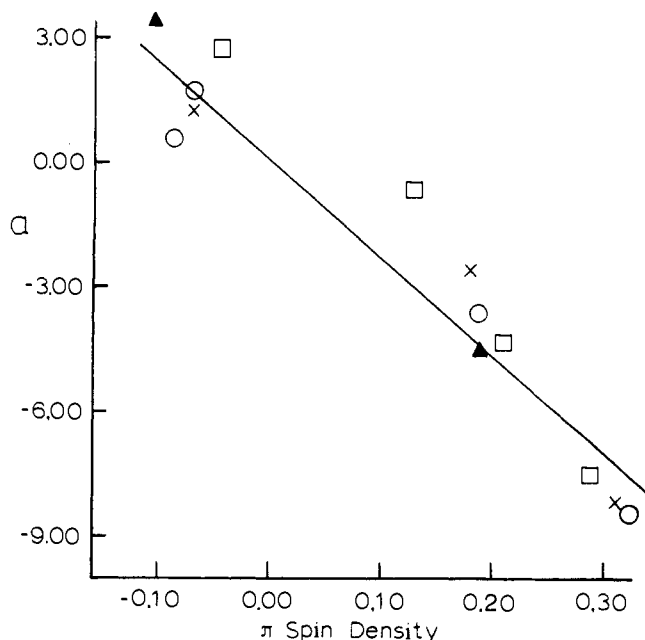
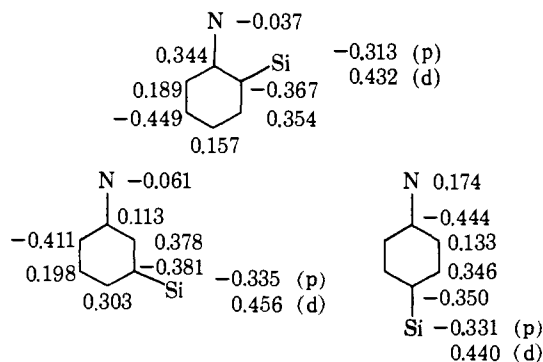


Figure 3. Plot of the CNDO/2 calculated π spin density against the ESR hyperfine coupling constants for the radical anions of: (X) trimethylsilylbenzene; and (▲) 4-trimethylsilyl-, (□) 3-trimethylsilyl-, and (○) 2-trimethylsilyl-*N,N*-dimethylaniline.

trimethylsilyl-*N,N*-dimethylaniline radical anion, based on the total electronic energies contained for the molecules.

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



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 π and d π coefficients are significantly larger than those obtained for the HFMO in the ground states of these molecules; viz., p π = 0.010, d π = 0.158 for 4-trimethylsilyl-*N,N*-dimethylaniline; p π = 0.012, and d π = -0.051 for 3-trimethylsilyl-*N,N*-dimethylaniline.⁸ 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 metal 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 π^* and d-p π^* interactions between silicon and the aromatic ring by the CNDO/2 calculations. Finally, it should be noted that the p orbital of silicon in the HFMO of the radicals is antibonding with respect to the methyl groups on silicon. This suggests that σ^* - π interactions in unsaturated organosilanes contribute significantly to the effects of silicon substitution in organic molecules. The extent of this contribution is currently under investigation in our laboratories.

Experimental Section

All boiling points are uncorrected. 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, Calif. ESR spectra were recorded using a Varian 4502-13 spectrometer equipped with 100-kHz field modulation and the Varian low-temperature probe. The synthesis and characterization of 3- and 4-trimethylsilyl-*N,N*-dimethylaniline have been reported previously.⁹

General Method for *o*-Lithio-*N,N*-dimethylanilines.¹¹ To a solution of the appropriate *N,N*-dimethylaniline in an equal volume of tetramethylethylenediamine was added 1 equiv of *n*-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. Normal derivatization consisted in the addition of the derivatizing reagent to the reaction mixture.²² 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. Final purification before spectroscopic measurements or analyses was achieved by preparative GLC using a 20-ft 30% SE-30 on Chromosorb W, stainless steel column generally operated at about 200° with a helium flow of about 150 ml/min.

2-Trimethylsilyl-*N,N*-dimethylaniline. This compound was prepared in 54% yield by inverse derivatization of *o*-lithio-*N,N*-dimethylaniline with trimethylchlorosilane (Aldrich): bp 91° (20 mm) [lit.²³ 104° (20 mm)]; NMR (CCl₄; Me₄Si) δ -0.26 (s, 9 H, SiMe₃), -2.64 (s, 6 H, NMe₂), -7.20 (m, 4 H, aromatic protons).

Anal. Calcd for C₁₁H₁₉NSi (mass 193): C, 68.31; H, 9.82; N, 7.26. Found (mass spectrum parent, 193): C, 68.62; H, 9.88; N, 6.96.

2-Trimethylsilyl-5-methyl-*N,N*-dimethylaniline. Normal derivatization of ortho-lithiated *N,N*-dimethyl-*m*-toluidine with trimethylchlorosilane prepared by the general method with stirring under argon for 3 hr gave 1.5 g (48.7% yield) of 2-trimethylsilyl-5-

methyl-*N,N*-dimethylaniline:²⁴ bp 102° (10 mm); NMR (CCl₄; Me₄Si) δ -0.22 (s, 9 H, SiMe₃), -2.30 (s, 3 H, 5-Me), -2.60 (s, 6 H, NMe₂) -7.06 (d, 1 H, H₄), -7.18 (s, 1 H, H₆), -7.46 (d, 1 H, H₃); J_{34} = 8 Hz.

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

3-Trimethylsilyl-6-methyl-*N,N*-dimethylaniline. Bromination of *N,N*-dimethyltoluidine (Aldrich) by the procedure of Gorvin¹³ gave a 33% yield of 3-bromo-6-methyl-*N,N*-dimethylaniline. Derivatization in the normal manner with trimethylchlorosilane of 3-lithio-6-methyl-*N,N*-dimethylaniline, prepared by lithium-halogen exchange,²⁵ gave a 61% yield of 3-trimethylsilyl-6-methyl-*N,N*-dimethylaniline: bp 114–115° (10 mm); NMR (CCl₄; Me₄Si) δ -0.23 (s, 9 H, SiMe₃), -2.31 (s, 3 H, 6-Me), -2.72 (s, 6 H, NMe₂), -7.09 (s, 2 H, H_{4and5}), -7.16 (s, 1 H, H₂).

Anal. Calcd for C₁₂H₂₁NSi (mass 207): C, 69.49; H, 10.26. Found (mass spectrum parent 207): C, 69.25; H, 9.90.

2-*d*-4-Trimethylsilyl-*N,N*-dimethylaniline. Normal derivatization with D₂O of 2-lithio-4-trimethylsilyl-*N,N*-dimethylaniline, prepared by ortho lithiation of 4-trimethylsilyl-*N,N*-dimethylaniline with stirring for 2 hr and refluxing for an additional hour, followed by the normal work-up gave an 81% yield of product: bp 127° (10 mm) (lit.⁹ bp 101° (1.3 mm); NMR (CCl₄; Me₄Si) δ -6.64 (d, ortho protons) and -7.36 (m, 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 D₂O of 4-lithio-*N,N*-dimethylaniline, prepared by lithium-halogen exchange with 4-bromo-*N,N*-dimethylaniline,²⁵ gave 2.5 g (82% yield) of 4-*d*-*N,N*-dimethylaniline: bp 76° (10 mm) (mass spec ratio of the 121–122 parent peaks indicated 87% deuteration); NMR (CCl₄; Me₄Si) δ -2.90 (s, 6 H, NMe₂), -6.68 (d, ~2 H, ortho protons), -7.20 (d, ~2 H, 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-*d*₂-*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; Me₄Si) δ -7.26 (m, ~3 H, ring protons)] indicated 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% product, bp 110° (10 mm). Based on the NMR [(CCl₄; Me₄Si) δ -7.07 (m, ~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 of 4-*d*-*N,N*-dimethylaniline using the procedure of Gorvin¹³ gave 1.3 g (32% yield) of monobrominated product. Lithium-halogen exchange²⁵ 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 indicat-

ed volume composition were transferred into the sample cell using standard high vacuum techniques. Otherwise the samples were prepared using previously described techniques,^{5a,26} using triply sublimed potassium metal as the reducing agent.

Theoretical Calculations. The CNDO/2 program employed was that of Pople and Beveridge¹⁵ and was obtained from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401. Standard bond angles and bond lengths were used²⁷ and 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°.²⁸ 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, toward the trimethylsilyl group. This configuration is based on the rotational angle for the lone pair which we have determined spectroscopically for the ground state.²⁹ 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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Chemical Pseudoexcitation and Paradoxical Orbital Interaction Effect

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Abstract: Some third-order configuration interaction (CI) perturbation energy terms for bimolecular interactions have been shown to be interpreted as representing the local excitation within one or both of the interacting molecules, induced by charge transfer (chemical pseudoexcitation). The chemical pseudoexcitation effect was more explicitly expressed by the second-order perturbation energy terms obtained on the assumption of the degeneracy of a particular transferred configuration with the original one. The following rules have been derived. (1) Some thermal reactions between strong donors and strong acceptors are endowed with some characteristics of the photochemical reactions of weaker donor-acceptor cases. (2) Some reactions normally requiring photoinduction may take place on, or may be accelerated by, a complex formation of one of the reactants with catalysts which enhances the donor-acceptor relationship. (3) Paradoxical orbital interaction, in which the HOMO-HOMO and/or the LUMO-LUMO interactions play a dominant role, is expected to govern some significant stages of a variety of reactions in place of the normal HOMO-LUMO interaction. The regioselectivity in two types of thermal 2 + 2 cycloaddition reactions between strong donors and strong acceptors, the mechanisms of thermal and photochemical reactions via charge-transfer complexes, and the mechanisms of thermal and photochemical electrophilic substitution in aromatic systems are generally discussed with some beautiful examples.

Perturbation approaches to chemical reaction mechanisms on the basis of molecular orbital (MO) method have given rise to the concept of orbital interaction. The electron delocalization due to the interaction between the "frontier" orbitals, the highest occupied (HO) MO of donor, and the lowest unoccupied (LU) MO of acceptor contributes dominantly not only to the stabilization of the interacting system but also to the intermolecular bond formation.¹⁻⁵ There may be no room for doubt about the role of the interaction between these particular orbitals in determining the stereochemical paths of various reactions which proceed through concerted or least-motion approach of reactants. This implies that the transferred configuration involving an electron shift from the HOMO of donor to the LUMO of acceptor is of a profound importance, when we describe the interaction in terms of the configuration function. Even in nonconcerted transformations composed of several distinguishable elementary processes, a certain electron configuration can be assigned to each step of the reaction. There may, however, be a number of equivocal processes which are located between the two extremes, concerted and step-by-step mechanisms. It would be a poor approximation to discuss such reactions only in terms of HOMO-LUMO interaction, namely, in terms of interaction between the transferred configuration and the original configuration. It is necessary to take the other orbital interactions into consideration, or to perform multiconfiguration interaction analysis.

The possibility of a drastic change in stereochemical path due to an electron transfer was first pointed out by one of the present authors (K.F.) in connection with a "symmetry-forbidden"⁶ reaction, an electrophilic cis-1,2 addition to olefinic double bonds.⁷ From a series of papers by Epiotis⁸ he developed a similar idea and discussed the mechanisms of a variety of thermal and photochemical reactions. The interactions between one transferred configuration and another,

between one locally excited configuration and another, and between a transferred configuration and a locally excited configuration should be studied in order to discuss such problems in a strict way. The roles of the above configuration interactions in reaction mechanisms have not been discussed in detail so far⁵ while the significance of the interaction of the original electron configuration with the transferred configuration has been fully discussed together with the interaction of the original configuration with the locally excited configuration.⁹

The purpose of the present paper is to present in general a theoretical basis of the roles of the various configuration interactions not necessarily involving the zero configuration, by analyzing the second-order perturbed wave function and the third-order perturbed energy for nondegenerate systems, and the first-order perturbed wave function and the second-order perturbed energy for degenerate systems. It is also aimed to relate the concept of such configuration interactions to the reaction mechanisms, especially to the intermediary processes between the concerted and the stepwise reactions, and between the thermal and the photochemical reactions. The current topics in organic chemistry would be quoted to visualize the theoretical concept in a chemically graspable manner.

Theoretical Background

The background of the present work is found in the perturbation theory based on the concept of configuration interaction as described in our previous paper.⁵ Suppose that a ground-state molecule (A) weakly interacts with a ground-state partner (B). The occupied and the unoccupied MO's of A and those of B are denoted by the letters *i*, *j*, *k*, and *l*, respectively. We use an arrow to signify an electron shift, for instance, *i* → *l* stands for the electron transfer from the *i*th occupied orbital of A to the *l*th unoccupied MO of B, and *i* → *j* means an electron promotion from the