

value of $\lambda = \rho_R/\rho_I$ with eq 1 will relieve the curvature shown.

Comparison of the various ρ values for F nmr shifts obtained in this study leads to the conclusion that π bond inductive effects follow the σ_I scale and contribute substantially to observed shifts.

Implied applications of eq 1 to structural characterization of reaction transition states are supported

by the results of this study. Ehrenson, Brownlee, and Taft have discussed such applications.³

Acknowledgment. We are pleased to acknowledge the contribution of Dr. John Thompson of unpublished results and general assistance at the outset of this work. We are also indebted to Dr. R. G. Pews for samples of *trans*-4'-substituted-4-fluorostilbenes.

Bonding Studies in Group IV Substituted Anilines.

III. Electron Spin Resonance Spectra of the Radical Cations and the Ground-State Bonding Description¹

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Abstract: The radical cations of *p*-*tert*-butyl-, *p*- and *m*-trimethylsilyl-, and *p*-trimethylgermyl-*N,N*-dimethylaniline, generated electrolytically in acetonitrile with sodium perchlorate as the supporting electrolyte, have been studied by esr spectroscopy. These first examples of group IV organometallic cation radical esr spectra provide insight as to the bonding interactions in the ground states of these molecules. Semiempirical molecular orbital calculations using the CNDO/2 approximation, which correlate well with experimental ground-state properties and radical cation spin densities, indicate that both hyperconjugative $p-\pi$ interaction and $d\pi$ interaction contribute to the stabilization of the ground state observed when carbon is replaced with silicon. Based on the results of the CNDO/2 calculations, the interaction of the *d* orbitals appears more important than hyperconjugation in the ground state and accounts almost entirely for the stabilization of the highest occupied molecular orbital.

The electron spin resonance spectra of several anion radicals containing group IV metals have been reported.² While these esr experiments have demonstrated a small delocalization of the unpaired electron through the *d* orbitals of the metal, they suffer from the disadvantage that the odd electron occupies a π^* molecular orbital. The *d*-orbital interactions observed are therefore excited state interactions, and the conclusions strictly are valid for only ($p \rightarrow d$) π^* overlap.³ In a radical cation the unpaired electron resides in a bonding molecular orbital providing a system more appropriate for the study of ground-state interactions.

In our studies of the ground-state properties of group IV substituted anilines, we observed a small but significant increase in the ionization potential of the molecules when silicon or germanium was substituted for carbon. The results indicated a stabilization of the highest filled molecular orbital (HFMO) for *p*-tri-

methylsilyl- and *p*-trimethylgermyl-*N,N*-dimethylaniline of 0.30 and 0.24 eV, respectively, relative to the *p*-*tert*-butyl compound.⁴ This is consistent with electron withdrawal from the HFMO by the trimethylsilyl or trimethylgermyl group. Such ground-state stabilizations are commonly observed in unsaturated organosilicon compounds and have generally been attributed to *d*-orbital interaction with the bonding π orbitals. An alternative explanation has been suggested which ascribes the stabilization to a $\sigma-\pi$ or hyperconjugative interaction between the metal and the unsaturated system.⁵ Although the hyperconjugative description of the bonding in group IV substituted π systems appears reasonable, and has been suggested for other systems,⁶ very little experimental evidence for this type of $\sigma-\pi$ interaction appears in the literature.^{5,6} Of this evidence, most is based on correlations with charge transfer data. We found that such charge transfer studies provide unreliable measurements of ground-state energies in our studies of group IV substituted anilines.⁴

In order to determine whether it is more appropriate to attribute the electron withdrawal to *d*-orbital interaction with the ground-state molecular orbitals or to a hyperconjugative $\sigma-\pi$ effect, we have investigated the properties of the radical cations of the para-substituted

(1) For paper II in this series, see M. J. Drews and P. R. Jones, *J. Organometal. Chem.*, **44**, 253 (1972).

(2) E. S. Kean, K. Fisher, and R. West, *J. Amer. Chem. Soc.*, **94**, 3247 (1972); A. L. Allred and L. W. Bush, *ibid.*, **90**, 3352 (1968); E. G. Janzen, J. B. Pickett, and W. H. Atwell, *ibid.*, **90**, 2719 (1968); P. R. Jones and R. West, *ibid.*, **90**, 6978 (1968); F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, *Helv. Chim. Acta*, **51**, 707 (1968); E. G. Janzen and J. B. Pickett, *J. Amer. Chem. Soc.*, **89**, 3649 (1967); M. D. Curtis and A. L. Allred, *ibid.*, **87**, 2554 (1965); G. R. Husk and R. West, *ibid.*, **87**, 3993 (1965); J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); R. D. Cowell, G. Urry, and S. I. Weissman, *J. Amer. Chem. Soc.*, **85**, 822 (1963); M. G. Townsend, *J. Chem. Soc.*, 51 (1962).

(3) For recent reviews of this area, see C. J. Attridge, *Organometal. Chem. Rev., Sect. A*, 323 (1970); "Electronic Transitions in Organometalloids," B. G. Ramsey, Ed., Academic Press, New York, N. Y., 1969; "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968.

(4) P. R. Jones, M. J. Drews, J. K. Johnson, and P. S. Wong, *J. Amer. Chem. Soc.*, **94**, 4595 (1972).

(5) C. G. Pitt, *J. Organometal. Chem.*, **23**, C35 (1970); C. Curran, R. Witucki, and P. McCusker, *J. Amer. Chem. Soc.*, **72**, 4471 (1950).

(6) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 829 (1970); H. Bock and H. Alt, *ibid.*, **92**, 1569 (1970), and references contained therein.

anilines. Latta and Taft have reported the esr spectra for a series of substituted *N,N*-dimethylaniline radical cations which were generated electrolytically.⁷ We chose the group IV substituted *N,N*-dimethylanilines for this study because of the potential accessibility of their radical cations.

Experimental Section

Compounds and Reagents. The synthesis and characterization of all the compounds involved in this study, along with the purification of solvents and supporting electrolytes, have been described previously.⁴

Generation of the Cation Radicals. The high reactivity of the desired cation radicals¹ required some modifications of the techniques usually employed for the electrolytic generation of radicals.⁷ The Varian V-4566 electrolytic cell was modified by the addition of an H compartment to the top part of the cell to provide a mercury pool cathode. In filling the cell a bubble of inert gas, usually argon, was trapped immediately below the flat part of the cell. The platinum gauze anode was centered in the flat portion of the cell. This configuration permitted high concentrations of the very unstable cations to be generated in a short period of electrolysis time. The bubble, along with the location of the cathode, helped to prevent the diffusion of unoxidized parent species into the cavity area and encouraged the migration of the cations up and out of the cavity before any secondary reactions could occur.

The absence of complicating oxidative steps at potentials more anodic than the initial cation radical formation, as shown by the kinetic studies of the radicals,¹ made strict control of the working electrode's potential unnecessary for the esr studies. The power supply was a simple Heathkit ID-32 dc power source, the applied voltages were measured with a Heathkit VOM IM-25, and the current flow through the cell was monitored with a microammeter.

Acetonitrile was used as the solvent with the concentration of the compound to be electrolyzed generally about 2.0 mM. It was found that when tetra-*n*-butylammonium perchlorate rather than sodium perchlorate was used as the supporting electrolyte, a concentration of the radical cation sufficient to obtain a resolved spectrum could not be obtained. The reason for this phenomenon is not understood, but in similar studies of other substituted *N,N*-dimethylaniline cation radicals the supporting electrolyte was generally sodium perchlorate.^{7,8}

Under these conditions no esr spectrum other than that of the initially formed radical cation was observed. If, however, the "normal" configuration of the electrolytic cell was used with the mercury pool cathode at the bottom of the cell, the initial spectrum decayed rapidly. Continued electrolysis of the resulting blue solution gave rise to the spectrum of *N,N,N',N'*-tetramethylbenzidine.⁹

Esr Spectra. A Varian V-4502 esr spectrometer with a 9-in. electromagnet was used for these studies. The spectra were measured at room temperature using 100-kHz field modulation and the V-4532 dual cavity with Fremy's salt in the reference cavity to calibrate the measurement of the hyperfine coupling constants. The isotropic *g* factors were determined for each of the radicals and were essentially the same, 2.0033 ± 0.0002 .

Theoretical Calculations. The CNDO/2 program employed was that written by Pople and Beveridge,¹⁰ and was obtained from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401. Standard bond angles and bond lengths were used¹¹ and were not varied for the cations or neutral molecules. For all the molecules the dimethylamino group was treated as planar with the C-N-C angle of 120° in the plane of the aromatic ring.

(7) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

(8) R. N. Adams, E. T. Sed, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, and D. W. Leedy, *ibid.*, **88**, 3498 (1966).

(9) The solutions which gave the spectrum of the parent cation radical were bright yellow in color. With our cell configuration, as the cation migrated out of the cavity, the blue color appeared in the area above the cavity, below the cathode, supporting our conclusion that the parent cation radicals are destroyed by reaction with unoxidized compounds (ref 1).

(10) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(11) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11, 140, 172, 199 (1958).

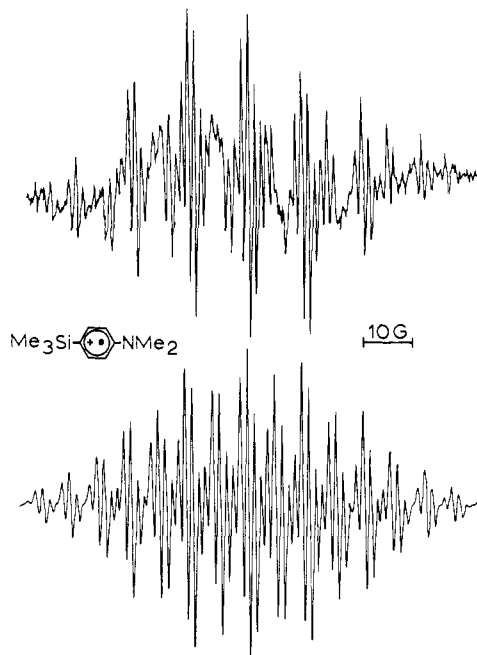


Figure 1. Esr spectrum of the radical cation of *p*-trimethylsilyl-*N,N*-dimethylaniline: upper, experimental; lower, computer simulated using Lorentzian line shapes and a line width of 0.2 G.

Results

The group IV substituted *N,N*-dimethylaniline cation radicals are very unstable species with half-lives in the presence of unoxidized parents ranging from 3.4 sec for *p-tert*-butyl-*N,N*-dimethylaniline to less than 7 msec for *N,N*-dimethylaniline itself.¹ Despite this high reactivity, with the experimental modifications discussed above, we were able to obtain resolved esr spectra for the *p-tert*-butyl-, *p*-trimethylsilyl-, and *p*-trimethylgermyl-*N,N*-dimethylaniline cation radicals.

The esr spectrum of the radical cation of *p*-trimethylsilyl-*N,N*-dimethylaniline and a computer simulation of the spectrum are shown in Figure 1. Because of the instability of the radical, splittings smaller than 0.2 G could not be observed. However, the inclusion of a hyperfine coupling constant (hfcc) of 0.1 G, assigned to the trimethylsilyl protons, greatly improved the fit between the simulated and experimental spectra. The spectrum's overall features are similar to those of the *p*-methyl-*N,N*-dimethylaniline radical cation reported by Nelson.¹² The hfcc's listed in Table I were assigned by analogy with the coupling constants

Table I. Esr Data for Para-Substituted *N,N*-Dimethylaniline Radical Cations

Substituent	a_N	a_{NCH_3}	$a_{H(o)}$	$a_{H(m)}$	a_{MCH_3}
CMe ₃	11.30	12.20	5.20	1.30	0.40
SiMe ₃	11.40	12.60	5.35	1.50	<0.1 ^a
GeMe ₃	11.30	12.50	5.28	1.47	<0.1 ^a
Me ^b	11.17	12.22	4.25	1.82	
OMe ^b	10.00	10.40	5.21	1.36	
F ^b	11.68	12.95	5.24	1.38	
NO ₂ ^b	12.80	14.83	5.86	1.87	

^a Estimated. ^b Reference 7.

(12) R. F. Nelson and M. Melicharek, *J. Electroanal. Chem. Interfacial Electrochem.*, **26**, 201 (1970).

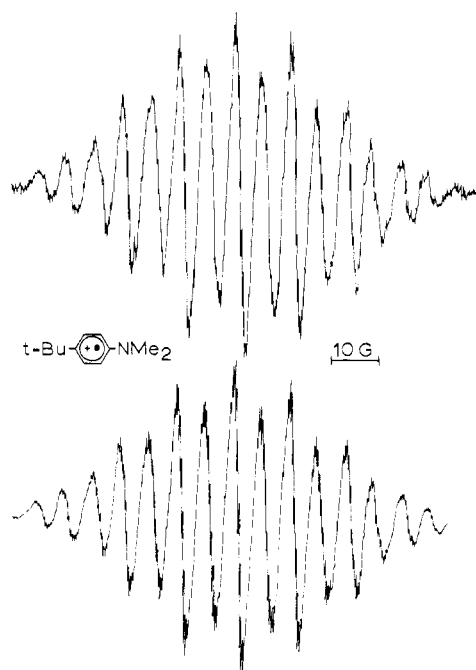


Figure 2. ESR spectrum of the radical cation of *p*-*tert*-butyl-*N,N*-dimethylaniline: upper, experimental; lower, computer simulated using Lorentzian line shapes and a line width of 0.05 G.

reported by Latta and Taft for other para-substituted *N,N*-dimethylaniline cation radicals,⁷ and represent the best fit with the experimental spectrum.

Qualitatively, the ESR spectrum of *p*-trimethylgermyl-*N,N*-dimethylaniline radical cation resembles that of its silicon analog. As indicated by the kinetic studies, this radical was even less stable than the *p*-trimethylsilyl radical. Experimental splittings which could be assigned to the methyl protons of the trimethylgermyl group were not observed, but the fit of the simulated spectrum was improved by adding a 0.1-G hfcc for these protons. The hfcc's which give the best fit with the experimental spectrum are listed in Table I.

Figure 2 illustrates the experimental and simulated ESR spectrum of the *p*-*tert*-butyl-*N,N*-dimethylaniline cation radical. As can be seen in the spectrum, the splitting due to the *tert*-butyl group protons was resolved for this more stable cation radical and found to be 0.40 G. The increased complexity of the spectrum introduced by the additional lines made the assignment of the other hyperfine coupling constants for the radical a great deal more difficult. The values of these coupling constants listed in Table I were obtained by assuming a linear relationship between the π spin densities (listed in Table III), calculated using the CNDO/2 approximation,¹⁰ and the proton or nitrogen coupling constants observed in the ESR spectra. The comparison shown in Figure 2 of the experimental spectrum with the spectrum simulated using these hfcc's indicates the excellent agreement which was obtained.

The radical cation of *m*-trimethylsilyl-*N,N*-dimethylaniline has been prepared. Unfortunately, the lack of symmetry in this species leads to severe overlapping of the lines in its ESR spectrum. To date, we have not been able to resolve the spectrum sufficiently to obtain meaningful data for the assignment of the hyperfine

interactions. Attempts to obtain the ESR spectrum of the parent of the series, *N,N*-dimethylaniline cation radical, were also unsuccessful. This was anticipated in view of its great susceptibility to further reaction indicated by the kinetic results and is consistent with the observations of other workers.^{7,13}

Table I summarizes the ESR results. Included in this table for purposes of comparison are data reported by Latta and Taft⁷ for some other *N,N*-dimethylaniline radical cations with representative electron-withdrawing and releasing substituents. The general trend observed is that, as the electron withdrawing effect of the para substituent increases, all of the hyperfine coupling constants increase. On this basis it may be concluded that, in the radical cations, the trimethylsilyl and trimethylgermyl substituents are either electron-withdrawing or weaker electron donors than the *tert*-butyl group.

Hückel molecular orbital calculations treating the dimethylamino group and the group IV substituent as heteroatoms attached to the benzene ring were performed.¹⁴ For the heteroatom parameters the values of h and k chosen were those used by Allred and co-workers because they represented an internally self-consistent data set for the three substituent groups.¹⁵ However, the auxiliary inductive parameters employed by these workers were not included in the calculations. This decision was based on the consideration that the strong electron-donating effect of the dimethylamino group would tend to reduce the $+I$ effect of other ring substituents. Turner has observed that the effect of two strongly donating substituents on an aromatic ring is usually less than the sum of the individual substituent effects.¹⁶ The energies and one-electron π densities (c_i^2) of the highest filled molecular orbitals obtained are given in Table II.

Table II. Results of Hückel Calculations for the Group IV Substituted *N,N*-Dimethylanilines

Substituent	E_{HOMO}^a	c_N^2	c_o^2	c_m^2	c_M^2	C-M bond order
H	0.4092	0.7671	0.0632	0.0031		
<i>p</i> -Me ₃ C	0.3914	0.7284	0.0622	0.0077	0.0164	0.1743
<i>p</i> -Me ₃ Si	0.4184	0.7757	0.0624	0.0015	0.0055	0.1957
<i>p</i> -Me ₃ Ge	0.4138	0.7707	0.0628	0.0022	0.0030	0.1397
<i>m</i> -Me ₃ Si	0.4096	0.7687	0.0651	0.0029	0.0002	0.1827

^a In units of β .

The Hückel calculations gave excellent correlations with experimental ionization potentials and base strengths,⁴ and the nitrogen one-electron densities were linearly related to the experimental a_N .¹⁷ It can be seen by comparing Table I with Table II that there is good qualitative agreement between the experimental hyperfine coupling constants of the radical cations and the Hückel calculated electron distribu-

(13) T. Mizoguchi and R. N. Adams, *J. Amer. Chem. Soc.*, **84**, 2058 (1962).

(14) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(15) M. D. Curtis, R. K. Lee, and A. L. Allred, *J. Amer. Chem. Soc.*, **89**, 5150 (1967); M. D. Curtis and A. L. Allred, *ibid.*, **87**, 2554 (1965).

(16) D. W. Turner, D. P. May, and A. D. Baker, *J. Chem. Soc. B*, 22 (1968).

(17) M. J. Drews, Ph.D. Thesis, North Texas State University, Dec 1971.

tions in the HFMO. This agreement with experiment justifies our neglect of the auxiliary inductive parameters for this system. It is of interest to compare the C-M bond orders listed in Table II. The π bond order between the group IV substituent and the ring increases: $p\text{-Me}_3\text{Ge} < p\text{-Me}_3\text{C} < m\text{-Me}_3\text{Si} < p\text{-Me}_3\text{Si}$. These Hückel results are inconsistent with those of the kinetic studies on the radical cations, in which we found the order of stability toward cleavage of the C-M bond to be $p\text{-Me}_3\text{Ge} < p\text{-Me}_3\text{Si} < m\text{-Me}_3\text{Si} < p\text{-Me}_3\text{C}$.¹

The biggest disadvantage of Hückel calculations applied to these molecules is that an *ab initio* assumption of π bonding between the atoms included in the calculation is made and only the extent of this π bonding is varied. The good agreement with experiment suggests that π bonding between the group IV element and the aromatic ring is significant. However, no differentiation between hyperconjugative and d-orbital effects is possible. For this reason we also performed semiempirical SCF-MO calculations which do not involve the *ab initio* assumption of π interactions for these molecules. The CNDO/2 approximation was chosen because it has recently been extended to include third row elements and it has not been generally applied to such large molecules containing silicon.¹⁸

The results of the CNDO/2 calculations for the radical cations are given in Table III. The calcula-

Table III. CNDO/2 π Spin Densities for Para-Substituted *N,N*-Dimethylaniline Cation Radicals

Substituent	ρ_N^π	ρ_{o-C}^π	ρ_{m-C}^π	ρ_{p-C}^π
H ^a	0.6927	0.1337	-0.0677	0.1454
Me ₃ C	0.6608	0.1247	-0.0579	0.1453
Me ₃ Si	0.6890	0.1339	-0.0673	0.1275
Me	0.6490	0.1249	-0.0620	0.1487
F	0.6770	0.1272	-0.0624	0.1388
MeO	0.6069	0.1089	-0.0436	0.1248
Q_{av}^b	16.90	41.10	25.35	

^a Not included in the calculation of Q_{av} because of the lack of experimental hyperfine coupling constants. ^b Average value of the Q 's calculated from experimental a values and CNDO/2 determined ρ_i^π .

tions indicated that the spin density was concentrated predominantly in an orbital of the same symmetry as the symmetric π bonding orbital of benzene, π_{sym} .¹⁹ The average Q values listed in Table III were determined by assuming a McConnell-type relation between the experimental coupling constants and the calculated spin densities

$$a_i = \rho_i^\pi Q$$

where a_i is the experimental hfcc for the i th atom or a proton bonded to the i th atom and ρ_i^π is the π spin density at the i th atom.²⁰ The variation in the Q value for various positions in a radical is not unknown, and several attempts have been made to modify Mc-

(18) G. Szeimies, *Tetrahedron Lett.*, **58**, 5073 (1970), and references therein.

(19) That is, the e_g orbital of benzene which is symmetric with respect to reflection through the mirror plane passing through the 1,4 positions of the ring and perpendicular to the ring.

(20) H. M. McConnell, *J. Chem. Phys.*, **28**, 1188 (1958); **24**, 632, 764 (1956); H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

Connell's original relationship to account for these variations.²¹ It is interesting to note that the average of the Q values given in Table III is 27.78, in good agreement with the generally accepted value of Q for aromatic systems of 27 G.²¹ Considering the size of the molecules and the level of the CNDO/2 approximation, the correspondence between calculated spin densities and the experimental data seems to be reasonable. The trend observed here, as with the Hückel calculations, is for electron-withdrawing groups to increase the magnitude of the spin densities at all positions.

CNDO/2 calculations were also carried out for the ground states of these molecules. For the group IV substituted derivatives, the rotational orientation of the Me₃M group with respect to the aromatic ring was varied to determine the most stable configuration. The orientation of the Me₃M group with one of the methyl groups in the plane of the ring was found to give the lowest total electronic energy. This configuration was about 0.01 to 0.03 eV more stable than that with one of the methyl groups perpendicular to the ring. Although the rotational orientation of the Me₃M group had a small effect on the total electronic energy of the system, the effects on charge distributions and overlaps were negligible.

Table IV provides a comparison between calculated

Table IV. Comparison of CNDO/2 Calculated and Experimental Ground-State Properties for Some Substituted *N,N*-Dimethylanilines

RC ₆ H ₄ NMe ₂ R	E_{HFMO} , -au	$c_{Np\pi}^a$	$E_{p/2}^b$, V vs. sce	pK _a ^b
H	0.3923	0.658	0.74	4.35
<i>p</i> -Me ₃ C	0.3774	0.605	0.68	4.65
<i>p</i> -Me ₃ Si	0.3975	0.640	0.78	3.98
<i>m</i> -Me ₃ Si	0.3908	0.655	0.72	4.41
<i>p</i> -F	0.3890	0.623		3.92 ^d
<i>p</i> -Me	0.3727	0.575	0.70	4.94
<i>p</i> -MeO	0.3605	0.526	0.60 ^c	5.06 ^d

^a Coefficient of the nitrogen $p\pi$ orbital in the HFMO. ^b Reference 4. ^c Calculated from the $E_{1/2}$ value of 0.33 V vs. 0.01 N Ag⁺/Ag: A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4130 (1964), by adding 0.30 to correct to V vs. sce; E. S. Pysh and N. C. Yang, *ibid.*, **85**, 2124 (1963), and correcting to $E_{p/2}$; R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 709 (1964). ^d Calculated using the linear free energy relation given by J. Clark and D. D. Perrin, *Quart. Rev., Chem. Soc.*, **18**, 295 (1964).

and experimental ground-state properties for the *N,N*-dimethylanilines involved in this study. We have shown that the ionization potentials of these compounds are linearly related to their half-peak oxidation potentials.⁴ As a test of the CNDO/2 approximation, the calculated energies of the HFMO are plotted as a function of $E_{p/2}$ in Figure 3. In contrast to the findings of other workers,^{22,25,27} it can be seen that for this series of *N,N*-dimethylanilines the correlation is quite good.

The general trend apparent in Table IV is for the energy of the HFMO to decrease as the coefficient of the nitrogen $p\pi$ orbital increases. We pointed out

(21) For an excellent review of the problem of relating spin densities to hyperfine coupling constants, see J. R. Bolton in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 1.

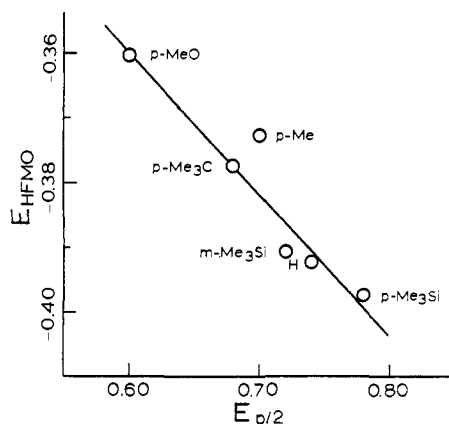


Figure 3. Plot of the CNDO/2 calculated energy of the HFMO against $E_{p/2}$ for the substituted *N,N*-dimethylanilines.

that the linear relation which exists between the pK_a 's and $E_{p/2}$ values might indicate that the pK_a 's of these anilines are related to the energy of their HFMO's.⁴ The CNDO/2 results now provide theoretical support for this suggestion. As the HFMO is stabilized, the contribution of the lone-pair orbital to the π system increases and the base strength decreases. Figure 4 clearly illustrates this trend, showing decrease in pK_a as the delocalization of the nitrogen lone pair increases. Only two compounds, *p*-fluoro- and *p*-trimethylsilyl-*N,N*-dimethylaniline, deviate significantly from the correlation. Bloor and Breen have reported some anomalous results for CNDO/2 calculations on fluorobenzene.²² With the *p*-trimethylsilyl compound, the calculations suggest that the lone pair orbital involvement in lower lying occupied molecular orbitals is greater, as will be shown in Table VI.

One further comparison of experimental and calculated ground-state properties is noteworthy. The experimental dipole moment of *N,N*-dimethylaniline is 1.48 D,²³ compared with the CNDO/2 calculated moment of 1.13 D. The low calculated value of the dipole moment may well be due to our choice of a planar configuration for the dimethylamino group. In their calculation for aniline, Bloor and Breen observed that the planar configuration of the NH_2 group gave a low dipole moment while a pyramidal configuration gave excellent agreement with experiment.²² These authors note that the charge distributions for the two conformations are almost identical and suggest that the CNDO/2 method is potentially very useful for calculating conformations by comparing calculated and experimental dipole moments. In this light, the excellent agreement we obtained for *p*-trimethylsilyl-*N,N*-dimethylaniline between the calculated moment of 1.85 D and the experimental value of 1.84 D²⁴ supports our choice of the planar configuration of the dimethylamino group for this molecule. The correspondence adds weight to the bonding description of the silyl compounds given by the CNDO/2 approximation.

Discussion

The CNDO/2 approximation has recently been the object of several critical papers. In a review on photo-

(22) J. E. Bloor and D. L. Breen, *J. Phys. Chem.*, **72**, 716 (1968).
 (23) S. W. Tucker and S. Walker, *J. Chem. Phys.*, **52**, 2545 (1970).
 (24) H. Sofer and T. DeVries, *J. Amer. Chem. Soc.*, **73**, 5817 (1951).

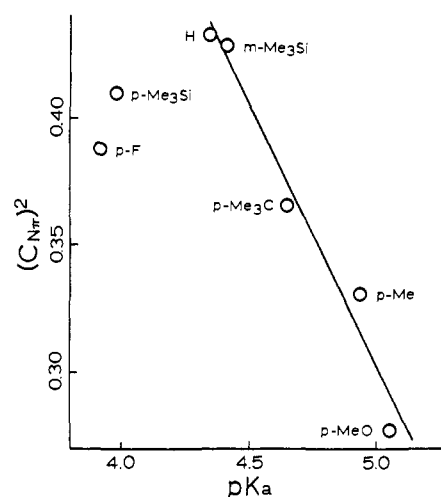
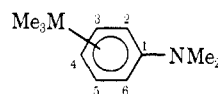


Figure 4. Relation between the base strengths of the substituted *N,N*-dimethylanilines and the square of the CNDO/2 coefficient of the nitrogen lone-pair orbital in the HFMO.

electron spectroscopy,²⁵ Worley points out that the ionization potentials calculated using Koopmans' theorem²⁶ are usually about 4.0 eV too high. Bloor and Breen have shown that although CNDO/2 generally gives poor results for ionization potentials of substituted benzenes, relative values for a series of closely related compounds are more reliable.²² Jesaitis indicates that CNDO/2 gives good agreement with experimental charge distributions and dipole moments but poor results for reaction and atomization energies.²⁷ In view of the good correspondence between experimental and calculated properties of the substituted anilines which we have obtained, a discussion of the CNDO/2 bonding description seems worthwhile.

In Tables V and VI, the numbering given below was used. Table V gives the atomic orbital coefficients



for the HFMO. The orbital is clearly a π_{sym} 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 substituent and the ring for the carbon and fluorine substituents.

With the trimethylsilyl derivative, the node is shifted and appears close to the silicon nucleus. (Compare the coefficient of -0.127 for the $p\pi$ orbital of the *tert*-butyl carbon with $+0.010$ for the silicon $p\pi$ orbital in *p*-trimethylsilyl-*N,N*-dimethylaniline.) Apparently, the contribution of the silicon $d\pi$ orbital to the HFMO affects the position of this node in the molecular orbital. The fact that a node in the molecular orbital bearing the unpaired electron occurs so close to the silicon nucleus may account for the smaller coupling constants of the trimethylsilyl protons compared to those for the *tert*-butyl protons. The coefficients indicate that the major interaction between silicon and this orbital is of the $d-p\pi$ type and that $\sigma-\pi$ interactions do not contribute significantly to the stabilization of the HFMO. It is also apparent that the coefficients

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Table V. CNDO/2 Coefficients for the HFMO of the Group IV Substituted Anilines^a

Substituent	Atoms						M	
	N	1	2	3	4	p	d ^b	
H	0.658	-0.265	-0.321	0.119	0.399			
4-Me	0.575	-0.301	-0.293	0.181	0.408	-0.136		
4-Me ₃ C	0.605	-0.296	-0.304	0.166	0.406	-0.127		
4-Me ₃ Si	0.640	-0.234	-0.318	0.098	0.382	0.010	-0.158	
3-Me ₃ Si	0.656	-0.273	-0.321	0.116	0.392	0.012	-0.051	
			-0.314 ^c	0.128 ^d				
4-F	0.623	-0.291	-0.308	0.163	0.394	-0.204		

^a In as much as this is a π_{sym} 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. ^b In the set-up of the overlap integrals the orientation of this d π orbital is such that a negative coefficient indicates positive overlap. ^c Carbon 6. ^d Carbon 5.

Table VI. CNDO/2 Net Atomic Charges for the Group IV Substituted *N,N*-Dimethylanilines

Substituent	Δq^a	Atom							Substituent orbitals' density	
		N	1	2	3	4	M	M-CH ₃ ^b	p	d
H	Tot	-0.152	0.155	-0.062	0.034	-0.031				
	σ	-0.319	0.091	0.028	-0.001	0.032				
	π	0.167	0.064	-0.090	0.035	-0.063				
4-Me ₃ C	Tot	-0.153	0.145	-0.054	0.010	0.000	0.053	-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	
4-Me ₃ Si	Tot	-0.149	0.178	-0.082	0.093	-0.140	0.136	-0.191	1.762	1.246
	σ	-0.329	0.080	0.025	0.006	-0.113	-0.016		1.165	0.995
	π	0.180	0.098	-0.107	0.087	-0.027	0.152		0.597	0.251
3-Me ₃ Si	Tot	-0.153	0.134	-0.001	-0.085	0.032	0.144	-0.191	1.765	1.235
	σ	-0.317	0.088	0.033	-0.142	0.041	-0.023		1.168	0.999
	π	0.164	0.046	-0.034	0.057	-0.009	0.167		0.597	0.236

^a Excess total charge density on the atom indicated (ref 22). ^b Average Δq for the three methyl carbons of the Me₃M group.

of the ring carbon atoms are rather insensitive to the nature and location of the substituent, while the extent of d-p π interaction is very sensitive to the π density of the carbon to which silicon is attached.

In order to assess the total effect of metal substitution in these systems, it is necessary to consider the interactions in all of the occupied molecular orbitals. The most efficient method of doing this is to examine the total charge perturbations and bond orders for the orbitals of interest. Table VI lists the "formal charges," Δq ,²² and the total electron densities for the substituent's p and d orbitals. These have been separated into σ and π components.

The greater involvement of the nitrogen lone-pair orbital in lower lying occupied molecular orbitals is apparent in its increased positive Δq_{π} for the 4-trimethylsilyl compound. A general tendency for electron density to be shifted toward the silicon end of the molecule can be observed. This electron density accumulates at the silicon methyl carbons. The +I inductive effect of silicon shows up as increased σ electron density at its point of attachment. Along with this there is a decrease of π density at the same carbon. A considerable redistribution of electron density within the p and d orbitals of silicon occurs both in the σ and π system, evidently stabilizing the accumulation of negative charge at the silicon-methyl carbons.²³

(28) It should be noted that while only one d orbital is of the proper symmetry and spatial orientation to overlap with the aromatic π system, all of the d orbitals can interact with carbons of the trimethylsilyl group

An indication of the relative importance of d-p π bonding and p-p π hyperconjugation for the ground state is obtained from an examination of the off-diagonal terms of the CNDO/2 density matrices for the group IV substituted *N,N*-dimethylanilines (Table VII). It can be seen that the position of silicon sub-

Table VII. CNDO/2 Bond Densities^a and Bond Orders^b for the Interaction between the Group IV Element and Its Ring Carbon for Substituted *N,N*-Dimethylanilines

Substituent orbitals	Substituent		
	<i>p</i> -Me ₃ C	<i>p</i> -Me ₃ Si	<i>m</i> -Me ₃ Si
s	0.678	0.679	0.678
p σ	1.260	1.100	1.100
d σ		0.832	0.842
p π	0.176	0.209	0.192
d π		0.363	0.321
σ BO	0.969	1.306	1.310
π BO	0.088	0.286	0.256
Total BO	1.057	1.592	1.566

^a Total bonding density minus antibonding density for the orbitals indicated. ^b Bond density/2.

stitution has little influence on its σ bonding with the ring. The total hyperconjugative p π interaction in the ground state is greater for both *p*- and *m*-trimethyl-

in a σ or π fashion. It is our view that the single d π orbital provides the means of transmission of electron density from the π system to the ample electronic storehouse formed by the p and d orbitals of the trimethylsilyl group.

silyl-*N,N*-dimethylanilines than for the *tert*-butyl compound. However, the total interaction of the *d* orbitals with the π system is significantly larger than the $p\pi$ interaction for the silicon compounds. The $p\pi$ and $d\pi$ interactions between silicon and the ring decrease as the π density at the carbon to which the trimethylsilyl group is attached decreases.

Our results are in substantial agreement with recently published results of Kawamura and Kochi.²⁹ These authors conclude from a study of hfcc's and *g* values for a series of neutral radicals [(CH₃)₃MCH₂CH₂·, M = C, Si, Ge, Sn] that both *p*-*d* and hyperconjugative interactions provide delocalization of the odd electron to the β C-M σ bond. Further, both interactions are of the same order of magnitude and both increase with increasing atomic number of the metal.²⁹ On this basis we might suggest that the interactions in *p*-trimethylgermyl-*N,N*-dimethylaniline, for which we could not perform CNDO/2 calculations, are sim-

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ilar to those in the trimethylsilyl compounds. We do not agree with the conclusions of Symons and co-workers who, on the basis of coupling constants alone, ruled out *p*-*d* π interactions for alkyl radicals containing Sn, P, or As in the β position.³⁰

Although the CNDO/2 calculations indicate some contribution of the $p\pi$ orbital of silicon to the ground-state molecular orbitals, the larger coefficients for this orbital occur in the unoccupied molecular orbitals. The effect of group IV elements on the excited states of these molecules will be discussed in the following paper.

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Interchange of Functionality in Conjugated Carbonyl Compounds through Isoxazoles

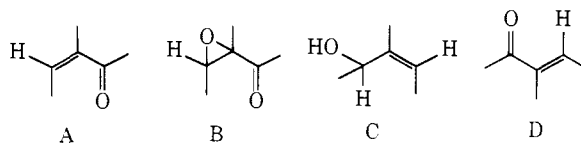
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Abstract: Five isoxazoles were prepared in good to excellent yield by a new method involving oxidation of certain α,β -unsaturated ketoximes with iodine-potassium iodide in aqueous tetrahydrofuran in the presence of bicarbonate. Catalytic hydrogenation of the isoxazoles gave vinylogous amides while reduction with sodium and 3 equiv of *tert*-butyl alcohol in liquid ammonia yielded the β -aminocarbonyl compounds in excellent yields. The corresponding α,β -unsaturated carbonyl compounds were available from the crude amines by thermolysis or treatment with acidic catalysts. This new method for the transposition of functionality within α,β -unsaturated carbonyl compounds was used to convert the three ionones **1a**, **1b**, and **1d** to the corresponding damascones **4a**, **4b**, and **4d**. The method is also suitable for the preparation of unsaturated aldehydes, but the starting material cannot be an aldoxime because the resulting isoxazole is too unstable in the basic medium necessary for its creation.

Since the recognition of β -damascenone (**4c**)¹ as an important constituent of Bulgarian rose oil and raspberry aroma,² its chemical synthesis has received much attention.^{1,3-5} Added impetus to develop efficient syntheses for this class of compounds was provided when β -damascone (**4a**) was found in Burley tobacco.⁶ Both it and its α (**4b**)⁷ and γ isomers⁸ have been synthesized by multistep procedures from starting materials containing fewer carbon atoms. The readily available and inexpensive α - and β -ionones (**1b** and **1a**)

represent ideal raw materials for the synthesis of the corresponding damascones (**4b** and **4a**). The hitherto most efficient method for the transposition of carbonyl group and double bond in conjugated ketones was discovered by Wharton.⁹ He found that treatment with hydrazine of an epoxy ketone **B**, available by oxidation of the corresponding α,β -unsaturated ketone **A**, gave the allylic alcohol **C**, oxidizable, unless tertiary, to the transposed conjugated ketone **D**.



Both epoxydihydro- α -ionone and its γ isomer were submitted to the Wharton reaction, but the results were

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