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HYPERCONJUGATIVE vs. *d* ORBITAL EFFECTS IN UNSATURATED SILANES

I. THE ENERGY LEVELS IN *para*-GROUP IV-SUBSTITUTED ANILINES

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Summary

The energy levels of a series of *para* substituted *N,N*-dimethylanilines $p\text{-MH}_n\text{Me}_{3-n}\text{C}_6\text{H}_4\text{NMe}_2$ (n = 0-3, M = C or Si) for the ground and lower lying excited states have been determined in acetonitrile solution. The levels for the carbon compounds are all slightly destabilized relative to *N,N*-dimethylaniline and the effects are rather insensitive to n. The stabilizations produced by silicon substituents on all levels are markedly affected by silicon's substituents, showing increasing perturbations with increasing n. It is concluded that variations in the interaction of the σ^* system of the silyl substituent with the aniline π system, and not *d* orbital interactions, account for the trends observed.

Introduction

It has become increasingly apparent in recent years that properties of organosilicon molecules traditionally ascribed to *d* orbital interactions [1] may, in many cases, be explained by consideration of σ—π hyperconjugative effects. Both Pitt and Schweig have recently applied the perturbational molecular orbital treatment of hyperconjugation, in conjunction with CNDO/2 calculations, to rationalize trends in the experimental properties of organosilicon compounds with good success [2,3]. In a recent quantum chemical study of the effects of silyl substituents in phenyl and benzylsilanes, Ponec and Chvalovsky found that charge transfer spectra with tetracyanoethylene as the acceptor could be interpreted by interaction of the σ^* orbitals of the Si—X bonds, without assuming participation of silicon *d* orbitals [4]. The ultraviolet spectra of a series of silyl substituted benzenes $\text{PhSiH}_n\text{Me}_{3-n}$ (n = 0-3) have been interpreted solely on the basis of hyperconjugative interactions [5]. In contrast, studies of the photoelectron spectra of silylbenzene and trimethylsilylbenzene led McLean to conclude that there must be some stabilization due to interaction with the Si *d* and σ^*(Si—H) orbitals [6].

Studies in our laboratories of the effect of the trimethylsilyl substituent on the ground states [7], excited states [8], and radical anions [9] of *N,N*-dimethylaniline have indicated that, on the basis of CNDO/2 calculations, both p—d_π and p—p_π interactions were important in these systems. To differentiate between these two types of interaction we have undertaken studies to determine how successive replacement of methyl groups in the trimethylsilyl substituent with hydrogen affects the bonding interaction between silicon and the ring π system.

Our basic premise is that σ—π interactions between silicon and π electron systems should be much more sensitive to the nature of silicon's σ bonded substituents than d—π interactions. Presently available data in the literature provide a means to obtain reliable estimates of the σ, σ^*, and *d* orbital energies for various silicon containing substituents (Fig. 1). To illustrate, combination of photoelectron data with vacuum ultraviolet data for silane and tetramethylsilane shows that the term value (ionization potential) for the 3*d* level is essentially constant. Values of 1.61 and 1.66 eV for silane and tetramethylsilane, respectively, have been reported [10].

On the other hand, the term values for the $n + 1t_2$, σ^*(Si—X), levels vary significantly from 4.67 eV for silane to 3.94 eV for tetramethylsilane. These estimates of the ionization energies of the t_2, σ^* levels are obtained from the values assigned to the $nt_2 \rightarrow n + 1t_2$ transitions [10], and the photoelectron ionization energies for the originating orbitals. The ionization energies of the $1t_2$, σ(Si—H), level in silane average to 12.62 eV [11]*.

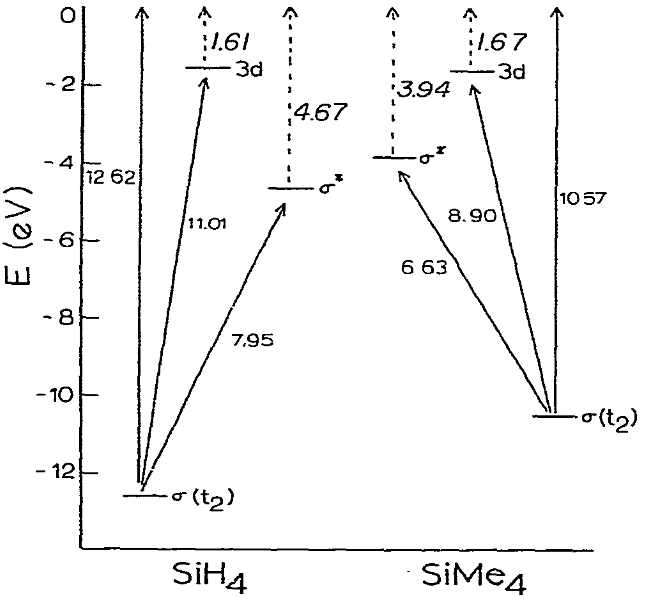

Fig. 1. Estimation of the relative energies of the σ^* and 3*d* levels for silane and tetramethylsilane.

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[*] These t_2 ionizations are split by Jahn—Teller distortions of the ion in the photoelectron experiment [11].

The corresponding ionization of the $3t_2$, σ(Si—C), level in tetramethylsilane occurs at 10.57 eV [12]. It is components of the levels of T_2 symmetry which have the correct symmetry for interaction with a π system when silane becomes the silyl group, or when tetramethylsilane becomes a trimethylsilyl group [13].

While there are also $3d$ orbitals of T_2 symmetry, experimental evidence indicates that mixing of d orbitals with the σ molecular orbital systems is not significant for the methylsilanes [14], or for silane itself [15]. These conclusions are supported by the near constancy of the $3d$ term values for these molecules [10]. Thus, for a series of molecules related in all respects except for the substitution of hydrogens for methyl groups on silicon, one would anticipate variations in effects due to σ—π interactions, but near constancy in effects due to d orbital involvement in the bonding. We report a study of these effects on a series of *p*-silicon- and *p*-carbon-substituted *N*,*N*-dimethylanilines in this paper.

Experimental

Oxidation potentials were determined as has been described previously [7]. Ultraviolet spectra were obtained using a Cary 14 spectrometer and 10 mm quartz cells. The temperature was unregulated ambient, generally about 23°C. Samples for the measurement of extinction coefficients were prepared by standard dilution methods. The spectra with severely overlapping bands were analyzed using the non-linear least squares program, MROCOS, obtained from Oak Ridge National Laboratory, Oak Ridge, Tennessee. 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. Melting points and boiling points are uncorrected.

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. All anilines were purified by GLC collection using a 20′ × 3/8″ stainless steel column of 30% SE-30 on 45/60 mesh Chromasorb W at ca. 200°C for characterization and prior to the measurements made in this study.

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) with dimethylsulfate [16]; b.p. 92°C/10 Torr (Lit. [17]: 104°C/18 Torr).

p-Isopropyl-N,N-dimethylaniline was synthesized by methylation of *p*-isopropylaniline prepared from cumene (Eastman) using the procedure of Hansch and Helmkamp [18]; b.p. 88-89°C/10 Torr (Lit. [18]: 111-112°C/16 Torr).

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

p-Silyl-N,N-dimethylaniline was synthesized by lithium aluminum hydride reduction of *p*-trichlorosilyl-*N*,*N*-dimethylaniline, which was prepared by inverse derivatization of *p*-lithio-*N*,*N*-dimethylaniline [19] with tetrachlorosilane (PCR) in tetrahydrofuran. An overall yield, based on *p*-bromo-*N*,*N*-dimethylaniline, of 20% was obtained; b.p. 82°C/3 Torr; m.p. 48°C (Lit. [20]: b.p. 81°C/5 Torr; m.p. 45-50°C).

Anal.: Found: C, 63.30; H, 8.66; N, 9.18. $C_8H_{13}NSi$ calcd.: C, 63.51; H, 8.66; N, 9.26%. 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, which was obtained from the inverse derivatization of *p*-lithio-*N*,*N*-dimethylaniline with methyltrichlorosilane (Columbia) in tetrahydrofuran; b.p. 107°C/10 Torr (Lit. [20]: 110°C/16 Torr).

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

p-Dimethylsilyl-N,N-dimethylaniline was prepared by inverse derivatization of *p*-lithio-*N*,*N*-dimethylaniline with dimethylchlorosilane (PCR) in tetrahydrofuran, 67% yield; b.p. 120°C/10 Torr (Lit. [20]: b.p. 122°C/14 Torr).

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

Results

The half peak oxidation potentials for the *para* series of carbon and silicon *N*,*N*-dimethylanilines were determined by cyclic voltammetry in acetonitrile solution using tetrabutylammonium perchlorate as the supporting electrolyte. These are listed in Table 1 along with proton NMR data for the compounds. The silicon compounds consistently have higher oxidation potentials than their carbon analogs. Further, there is a distinct trend towards increasing oxidation potential as methyl groups are replaced by hydrogen in the silicon series.

The chemical shifts for a series of substituted aromatic systems can provide information about the electronic nature of the substituents [21]. The proton chemical shifts listed in Table 1 for the *para*-substituted *N*,*N*-dimethylanilines show that the aromatic protons and the dimethylamino protons in the silicon compounds are deshielded compared to their carbon analogs. This indicates that the silyl groups are electron-withdrawing, or, at least, less electron releasing than the alkyl groups, and is consistent with the oxidation potentials. In the silicon

TABLE 1

GROUND STATE PROPERTIES OF *para*-SUBSTITUTED *N*,*N*-DIMETHYLANILINES

Substituent R	$E_{p/2}$[a] (V vs. SCE)	PMR[b]						
		δ(M—H)	*J* (Hz)	δ(M—CH₃)	δ(N—CH₃)	δ(H_o)	*J* (Hz)	δ(H_m)
H	0.74[c]	—		—	2.85	6.76		6.76
CH_3	0.70[c]	2.23		—	2.91	6.54	8	6.92
CH_2Me	0.70	2.56	6	1.18	2.92	6.57	8	6.94
$CHMe_2$	0.71	2.74	7	1.15	2.76	6.40	8	6.80
CMe_3[c]	0.68	—		1.30	2.90	6.70	8	7.24
SiH_3	0.86	4.26		—	3.00	6.68	8	7.42
SiH_2Me	0.85	4.38	4	0.34	3.02	6.68	8	7.39
$SiHMe_2$	0.83	4.46	4	0.27	2.95	6.66	8	7.34
$SiMe_3$[c]	0.78	—		0.20	2.90	6.58	9	7.25

[a] Determined in acetonitrile with tetrabutylammonium perchlorate as the supporting electrolyte. [b] Carbon tetrachloride solution with tetramethylsilane as internal reference, in δ (ppm). [c] Ref. 7.

TABLE 2

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

Substituent	Transition					
	LE_α		CT_s		CT_a	
	λ_{max} (Å)	$\epsilon_{max} \times 10^{-3}$	λ_{max} (Å)	$\epsilon_{max} \times 10^{-4}$	λ_{max} (Å)	$\epsilon_{max} \times 10^{-4}$
H	2998	2.78	2517	1.62	2007	2.17
CH_3	3064	2.03	2543	1.37	2032	1.92
CH_2Me	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_2Me	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

[a] Ref. 7.

series of compounds the aromatic and dimethylamino protons move downfield as methyl groups on silicon are replaced by hydrogen, while the opposite trend is observed for the silyl hydrogens. Both trends show that the electron accepting ability of the silyl group increases as the number of hydrogens on silicon increases.

The solution ultraviolet spectra of substituted anilines show three distinct bands. In order of increasing energy, these have been assigned as the LE_α, a localized aromatic excitation; the CT_s band, corresponding to charge transfer from nitrogen to the symmetric π^* orbital; and the CT_a band, representing charge transfer excitation from nitrogen to the antisymmetric π^* orbital [22]. While there has been some question of these assignments [23], it will suffice for our purposes to use these labels for the excited states. The wavelengths and relative intensities of the bands for the *para* series of compounds, (determined in acetonitrile solution) are listed in Table 2. All of the bands are shifted slightly to the red for both the alkyl and silyl substituted *N,N*-dimethylanilines. However, the larger red shift for the CT_s transition in the silyl compounds is only consistent with a greater stabilization for their excited states compared to the carbon compounds. We also note that the intensities of the LE_α and CT_s transitions are consistently greater in the silicon compounds than in the carbon compounds. This would be in accord with greater delocalization of charge in the excited states of the silylanilines. Solvent effects on the ultraviolet spectra of these systems show that there is greater charge separation in the excited states than in the ground states [8].

Discussion

By making use of the correlation which we have developed between the photoelectron ionization energies and electrolytic oxidation potentials, it is possible to calculate good estimates of the ground state energies of substituted *N,N*-dimethylanilines [7]. Combining these results with the ultraviolet data, and

TABLE 3

RELATIVE GROUND AND EXCITED STATE ENERGIES[a] FOR *para* GROUP IV SUBSTITUTED *N,N*-DIMETHYLANILINES

Substituent	State G^b	LE_α	CT_s	CT_a
H	7.62	3.49	2.70	1.45
CH_3	7.50	3.45	2.62	1.40
CH_2Me	7.50	3.42	2.64	1.39
$CHMe_2$	7.53	3.45	2.65	1.43
CMe_3	7.44	3.33	2.55	1.31
SiH_3	7.98	3.93	3.37	1.88
SiH_2Me	7.95	3.89	3.33	1.83
$SiHMe_2$	7.89	3.82	3.21	1.76
$SiMe_3$	7.74	3.57	3.08	1.63

[a] In eV (—1), acetonitrile solution. [b] Calculated using the relation between $E_{p/2}$ and *IP* given in Ref. 7.

assuming Koopmans' theorum gives a means of comparing the relative energies of the ground states and lower lying excited states for the series of molecules. The results of these calculations are given in Table 3. In Fig. 2. we have plotted the perturbations of the energy levels of *N,N*-dimethylaniline produced by the carbon and silicon substituents.

It is clear from Fig. 2 that the major effect of the carbon substituents on

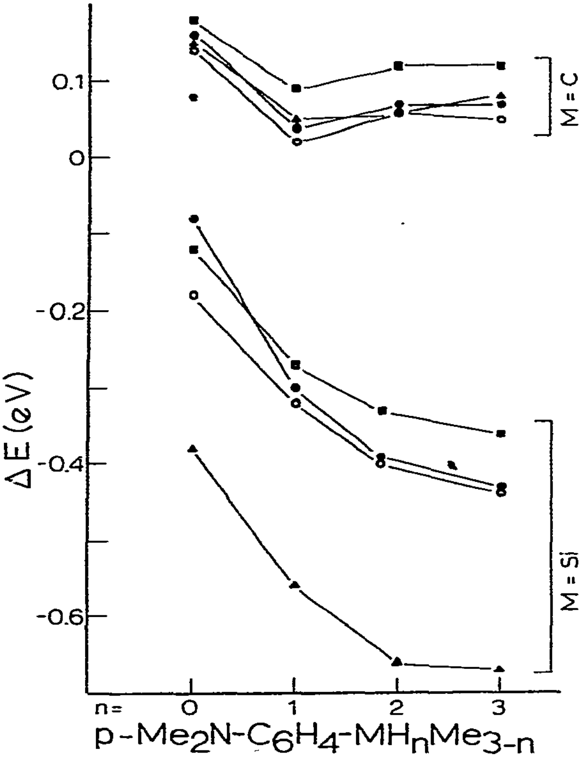

Fig. 2. Perturbation in *N,N*-dimethylaniline energy levels produced by carbon and silicon substituents: ■ = G, ● = LE_α, ▲ = CT_s, ○ = CT_a.

all of the energy levels is a small destabilization. All of the energy levels are affected to approximately the same extent and there is little variation in the series methyl through t-butyl although a slight decrease in the electron releasing ability of the substituent is observed as methyl groups are replaced by hydrogen.

In contrast, the effect of the silicon substituents on the energy levels is stabilization to a much greater extent than the destabilization produced by the carbon substituents. While the effects on each of the states are nearly parallel, the stabilization of the symmetric excited state, CT_s, is nearly twice as large as the effects on the other states. This is consistent with the fact that the π^* symmetric orbital has large density at the *para* positions and should thus be most sensitive to perturbations produced by π interactions. We further note that the perturbations increase significantly as methyl groups on silicon are replaced by hydrogen. These effects are parallel to the decrease in energy of the σ^* level of the silyl substituent which has the appropriate symmetry for π interaction. It is well known that perturbations of energy levels increase as the energy match between the interacting orbitals improves [2,3]. It should be emphasized that, on the basis of symmetry alone, it is not possible to differentiate between *d* orbital interaction and/or hyperconjugative interaction with the π system in a series of unsaturated silanes. However, considering the near constancy of the *d* orbital energy for the silicon substituents involved in this study, we are led to the conclusion that the variations observed must be attributed to variations in the interactions of the σ orbital systems of the silyl substituent with the aromatic π system. We believe that the major interaction in the silyl substituted anilines is between the σ^* levels of the silyl substituent and the symmetric π and π^* orbitals of *N,N*-dimethylaniline. This conclusion is supported by electron spin resonance studies of the radical anions of the *para*-silyl substituted anilines [24].

It is of interest to note that the perturbations produced by silyl substituents in the aniline systems are much larger than the perturbations produced in benzene itself [25]. This is clearly due to a better energy match between the interacting orbitals in the anilines than in the silylbenzenes. With the experimental data presently available on the ground and excited state energies of the components, a detailed perturbational analysis of at least the silyl- and trimethylsilyl-substituted aromatic systems should now be possible, and highly desirable. We would encourage workers more skilled than ourselves in quantum mechanical manipulations to perform these analyses. A similar investigation of the methylsilyl and dimethylsilyl systems must await the analysis and assignment of the vacuum ultraviolet spectra of the methylsilanes [26].

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