BONDING STUDIES IN GROUP IV SUBSTITUTED ANILINES

IV*. EXCITED STATE INTERACTIONS IN THE TRIMETHYL DERIVATIVES

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Summary

The solution ultraviolet spectra for N,N-dimethylaniline, p-t-butyl-, and p-trimethylsilyl-, p-trimethylgermyl-, and m-trimethylsilyl-N,N-dimethylaniline in acetonitrile and pentane are reported. The Group IV substituents perturb the excited states to a much larger extent than the ground states. Both the symmetric and antisymmetric π^* levels are affected by π interaction with the trimethylsilyl and trimethylgermyl substituents. The magnitude of the effects are proportional to the π density at the point of substitution. Simple Hückel calculations correlate well with experimental transition energies. The model appears to exaggerate π interactions between silicon or germanium and the π^* molecular orbitals.

Introduction

In the preceding paper in this series [1] we discussed the ground state properties and bonding in a series of *para* Group IV substituted N,N-dimethylanilines and m-trimethylsilyl-N,N-dimethylaniline. The small stabilizations of the ground states observed when silicon or germanium was substituted for carbon in these compounds were attributed, on the basis of CNDO/2 calculations, to a combination of d_π interaction and hyperconjugative p_π interaction. Recently our CNDO/2 results have been shown to correlate well with changes in ^{13}C chemical shifts [2]. Having established the relative energies of the ground states for this series we were in a position to investigate the perturbations which Group IV metalloids have on the excited states. This paper deals with the results of the investigation of solution ultraviolet spectra.

Helpful to the understanding of the effects of Group IV metal substitution on the excited states of N,N-dimethylanilines is the correct assignment of the state symmetry corresponding to the observed ultraviolet transitions. One available theoretical model for substituted N,N-dimethylanilines is the composite π system developed by Murrell [3]. This model was applied successfully to N,N-
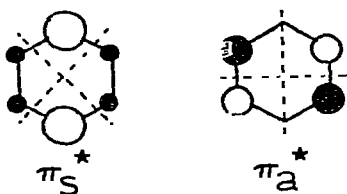
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* For part III see ref. 1.

π_s^{*} π_a^{*}

Fig. 1 Simple Hückel orbitals for the symmetric, π_s^{*} and antisymmetric, π_a^{*} antibonding orbitals of benzene

dimethyl- and other N-alkylated anilines by Kimura and coworkers [4]. In this approach the chromophore is treated as a combination of two or more simpler systems. For N,N-dimethylaniline the systems chosen are the benzene ring and the dimethylamino group. The excited states may be classed as symmetric (s) or antisymmetric (a) with respect to the mirror plane perpendicular to the aromatic ring and containing the nitrogen atom (Fig. 1)

In order of increasing energy the transitions observable in solution spectra are the LE_α band, a localized excitation to the antisymmetric π^{*} orbital; the CT_s band, a band corresponding to charge transfer from nitrogen to the symmetric π^{*} orbital; and the CT_a band, a charge transfer transition to the antisymmetric π^{*} orbital [5]. In this report we examine the effect of Group IV substitution on these excited states.

Experimental

All of the solution spectra were determined using a Cary 14 spectrophotometer using quartz cells with a 10 mm path length. The temperature was unregulated ambient, generally about 23°. Samples for the measurement of extinction coefficients were prepared by standard dilution techniques. All of the extinction coefficients in a particular solvent were determined using the same batch of purified solvent.

Acetonitrile (Matheson—Coleman—Bell, Spectroquality) was purified as described previously [6]. The n-pentane (Phillips, 99.5 mol %) was stirred at room temperature with concentrated sulfuric acid for 10-20 h, and distilled under an inert atmosphere of argon immediately prior to use. Solvent prepared in this manner typically had an absorbance of less than 0.6 at 195 nm vs. air.

All of the anilines were purified by preparative GLC immediately prior to use. Their synthesis and characterization have been described previously [6].

Results

The solution spectra of all the anilines in this study show three major bands in the near ultraviolet region. The wavelengths and relative intensities of the bands for both acetonitrile and pentane solutions are listed in Table 1. As the polarity of the solvent decreases the transitions all shift to shorter wavelengths, indicating a greater degree of charge separation in the excited states than in the ground states. This is anticipated for the charge transfer bands. In the composite π system model there is significant mixing of the LE_α state with the charge transfer state of the same symmetry, CT_a [4]. Thus the solvent shift observed for the

TABLE 1

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

Substituent	Solvent [a]	$[LE_a]$ λ_{max} (nm)	log ε_{max}	$[CT_s]$ λ_{max} (nm)	log ε_{max}	$[CT_a]$ λ_{max} (nm)	log ε_{max}
II	A	299.9	3.48	253.5	4.26	201.2	4.42
	B	296.9	3.32	250.1	4.11	201.0	4.28
p-Me$_3$C	A	301.6	3.35	253.3	4.30	201.9	4.46
	B	299.7	3.41	251.8	4.26	202.2	4.39
p-Me$_3$Si	A	297.5	3.56	255.8	4.40	203.1	4.36
	B	294.0	3.45	253.2	4.38	202.9	4.33
p-Me$_3$Ge	A	300.4	3.40	252.4	4.33	204.5	4.36
	B	297.5	3.38	259.7	4.34	203.5	4.34
m-Me$_3$Si	A	310.0	3.30	258.2	4.15	212.3	4.40
	B	306.2	3.48	255.1	4.20	211.5	4.17

[a] A, acetonitrile; B, pentane.

LE_α band is consistent with the model we have chosen. It is of interest to note that the bathochromic shifts observed with increasing solvent polarity are smallest for p-t-butyl-N,N-dimethylaniline, suggesting a lower degree of charge separation in its exited states than for the other anilines.

All of the compounds give similar spectra in the low energy region. The spectrum of p-t-butyl-N,N-dimethylaniline most closely resembles that of the parent compound, indicating that the t-butyl group causes only small perturbations of the N,N-dimethylaniline excited states. Most of the bands are shifted slightly to the red, consistent with the destabilization of the ground state we observed for the p-butyl compound [1].

The spectra of the silyl and germyl compounds are clearly more perturbed than that of p-t-butyl-N,N-dimethylaniline. The greatest bathochromic shift for CT_s occurs with p-trimethyl-silyl-N,N-dimethylaniline while CT_a experiences the largest red shift in the m-trimethylsilyl compound. The LE_α band is blue-shifted for p-trimethylsilyl-N,N-dimethylaniline, slightly shifted to the red for the p-trimethylgermyl compound, and shows the largest red shift for m-trimethyl silyl-N,N-dimethylaniline.

Discussion

We have measured the ionization potentials of the molecules using a correlation between photoelectron ionization potentials and electrolytic oxidation potentials [6*]. Assuming Koopmans' theorem [8] it is possible to compare the relative energies of the lower lying excited states qualitatively.

Table 2 gives these energies calculated from the ultraviolet spectra in pentan and the ionization energies. Figure 2 is a plot of these data which also shows the perturbations of the ground state, G, and the three excited states, LE_α, CT_s and CT_a are consistent with what would be expected on the basis of the simple Hücke orbitals related to these states [4, 5].

TABLE 2

RELATIVE GROUND AND EXITED STATE ENERGIES FOR SOME GROUP IV SUBSTITUTED ANILINES

Substituent	State			
	G [b]	LE_α	CT_s	CT_a
H	7.62	3.44	2.66	1.45
p-Me$_3$C	7.44	3.30	2.51	1.31
p Me$_3$Si	7.74	3.52	3.02	1.63
p-Me$_3$Ge	7.68	3.51	2.90	1.59
m-Me$_3$Si	7.56	3.51	2.70	1.70

[a] In eV (−1). [b] Ref. 6.

* The direct assignment of ionization potentials from photoelectron spectra of these molecules, while desirable, is unfortunately not possible at this time. The ionizations of the nitrogen lone pair, the benzene π system and the silicon—carbon skeleton all lie in the region 7-10 eV and are not well resolved [7].
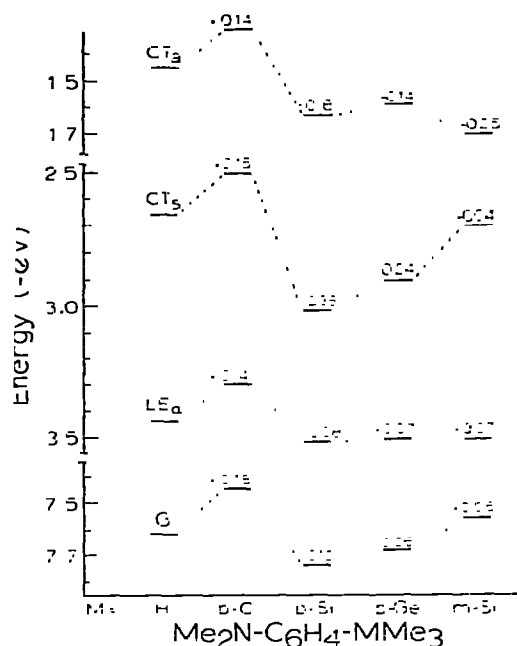
Fig. 2. Relative experimental energies for the ground and excited states of some trimethyl-Group IV-ubstituted-*N,N*-dimethylanilines.

The results for *p*-t-butyl-*N,N*-dimethylaniline are illustrative of a substituent whose predominant perturbing effect is an electron releasing, $+I$ inductive effect. The ground state and the excited states to a lesser extent show destabilizations due to electron release by the t-butyl group which interacts with the ring mainly through the σ electron system. As a result its effects are relatively independent of the π orbital symmetry of the various states. The slight bathochromic shifts observed in the spectrum on t-butyl substitution of *N,N*-dimethylaniline, Table 1, are apparently due to a larger inductive destabilization of the ground state than of the excited states.

Our CNDO/2 calculations for the ground states of *p*- and *m*-trimethylsilyl-*N,N*-dimethylaniline showed that the trimethylsilyl group is strongly electron releasing to the σ system of these compounds. Despite this electron releasing effect in the σ system, the net perturbation of the ground state produced by silicon substitution is electron withdrawal and stabilization of the ground state [1]. This effect is even more pronounced in the excited states. In the absence of π electronic effects one would expect inductive destabilization of the levels for the trimethyl-silyl substituted anilines to be larger than those observed for the t-butyl case. It can be seen in Fig. 2 that just the opposite is the case. The excited states are stabilized for *p*-, *m*-trimethylsilyl-, and *p*-trimethylgermyl-*N,N*-dimethylaniline compared to the t-butyl compound. Further, the extent of the stabilization is in agreement with what would be expected on the basis of π interaction. For the *para*-substituted compounds the symmetric excited state, CT_s, which has large density at the point of substitution is stabilized to the greatest extent. In *m*-trimethylsilyl-*N,N*-dimethylaniline the antisymmetric excited state, CT_a, shows the greatest stabilization.

It is interesting to note that the antisymmetric excited states are also stabi
ized to some extent in the *para* substituted silicon and germanium compounds.
In the simple Hückel orbitals a node is found at the *para* positions in the anti-
symmetric $\pi^{\star}$ orbitals. A stabilization of the antisymmetric excited states for
the *para* compounds could indicate that there is a through-space π interaction
between the silicon or germanium and the ring carbons *ortho* to the Group IV
substituent.

On the basis of ESR and CNDO/2 results which we have obtained for the
radical anions of the trimethylsilyl substituted compounds [9], we believe that
all of the excited state stabilizations observed are due to interaction of both the
d and *p* orbitals of silicon with the $\pi^{\star}$ orbitals of the aromatic system.

Hückel calculations

The large π interactions suggested by our experimental results led us to
attempt simple π molecular orbital calculations and test their applicability to
these molecules. The heteroatom model was used for the Hückel calculations
[10]. Both the dimethylamino and the other substituent group were treated
as heteroatoms attached to the benzene ring. The parameters, *h* and *k*, used for t
t-butyl, trimethylsilyl and trimethylgermyl substituents were those of Curtis and
Allred [11]. These were chosen because they represent an internally self consiste
data set for the groups and had been shown to fit more than one set of experime
al data. Because there is evidence that strong electron-donating groups such as
the dimethylamino group tend to reduce the +*I* effect of other ring substituents
[12], the auxiliary inductive parameters for the Group IV substituent groups wei
not employed in our calculations.

The transition energies were calculated in units of β by obtaining the differ-
ence between the appropriate Hückel orbital energies (eqn. 2). The value of the
resonance integral, $\beta^{\star}$, was determined for each transition by dividing the ob-
served transition energy in the spectrum of *N,N*-dimethylaniline by the Hückel
orbital energy difference. From the value of $\beta^{\star}$ obtained for the LE_{α} transition
and the experimental ionization potential of *N,N*-dimethylaniline the value of
the coulomb integral, α, was calculated. Using these values of α and β the ioniza-
tion potentials, $-E_{IP}$, and the transition energies, E_t, were calculated for the othei
members of the series using eqns. 1 and 2 respectively, where λ_G and $\lambda^{\star}$ are the
coefficients of β obtained from the Hückel calculations for the ground and ap-

$$-E_{IP} = \alpha - \lambda_G \beta^{\star} \tag{1}$$

$$E_t = (\alpha - \lambda^{\star} \beta^{\star}) - (\alpha - \lambda_G \beta^{\star}) = (\lambda_G - \lambda^{\star})\beta^{\star} \tag{2}$$

propriate anti-bonding Hückel orbitals. The $\beta^{\star}$ represents an adjusted off-diago-
nal element for each transition, determined as described above. The experimental
and calculated results are shown in Table 3.

It can be seen in Table 3 that the agreement between the calculated and
observed transition energies is quite good. In fact, when one considers the sim-
plicity of the model and that it includes no consideration of the effects of con-
figuration interaction which might be expected to be large in these systems,
the agreement is remarkable. For this series of closely related molecules one migh

TABLE 3

EXPERIMENTAL ^{a} AND CALCULATED TRANSITION AND IONIZATION ENERGIES FOR SOME SUBSTITUTED ANILINES

	Transition			
	IP	LE_α	CT_s	CT_a
β^*	2.964	2.964	3.389	2.543
Substituent	Found (calcd)	Found (calcd.)	Found (calcd.)	Found (calcd.)
H	7.62	4.176	4.958	6.169
p-Me$_3$C	7.44	4.138	4.924	6.135
	(7.46)	(4.123)	(5.006)	(6.154)
p-Me$_3$Si	7.74	4.217	4.711	6.111
	(7.54)	(4.203)	(4.358)	(6.229)
p-Me$_3$Ge	7.68	4.168	4.775	6.093
	(7.53)	(4.191)	(4.402)	(6.220)
m-Me$_3$Si	7.56	4.050	4.861	5.863
	(7.51)	(3.684)	(4.914)	(4.547)

^{a} Given in eV using an α value of —6.30 eV.

expect the contributions of the various electron configurations to the excited states to be similar, in which case our β^* parameter would include these effects. We feel that the inherent uncertainty in the ionization potentials does not warrant a more sophisticated treatment of the data including configuration interaction at this juncture.

Nevertheless one further comparison of the experimental and calculated transition energies is cogent. The largest disparities occur for those transitions to states with large π densities at the point of silicon or germanium substitution: the CT_s for the *para* substituted compounds, and the LE_α and CT_a for the *meta*-trimethylsilyl compound. For each of these transitions the calculated energy is about 0.3 eV lower than the experimental value. This suggests that the simple Hückel model tends to overemphasize interactions between silicon or germanium and the π^* molecular orbitals. Indeed, recent results of Sipe and West show that modified values of the h and k parameters in the simple Hückel approximation, used to scale the coulomb and resonance integrals of the ordinary carbon—carbon bond to those for the heteroatom, give much better correlations with spin density in a series of trimethylsilyl-substituted benzene radical anions [13].

Acknowledgement

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