

# Substituted *N,N*-Dialkylanilines: Relative Ionization Energies and Proton Affinities through Determination of Ion-Molecule Reaction Equilibrium Constants

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The relative ionization energies and proton affinities of *N,N*-dimethyl-, *N,N*-diethyl-, and *N,N*-di-*n*-propylaniline, and meta- and para-methyl-substituted analogues (as well as *N,N*,3,5-tetramethylaniline and 4-chloro-*N,N*-diethylaniline) have been determined in the gas phase through measurements of the equilibrium constants of charge-transfer and proton-transfer reactions in an ion cyclotron resonance spectrometer. Absolute values are assigned to the ionization energies and proton affinities generated in these experiments. Comparison standards were the ionization potential (7.12 eV) and proton affinity (223.4 kcal/mol) for *N,N*-dimethylaniline taken from the literature. The heats of formation of the parent radical cations,  $M^+$ , and the corresponding protonated molecules,  $MH^+$ , vary in the same way, differing from one another by  $21 \pm 2$  kcal/mol over the entire set; that is, the radical cations of these compounds display a constant hydrogen affinity of  $74 \pm 2$  kcal/mol. This is interpreted to mean that all the compounds protonate at the nitrogen atom; previous work had suggested that meta-substituted isomers protonate on the ring. Further, it is demonstrated that variations in both the ionization energy and the proton affinity values upon changes in ring substitution can be predicted from the appropriate Hammett  $\sigma$  values, but not from the corresponding  $\sigma^+$  values; changes brought about by differing *N*-substituents correlate with  $\sigma^*$  values.

## Introduction

In recent years, developments in kinetic mass spectrometry have permitted the determination of equilibrium constants for ion-molecule equilibria in the gas phase.<sup>2-4</sup> Using this approach, an abundance of information about the thermochemistry of gas-phase ions has been generated:

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

For example, scales of relative basicities of numerous organic compounds have been derived from overlapping series of proton-transfer equilibrium constants;<sup>2</sup> quantitative information about the differences in the heats of formation of alkylcarbonium ions has been obtained from equilibrium constants of hydride-transfer and halide-transfer reactions.<sup>3</sup> Finally, studies of charge-transfer equilibria<sup>4</sup>



have been shown to give information about the relative adiabatic ionization energies of molecules A and B. That

is, the Gibbs free change associated with reaction 2 at any particular temperature is obtained from the equilibrium constant:

$$K_{eq} = ([B^+]/[A^+])([A]/[B]) \quad (3)$$

If the entropy change of reaction 2 is determined (by measuring the equilibrium constant as a function of temperature) or can be reliably estimated, the corresponding enthalpy changes of the reaction are obtained. In the case of charge-transfer reaction 2, the  $\Delta H^\circ$  of reaction corresponds to the difference in the adiabatic ionization energies of A and B.

This study was undertaken in an attempt to directly determine the relative free energies of ionization of *N,N*-dialkylanilines from observations of charge-transfer equilibria in the gas phase. These quantities are of interest for predicting the reactivities of the substituted anilines as initiators of polymerization; it has been shown that the initiation mechanism involves the formation of a charge-transfer complex and thus can be correlated with the ionization potentials of the initiating compounds.<sup>5</sup>

Most ionization energy data for this class of compounds have been obtained from analyses of the spectra of charge-transfer complexes. That is, in electron donor-

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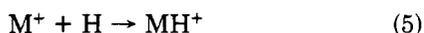
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acceptor complexes, absorption bands characteristic of neither the isolated donor or acceptor molecules are observed; these arise from a transition from the ground state of the molecular complex to an excited state in which an electron is largely transferred from the donor to the acceptor molecule. The maximum of this charge-transfer band,  $E_{ct}$ , is related to the ionization potential of the electron donor by the relationship

$$E_{ct} = IP - EA + C \quad (4)$$

where IP is the gas-phase ionization potential of the electron donor, EA is the gas-phase electron affinity of the acceptor, and C is a collective term for the solvation, polarization, and nonbonding contributions to the energy. Thus most of the quantitative ionization potential data on *N,N*-dialkylanilines<sup>6</sup> which can be related to the reactivity of this class of compounds as polymerization initiators have been obtained from such spectroscopic measurements made on charge-transfer complexes such as those proposed as intermediates in the initiating mechanism.<sup>5</sup> The possibility exists that the values may be influenced by the nature of the acceptor molecule or by solvent effects. Ionization potential data that are independent of the identity of the acceptor molecule or solvent could of course be obtained through standard mass spectrometric or photoelectron spectroscopic ionization onset measurements. Such determinations, however, are carried out individually for each separate compound, and the error limits on the absolute ionization potentials are usually sufficiently large that relative trends are not well-known for a series of compounds having similar ionization energies. Furthermore, at the present time few such values are available for substituted *N,N*-dialkylanilines.

It has also been seen that the ionization energies of organic molecules correlate with the corresponding proton affinities (PA). For example, it is a general observation that the hydrogen affinity of the parent radical cation is constant for a structurally or functionally related series of molecules.<sup>7</sup> The hydrogen affinity corresponds to the negative of the enthalpy change associated with the hypothetical process



Thus, the hydrogen affinity (HA) is given by

$$HA = \Delta H_f(M^+) + \Delta H_f(H) - \Delta H_f(MH^+) \quad (6a)$$

$$HA = IP + \Delta H_f(H) + PA - \Delta H_f(H^+) \quad (6b)$$

$$HA + 313.6 \text{ kcal/mol} = IP + PA \quad (6c)$$

Since HA is usually a constant for a particular compound type, a decrease in the ionization potential is predicted to be matched by an increase in the proton affinity in going from one molecule of a series to another of that series. Therefore, in the experiments reported here, the relative gas basicities of the various reacting pairs were determined from observations of the proton-transfer equilibrium constants



where the gas basicity is the free energy change associated

with reaction 7 and the proton affinity is the corresponding enthalpy change.

$$K_{eq} = ([AH^+]/[BH^+])([B]/[A]) \quad (8)$$

These results are interpreted in terms of the proton affinities of the *N,N*-dialkylanilines, and the correlation given in eq 6 is tested.

### Experimental Section

The experiments were performed in the NBS pulsed ion cyclotron resonance spectrometer which has been described before.<sup>8</sup> The experiments were completed before the recent modifications of the detection system of the instrument.<sup>8b</sup> Briefly, the two gases of interest are introduced into the reaction chamber of the spectrometer at a total pressure of approximately  $10^{-6}$  torr, and ionization is effected by a 3-ms pulse of 30-eV electrons (relative concentration of neutrals and ions, 1:10<sup>6</sup>). Since the reaction chamber is located between the poles of a magnet (magnetic field, 1.4 T), the positively charged ions are constrained to cyclic motion in the field and can be trapped for times as long as several seconds; under these conditions the ions undergo a sufficient number of collisions with the neutral molecules in the system that equilibria such as those represented in eq 2 and 7 can be achieved. The ions A<sup>+</sup> and B<sup>+</sup> or AH<sup>+</sup> and BH<sup>+</sup> were detected as a function of time using the detection system described elsewhere.<sup>8b,9</sup> The equilibrium constants (eq 3 and 8) then are simply obtained from the relative abundances of the reacting ions at long times (where the ratio of the abundances becomes constant in systems at equilibrium) and the known relative concentrations of compounds A and B. The temperature was measured by two thermocouples attached to the reaction cell, one in the vicinity of the filament and one at the opposite side of the cell. As described elsewhere,<sup>8</sup> the effective temperature of the reaction can be taken to be about 10 degrees higher than the temperature of the "cool" side of the cell.

Because the substituted *N,N*-dialkylanilines studied here have very low vapor pressures, and the instrument was not equipped with a specialized inlet system for such substances at the time these experiments were carried out, it was necessary to allow the various compounds to equilibrate their vapors in separate chambers of the inlet system for several hours before introducing the gases into the reaction chamber. After the two particular gases for a given set of measurements were introduced through two separate inlet systems and their pressures were measured with an ionization gauge, the charge-transfer equilibrium constants were determined. Then an excess of methane was added to form the MH<sup>+</sup> ions through proton transfer from CH<sub>5</sub><sup>+</sup>, and the proton-transfer equilibrium constant was determined. In every determination, the corrections were made for the presence of <sup>13</sup>C-labeled ions having a chemical identity the same as that of the ion one mass unit lower. Each reported equilibrium constant is an average of at least three determinations.

### Results and Discussion

Table I lists the equilibrium constants for charge-transfer reaction 2, and Figure 1 shows the resulting thermodynamic ladder of relative free energies of ionization of the substituted *N,N*-dialkylanilines. For most compounds included in the ladder, it can be seen in the figure that the precision of the various overlapping measurements of  $\Delta G^\circ$  is about 0.2–0.3 kcal/mol; because of the low vapor pressures of these compounds, the precision of these measurements is somewhat lower than that for similar determinations reported earlier for the alkyl- and halobenzenes.<sup>4</sup>

Let us consider the relationship of the values of  $\Delta G^\circ$  of reaction 2 given in Figure 1 to the differences in ionization

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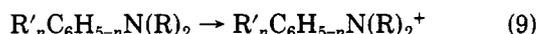
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Table I. Equilibrium Constants for Charge Transfer Processes [ $A^+ + B \rightleftharpoons B^+ + A$ ] in Substituted *N,N*-Dialkylanilines

A	B	T, K	$K_{eq}$	$\Delta G^\circ$ , kcal/mol
3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	320	4.5	-1.0
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	325	4.3	-0.9
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	283	4.1	-0.8
		327	5.7	-1.1
		346	4.8	-1.1
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	325	2.1	-0.5
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	325	1.4	-0.2
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	325	1.9	-0.4
C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	3-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	4.2	-0.9
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	3-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	4.8	-1.0
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	54	-2.6
C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	288	44	-2.2
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	550	20	-3.3
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> <sup>a</sup>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	550	61	-4.5

<sup>a</sup> Results from ref 11.

energies of the various compounds. The free energy changes of reaction 2 will be closely similar to the differences in the adiabatic ionization energies of A and B only if changes in symmetry or electronic degeneracy in the ionization process cancel for the two half reactions so that the entropy change of reaction 2 is close to zero. Since all the compounds studied here are *N,N*-dialkylanilines, each equilibrium measurement will involve two half reactions, both of which can be represented as



(where R and R' are alkyl groups). Any entropy changes associated with, for instance, a change of geometry upon ionization will be cancelled in the overall reaction, and it would be expected that these charge-transfer reactions would have no net entropy changes. It should be pointed out that in a previous study<sup>4</sup> carried out on the same ion cyclotron resonance instrument as that used here, the relative free energies of ionization of more than 40 organic compounds, primarily aromatics, were determined, and for reactions involving similar compounds (where changes in symmetry or the spin degeneracy of the electronic state cancelled for the two half reactions representing the ionization process) it was seen that the entropy changes were indeed close to zero. The scale of relative ionization energies derived from those results was seen to reproduce the energy differences between spectroscopically determined ionization potentials of the compounds within error limits of  $\pm 0.2$  kcal/mol or less in most cases. One result is given in Table I in which the temperature of the equilibrium constant determination was varied. Since, as expected, there is no effective change in the value of the free energy change with temperature, it can be concluded again that the measured values of  $\Delta G^\circ$  are effectively equal to the differences in the adiabatic ionization energies of A and B at a temperature in the range of 300 K. The scale of free energy changes (Figure 1) can therefore be equated with a corresponding scale of adiabatic ionization energies. The scale of relative ionization energies shown in Figure 1 is put on an absolute basis taking the well-established adiabatic ionization energy of *N,N*-dimethylaniline as a standard.<sup>10</sup> The ionization energy of this compound,  $7.12 \pm 0.03$  eV, is higher than that of other compounds studied here by a sufficiently large amount that a satisfactory

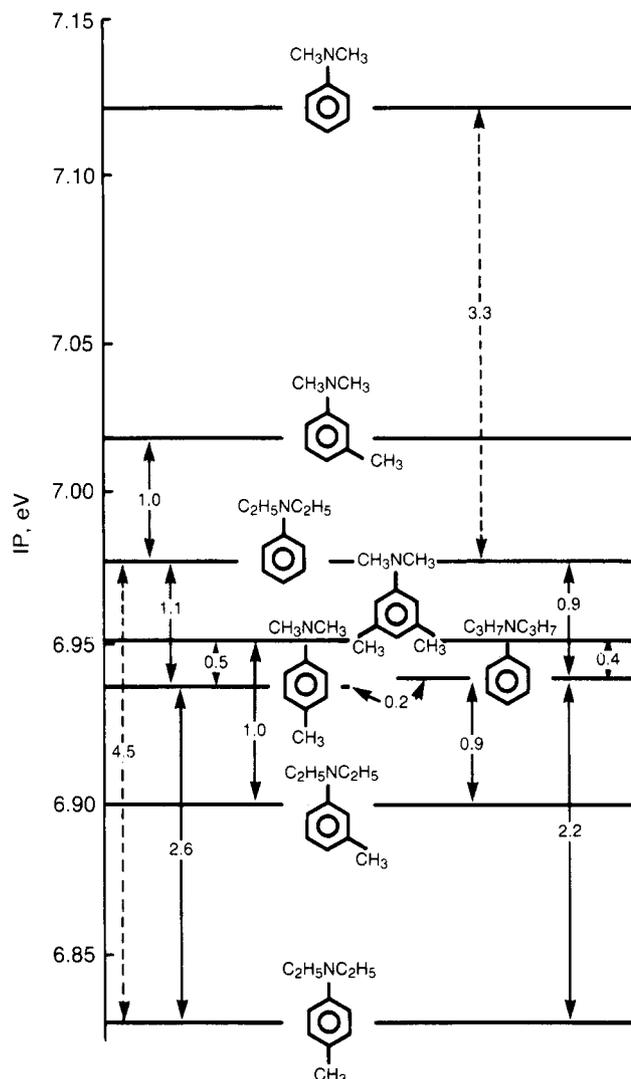


Figure 1. Thermochemical ladder showing the free energy changes (in kcal/mol) associated with charge-transfer reaction 2 derived from the equilibrium constant measurements presented in Table I. Since (see Discussion) these free energy changes can be assumed to be equal to the enthalpy changes for the reactions, the scale is effectively a scale of relative ionization energies; based on a value for the ionization potential of *N,N*-dimethylaniline of 7.12 eV (see Table II), the absolute ionization potential values shown on the scale at the left can be assigned. Free energy change values indicated by dotted lines were reported in ref 11.

equilibrium could not be achieved under the conditions of the ICR experiments (where the maximum  $\Delta G^\circ$  which can be measured is about 3 kcal/mol). Therefore, the ionization energy of this compound was related to the

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Table II. Ionization Energies (IE) of *N,N*-Dialkylanilines

compound	IE, eV		technique <sup>b</sup>	ref
	this work	lit.		
$C_6H_5N(CH_3)_2$		7.14	PI	10a
		7.13	PI	10b
		7.10	PI	10c
		7.10	PE	10d
		7.11	PE	10e
		7.15	PE	10f
		7.31	CTS	6a
		7.2	CTS	6b
		7.2	CTS	6c
		7.42	CTS	6d
	7.12*	evald		
$3-(CH_3)C_6H_4N(CH_3)_2$	7.02	7.06	PE	10e
$4-(CH_3)C_6H_4N(CH_3)_2$		7.35	CTS	6e
	6.93	6.95	CTEQ	11
		6.95	PE	10e
		6.9	PE	10g
$3,5-(CH_3)_2C_6H_3N(CH_3)_2$		7.33	CTS	6e
	6.95	7.25	CTS	6e
$C_6H_5N(C_2H_5)_2$		6.95	PE	10d
	6.98 <sup>a</sup>	6.95	CTEQ	11
		6.98	CTS	6e
		6.99	CTS	6e
	7.15	CTS	6f	
$3-(CH_3)C_6H_4N(C_2H_5)_2$	6.90	6.81	CTEQ	11
$4-(CH_3)C_6H_4N(C_2H_5)_2$	6.84	6.93	CTS	6e
$C_6H_5N(C_3H_7)_2$		6.93	CTS	6e
		6.96	CTS	6e
		7.15	CTS	6e

<sup>a</sup> Ionization energy scale standardized relative to this value; taken from equilibrium constant determination reported by Meot-Ner et al., relative to the ionization potential of *N,N*-dimethylaniline (evaluation shown here). See Discussion for reasoning leading to equating of relative free energy changes to relative enthalpy changes (i.e., to differences in ionization energies). <sup>b</sup>PI = photoionization onset; PE = photoelectron spectroscopy; CTEQ = charge-transfer equilibrium constant determination (high-pressure mass spectrometer); CTS = from optical spectrum of charge-transfer complex (eq 4).

thermodynamic ladder determined here by using the charge-transfer equilibrium constant determinations reported by Meot-Ner et al. (shown in Figure 1) from a high-pressure mass spectrometry study.<sup>11</sup>

Table II shows the ionization energies for this series of compounds assigned from the thermodynamic ladder of Figure 1 and taking the absolute value for the adiabatic ionization potential of *N,N*-dimethylaniline as base. These values are compared with ionization energies from the literature for those molecules for which other determinations have been made. The agreement with ionization energies from photoelectron spectroscopy and with the results of the equilibrium constant measurements in the high-pressure mass spectrometry study is good. These results demonstrate, however, that values for ionization energies estimated from charge-transfer spectra<sup>6</sup> (eq 4) show considerable scatter and often tend to be significantly higher than the correct adiabatic values. (A comparison of these values of ionization energies from charge-transfer spectra with the photoelectron spectra of these compounds, where available,<sup>10d-g</sup> demonstrates that these elevated values of the ionization energies can be attributed to experimental error since they do not correspond to either the vertical ionization potentials or to excited states of the ions.<sup>10d-g</sup>)

Table III gives the equilibrium constants and corresponding values of  $\Delta G^\circ$  determined from proton transfer reactions in these systems. Making the assumption that for these structurally related compounds, the entropy

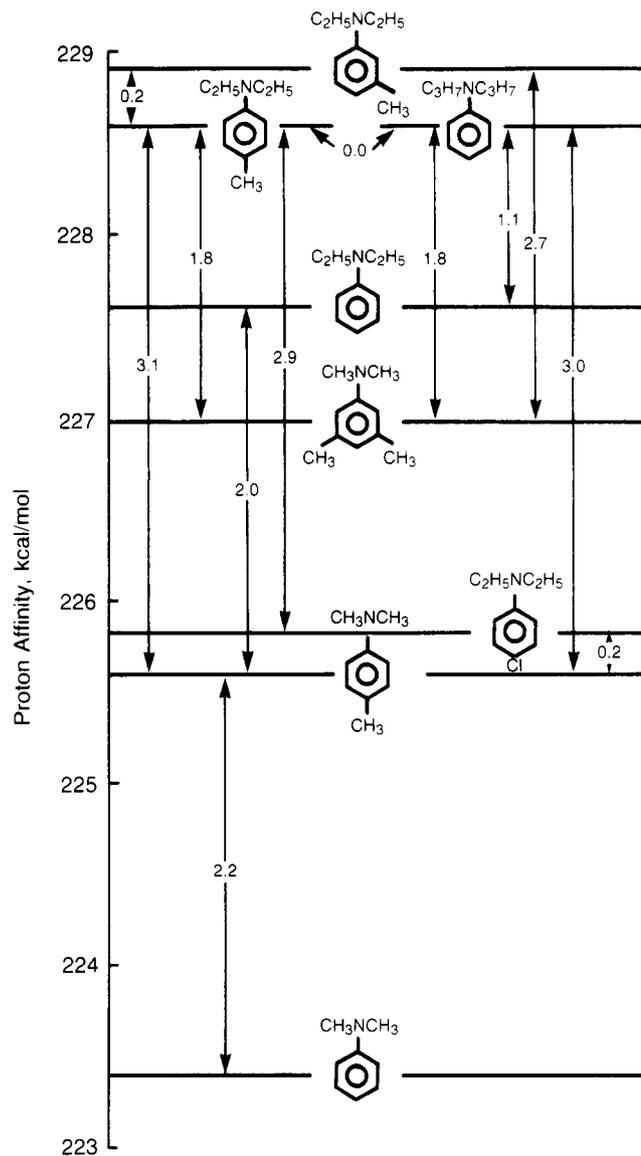


Figure 2. Thermochemical ladder showing the free energy changes (in kcal/mol) associated with proton-transfer reaction 7 derived from the equilibrium constant measurements presented in Table III. Since (see Discussion) these free energy changes can be assumed to be equal to the enthalpy changes for the reactions, the scale is effectively a scale of relative proton affinities; on the basis of a value for the proton affinity of *N,N*-dimethylaniline of 223.4 kcal/mol (ref 2a), the absolute proton affinity values shown on the scale at the left can be assigned.

change associated with reaction 7 will be effectively zero, the resulting scale of gas basicities shown in Figure 2 can be equated to the relative proton affinities for these compounds. Taking the previously determined value for the proton affinity of *N,N*-dimethylaniline, 223.4 kcal/mol, as base, absolute values can be assigned to this scale, as shown in Figure 2 and in Table IV.

The results obtained in this study are summarized in Table IV, where the absolute values assigned to the ionization energies and proton affinities are listed, and the values for the hydrogen affinities derived from eq 6 are also given. Results from the literature for the ionization energy<sup>12</sup> and proton affinity<sup>2+</sup> of aniline are included for purposes of comparison. It is seen that the heats of formation of the parent radical cations and the corresponding

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**Table III. Proton-Transfer Equilibrium Constants for Reactions [AH<sup>+</sup> + B → BH<sup>+</sup> + A] in Substituted *N,N*-Dialkylaniline Mixtures**

A	B	T, K	$K_{eq}$	$\Delta G^\circ$ , kcal/mol
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	318	35	-2.2
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	106	-3.0
4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	324	120	-3.1
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	68	-2.7
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	325	16	-1.8
C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	288	1.0	-0.0
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	325	5.7	-1.1
C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	1.3	-0.2
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	325	17	-1.8
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	288	35	-2.0
4-ClC <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	335	79	-2.9
4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	4-(ClC <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> )	325	1.4	-0.2

**Table IV. Ionization Energies (IE) and Proton Affinities (PA) of Substituted *N,N*-Dialkylanilines and Hydrogen Affinities (HA) of Corresponding Parent Radical Cations from Results of This Study**

M	$\Delta H_f(M)^a$	IE, eV (300 K)	$\Delta H_f(MH^+)^f$	PA	$\Delta H_f(MH^+)^f$	HA(M <sup>+</sup> )
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> <sup>b</sup>	21	7.68	198	209.5	177	73
C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	24	7.12 <sup>c</sup>	188	223.4 <sup>d</sup>	166	74
3-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	16	7.02	178	(224.5) <sup>e</sup>	(157) <sup>e</sup>	(73)
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(CH <sub>3</sub> ) <sub>2</sub>	17	6.93	177	225.6	157	72
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>	8	6.95	168	227.0	147	73
C <sub>6</sub> H <sub>5</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	9.5	6.98	171	227.6	148	74
3-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1	6.90	160	228.9	138	75
4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	3	6.83	160	228.6	140	72
4-ClC <sub>6</sub> H <sub>4</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>				225.6	142	
C <sub>6</sub> H <sub>5</sub> N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	1	6.93	161	228.6	138	75

<sup>a</sup> Reference 2a (kcal/mol). <sup>b</sup> Ionization energy (0 K) from ref 10; proton affinity from ref 2a. <sup>c</sup> Standard for relative ionization energy scale, see Table II. <sup>d</sup> Standard for relative proton affinity scale.<sup>2a</sup> <sup>e</sup> Result from ref 13c. <sup>f</sup> Cation heats of formation given using the stationary electron convention in which the integrated heat capacity of the electron is taken as zero at all temperatures.

**Table V. Summary of Hydrogen Affinities (HA) of Substituted Anilines<sup>a</sup>**

	HA, kcal/mol		HA, kcal/mol
aniline (N)	73	4-methylaniline (N)	72
3-methylaniline (C <sup>13b,c</sup> /N <sup>13a</sup> )	74	4-methyl- <i>N,N</i> -dimethylaniline (N)	72
<i>N</i> -methylaniline (N)	73	4-methyl- <i>N,N</i> -diethylaniline	72
<i>N</i> -methylaniline (N)	73	3-methoxyaniline (C) <sup>b</sup>	~74
<i>N,N</i> -dimethylaniline (N)	74	4-methoxyaniline (N) <sup>b</sup>	~64
3-methyl- <i>N,N</i> -dimethylaniline (N)	73	1,3-diaminobenzene (C <sup>13a</sup> )	74
<i>N,N</i> ,3,5-tetramethylaniline	74	1,4-diaminobenzene (N <sup>13a</sup> )	61
<i>N</i> -ethylaniline (N)	75	toluene (C) <sup>b</sup>	79
<i>N,N</i> -diethylaniline (N)	75	<i>m</i> -xylene (C) <sup>b</sup>	79
3-methyl- <i>N,N</i> -diethylaniline	74	<i>o</i> -xylene (C) <sup>b</sup>	77
<i>N,N</i> -dipropylaniline	75		

<sup>a</sup> N = conclusion reached in ref 13 that this compound is a nitrogen base. C = conclusion reached in ref 13 that this compound protonates on the aromatic ring. <sup>b</sup> Hydrogen affinities for these compounds calculated from data given in ref 2a and 12.

protonated molecules differ by  $21 \pm 2$  kcal/mol for the entire set. That is, the hydrogen affinities of the *N,N*-dialkylaniline cations are indeed constant.

In solution, anilines are known to undergo protonation at the nitrogen atom, but in the gas phase, evidence has been presented<sup>13</sup> that certain substituents on the ring, especially at the meta position, may cause the favored site of protonation to be on the ring. On the other hand, it has been suggested<sup>13</sup> that electron-donating groups in the para position or on the nitrogen stabilize the nitrogen base, causing nitrogen protonation to be favored. These conclusions were based on (a) comparisons of relative gas-phase basicities determined experimentally with those predicted from theory or from comparisons with trends in series of compounds known to protonate on the ring, (b) correlations of gas-phase basicities with solution basicities, where protonation is known to occur at the nitrogen

atom, or (c) correlations of gas-phase basicities with the experimental nitrogen 1s core electron ionization energies. Since the hydrogen affinity is simply the bond energy of the M<sup>+</sup>-H bond, one might expect that this quantity would differ for species protonated on the nitrogen atom or on the aromatic ring. To test this, an examination of the hydrogen affinities of the ions generated in 3-methoxyaniline and 4-methoxyaniline or in 1,3- and 1,4-diaminobenzene is useful. It was concluded in the earlier studies<sup>13a,b</sup> that 4-methoxyaniline and 1,4-diaminobenzene protonate at the nitrogen atom, while in both cases, the meta isomers protonate on the aromatic ring. (In the case of 3- and 4-methoxyaniline, both correlations with solution-phase basicity data,<sup>13b</sup> and a correlation with nitrogen ionization energies<sup>13a</sup> led to the same conclusion.) Values for the hydrogen affinities for the methoxyanilines and diaminobenzenes based on ionization potential<sup>13</sup> and proton affinity<sup>2a</sup> data from the literature are given in Table V. The ionization potentials of the methoxyanilines are not well established, and absolute values cannot be confidently assigned to the hydrogen affinities, but it appears (based on an internally consistent set of ionization potential determinations<sup>12</sup>) that the hydrogen affinity for the

(13) (a) Lau, Y. K.; Nishizawa, K.; Tse, A.; Brown, R. S.; Kebarle, P. *J. Am. Chem. Soc.* 1981, 103, 6291. (b) Summerhays, K. D.; Pollack, S. K.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* 1977, 99, 4585. (c) Pollack, S. K.; Devlin, J. L. III; Summerhays, K. D.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* 1977, 99, 4583.

para-substituted isomer is significantly lower than that of the meta-substituted compound, as is also the case for the diaminobenzene isomers, thus confirming our supposition that carbon protonation and nitrogen protonation should lead to differing values of the hydrogen affinity.

Table V also shows the hydrogen affinities for all the species studied here, as well as those of some related compounds which have been calculated from data in the literature.<sup>2,12</sup> The identification of these species as "carbon" or "nitrogen" bases from the earlier studies is also shown in the table. All the compounds except the para-substituted isomers exhibit hydrogen affinity values of  $74 \pm 1$  kcal/mol; values for para-substituted compounds are slightly lower ( $\sim 72$  kcal/mol). The interpretation of this result may be (a) our assumption that H atom affinities will differ for these carbon-protonated and nitrogen-protonated species is incorrect or more likely (b) that all these alkyl-substituted aromatic amines are protonated at the same site. It is not difficult to rationalize the conclusion that the meta-substituted anilines are not different in their site of protonation from the para-substituted compounds or compounds with no ring substituents; the conclusion that the meta-substituted compounds were carbon bases was based on a lack of correlation of the solution and gas basicities of 3-methoxyaniline and 3-methylaniline.<sup>13a</sup> However, a reexamination of those earlier results taking into account a reevaluation of the proton affinity scale<sup>2a</sup> shows that the 3-methylaniline (but not the 3-methoxyaniline) does correlate reasonably well with the solution phase data. This compound also was shown to correlate well with nitrogen 1s ionization energies,<sup>13a</sup> and the authors of that study concluded that its site of protonation did not necessarily differ from that of its isomers. It appears most likely that all the compounds of interest in this study protonate on the nitrogen atom.

Since the reactivities of the *N,N*-dialkylanilines as polymerization initiators have often been described in terms of the usual extra thermodynamic parameters, it might be expected that the trends in ionization energies and proton affinities with molecular structure could also be described in the language of linear free energy relationships

$$\log K/K^\circ = (\rho)(\sigma^x) \quad (10)$$

(where  $K$  is the rate constant or equilibrium constant of interest,  $K^\circ$  is the corresponding quantity for a reference compound or reaction, and  $\sigma^x$  is  $\sigma^+$ ,  $\sigma^*$ , or  $\sigma$ , as appropriate). In previous studies, kinetic data for initiating mechanisms with the electron-accepting constituent of the complex were predicted from the  $\sigma^+$  values for the ring substituents of the amine.<sup>5</sup> Similarly, variations in reactivity occurring when the substituents on the nitrogen atom of the amine are changed were correlated with the appropriate  $\sigma^*$  values that measure the inductive effect associated with a particular group, with respect to a reactive center.

It is seen that changes in both ionization energies and proton affinities as reported here do, as expected, correlate with the appropriate  $\sigma^*$  values when the nitrogen substituent is varied. Although the results of this study provide few experimental points with which to establish such a comparison, a statistical analysis of the changes brought about in ionization energies or proton affinities by variations in the identity of ring substituents indicates that correlation with Hammett  $\sigma$  values is better than correlation with  $\sigma^+$  values, which express resonance interactions between electron-supplying substituents and electron-deficient centers of the reacting system. For example, coefficients of determination for plots of the ionization energies of *N,N*-dimethylanilines with no ring substituents or with meta- and with para-methyl groups are 0.981 for correlation with  $\sigma$  and 0.545 for correlation with  $\sigma^+$ ; a similar analysis of the corresponding proton affinity data leads to coefficients of determination of 0.988 for correlation with  $\sigma$  and 0.900 for  $\sigma^+$ . The data for the diethylanilines lead to coefficients of determination of 0.979 ( $\sigma$  correlation) or 0.878 ( $\sigma^+$  correlation) for the ionization energies and 0.895 ( $\sigma$  correlation) or 0.567 ( $\sigma^+$  correlation) for the proton affinities. These results are apparently in contradiction to the prediction based on observed kinetic effects that the effects of ring substituents on the ionization potentials of substituted anilines should be related to the appropriate  $\sigma^+$  factors.<sup>5</sup>

### Conclusions

The ionization energies and proton affinities of *N,N*-dialkylanilines and their methyl-substituted analogues follow closely related trends in the gas phase; the heats of formation of the protonated molecules are, in every case,  $21 \pm 1$  kcal/mol lower than those of the corresponding molecular radical cations; i.e. the hydrogen affinities of the radical cations are all  $74 \pm 2$  kcal/mol. This invariance suggests that all these compounds undergo protonation on the nitrogen atom, including the meta-substituted isomers, which have previously been suggested to undergo ring protonation.<sup>13b,c</sup> Variations in the energy of ionization and of protonation with changes in molecular substituents can be correlated with  $\sigma^*$  factors for changes in the *N*-alkyl groups or with  $\sigma$  factors for changes in ring substituents.

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**Registry No.**  $C_6H_5N(CH_3)_2$ , 121-69-7; 3-( $CH_3$ ) $C_6H_4N(CH_3)_2$ , 121-72-2; 4-( $CH_3$ ) $C_6H_4N(CH_3)_2$ , 99-97-8; 3,5-( $CH_3$ ) $_2C_6H_3N(CH_3)_2$ , 4913-13-7;  $C_6H_5N(C_2H_5)_2$ , 91-66-7; 3-( $CH_3$ ) $C_6H_4N(C_2H_5)_2$ , 91-67-8; 4-( $CH_3$ ) $C_6H_4N(C_2H_5)_2$ , 613-48-9;  $C_6H_5N(C_3H_7)_2$ , 2217-07-4; 4- $ClC_6H_4N(C_2H_5)_2$ , 2873-89-4;  $C_6H_5NH_2$ , 62-53-3;  $H_2$ , 1333-74-0;  $H^+$ , 12408-02-5; 3-methylaniline, 108-44-1; *N*-methylaniline, 100-61-8; *N*-ethylaniline, 103-69-5; 4-methylaniline, 106-49-0; 3-methoxyaniline, 536-90-3; 4-methoxyaniline, 104-94-9; 1,3-diaminobenzene, 108-45-2; 1,4-diaminobenzene, 106-50-3; toluene, 108-88-3; *m*-xylene, 108-38-3; *o*-xylene, 95-47-6.