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Bond Dissociation Energies of the N–H Bonds in Anilines and in the Corresponding Radical Anions. Equilibrium Acidities of Aniline Radical Cations

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The homolytic bond dissociation energies (BDEs) for the N–H bonds in 21 anilines have been estimated by combination of the equilibrium acidities (pK_{HA}) and the oxidation potentials of their conjugate anions, $E_{ox}(A^-)$, in DMSO. The pK_{HA} and $E_{ox}(A^-)$ values for para-substituted anilinide ions have been found to be linearly correlated with Hammett σ^- constants, indicating that $E_{ox}(A^-)$ values for anilinide ions are dictated largely by their basicities and are perturbed to only a minor extent by the radical stabilizing or destabilizing effects of substituents. Detailed analyses of ΔpK_{HA} and $\Delta E_{ox}(A^-)$ values for substituted anilines, diphenylamines, and phenols and a comparison with values for α-substituted acetophenones have revealed close similarities in the ways in which substituents affect BDEs. The $pK_{HA^{\cdot+}}$ values for 19 radical cations derived from substituted anilines were found to fall in the range of 1.2–10, and $pK_{HA^{\cdot+}}$ values for 14 radical cations derived from diphenylamines and related compounds fell in the range of −0.13 to +4.7. A linear correlation of the oxidation potentials of anilines vs the acidities of the corresponding radical cations was observed. The BDEs of the N–H bonds in 10 radical anions derived from anilines, diphenylamines, and related compounds were estimated by a combination of the pK_{HA} values of the nitrogen acids with their reduction potentials. These estimates showed that addition of one electron weakened the N–H bonds by about 35–60 kcal/mol.

Introduction

In an earlier paper we reported estimates of the homolytic bond dissociation energies (BDEs) for the O–H bonds in 35 ortho-, meta-, and para-substituted phenols and the acidities of the O–H bonds in the corresponding radical cations.[1a] A plot of the oxidation potentials for meta-substituted phenoxide ions vs pK_{HA} values was found to be linear ($R^2 = 0.983$) over a range of 14 kcal/mol with a slope of −1.9 when both axes were expressed in kcal/mol, pointing to the presence of an inherent group electronegativity factor related to basicity that strengthens the O–H bonds in the phenols. (Henceforth kcal/mol will be abbreviated as kcal.) The bonds became progressively stronger as the electron-withdrawing power of the meta group increased, which was interpreted to mean that the stability of the corresponding radicals were being progressively destabilized by electron withdrawal. Estimates of radical stabilization energies (RSEs) were made from the ΔBDE values, relative to that of the O–H bond in phenol (~90 kcal). The RSEs (kcal) for para donor groups were found to increase in the following order: Me (1.1), *t*-Bu (1.1) < Ph (2.3) < MeO (5.3) < HO (8.3) < Me_2N (9.6) < NH_2 (12.6). The RSEs for para acceptor groups were found to be negative; i.e., the para acceptors destabilized the phenoxyl radicals in the following order: PhCO (−2.6) < MeCO (−2.9) < CN (−4.4) < NO_2 (−4.8) < CF_3 (−5.5). These radical-stabilizing and -destabilizing effects of donors and acceptors were attributed to the dual effects of substituents on radical stabilities, i.e., stabilizing by virtue of their ability to delocalize the odd electron, but destabilizing by virtue of their electron-withdrawing effects.[1b] A very good correlation ($R^2 = 0.992$) with a slope of 13.4 kcal was obtained for a plot of $E_{ox}(A^-)$ vs σ^+ over a range of greater than 40 kcal. (The slope was 9.8 when divided by 1.37 for comparison of pK_{HA} vs σ^+ plots.) A similar good correlation ($R^2 = 0.992$) was obtained for a plot of $E_{OX}(HA)$ vs $pK_{HA^{\cdot+}}$ for m-$GC_6H_4OH^{\cdot+}$ radical cations, but the points for para donors deviated from the line.[1a]

In the present paper we have estimated BDEs of the N–H bonds in 21 anilines, nine diphenylamines, and related nitrogen acids from pK_{HA} and $E_{ox}(A^-)$ values and compared the results with those for the phenols. The equilibrium acidities of anilines in dimethyl sulfoxide (DMSO) have been reported and discussed earlier.[2] At that time a Hammett plot ($\rho = 5.27$; $R^2 = 0.998$) was obtained for six meta points.

There is a paucity of data concerning the BDEs of N–H bonds in the literature. In their 1982 review McMillen and Golden gave BDE values for only seven N–H bonds; N–NH_2 (107 kcal), H–NHMe (100), H–N_3 (93), H–NMe_2 (91.5), H–NHPh (88), H–NMePh (87.5).[3] We have since reported BDEs for H–NHPh (92 ± 1), H–NPh_2 (87.5 ± 1), pyrrole (97), and hydrazoic acid (94)[4] and also for carbazoles,[5] carboxamides,[6a] thiocarboxamides,[6a] and amidines.[6b]

We have also reported estimates of radical cation acidities for numerous C–H acids,[7] but the only values for N–H acids that have been reported in the literature are

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Table I. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the N–H Bonds in Substituted Anilines and Acidities of the Corresponding Radical Cations

compd	pK_{HA}[a]	$E_{OX}(HA)$[c]	$E_{ox}(A^-)$[d]	$pK_{HA^{\bullet+}}$[e]	BDE_{HA}[f]
aniline ($C_6H_5NH_2$)	30.6	0.445	−0.992	6.4	92.3
p-$MeOC_6H_4NH_2$	32.5[b]	0.125	−1.188	10	90.4
p-$MeC_6H_4NH_2$	31.7[b]	0.305	−1.072	8.5	92.0
m-$MeOC_6H_4NH_2$	30.5	0.465	−0.919	7.2	93.9
p-$ClC_6H_4NH_2$	29.4	0.535	−0.915	5.0	92.4
m-$ClC_6H_4NH_2$	28.5	0.635	−0.855	3.4	92.6
o-$ClC_6H_4NH_2$	27.6	0.625	−0.779	3.9	93.1
p-$BrC_6H_4NH_2$	29.1	0.525	−0.905	5.0	92.3
m-$BrC_6H_4NH_2$	28.4	0.635	−0.825	3.8	93.2
p-$CNC_6H_4NH_2$	25.26	0.795	−0.550	2.6	95.2
o-$CNC_6H_4NH_2$	24.3	0.780	−0.497	2.8	95.1
m-$CNC_6H_4NH_2$	27.6	0.775	−0.735	2.1	94.1
p-$MeCOC_6H_4NH_2$	25.35	0.675	−0.600	3.9	94.2
p-$NO_2C_6H_4NH_2$	20.9	0.895	−0.227	2.0	96.7
m-$CF_3C_6H_4NH_2$	28.2	0.698	−0.701	4.6	95.7
p-$CF_3C_6H_4NH_2$	27.0	0.723	−0.597	4.7	96.5
3,5-$(CF_3)_2C_6H_3NH_2$	25.75	0.964	−0.491	1.2	97.2
m-$CF_3SO_2C_6H_4NH_2$	26.2	0.855	−0.584	1.9	95.7
o-NO_2-p-$ClC_6H_3NH_2$	18.9		−0.068		97.6
2,4,6-$Cl_3C_6H_2NH_2$	23.5		−0.433		95.5
C_6H_5NHMe	29.5	0.446	−1.054	4.2	89.3

[a] Equilibrium acidities measured in DMSO solution against two indicators or standard acids. The pK_{HA} values for most of these anilines have been reported earlier.[2] [b] Estimated from a linear Hammett correlation of pK_{HA} with σ^- for para-substituted anilines (see Figure 2). [c] In volts; irreversible oxidation potentials of neutral weak acids measured in DMSO solution. [d] In volts; irreversible oxidation potentials of the conjugate anions measured in DMSO solution. [e] Equilibrium acidities of radical cations estimated by using eq 2. [f] In kcal/mol, homolytic bond dissociation energies of the N–H bonds estimated by using eq 1.

those for phenothiazine (4–5 in H_2O[8] and 4.3 in DMSO[7a]), $Me_2NH^{\bullet+}$ (6.5–7.5 in H_2O),[9] and $PhNH_2^{\bullet+}$ (7 in H_2O).[10] We now report 33 $pK_{HA^{\bullet+}}$ values for radical cations derived from anilines, diphenylamines, and related compounds.

Results and Discussion

Hammett-Type Correlations for Anilines and Phenols. The equilibrium acidities of aniline and 20 of its ortho, meta, and para derivatives are summarized in Table I. A plot of the pK_{HA} values for weak para-acceptor and meta-substituted phenols in DMSO (p-MeO, H, p-Cl, p-Br, m-Cl, m-CF_3, m-CN) vs those of the corresponding anilines was linear ($R^2 = 0.989$) with a slope of 1.04.[2] A plot of the pK_{HA} values for para-substituted anilines vs σ^- (Figure 1) was much more scattered ($R^2 = 0.963$; $\rho^- = 7.6$ kcal), as was a corresponding σ_p^- plot (Figure 2) for phenols ($R^2 = 0.938$; $\rho^- = 6.5$).

Data for para-donor anilines is sparse because their low acidities make pK_{HA} measurements difficult in DMSO, and a plot of $E_{ox}(A^-)$ values vs σ^+ comparable to that observed for phenols ($\rho^+ = 13.4$ kcal) could not be made.

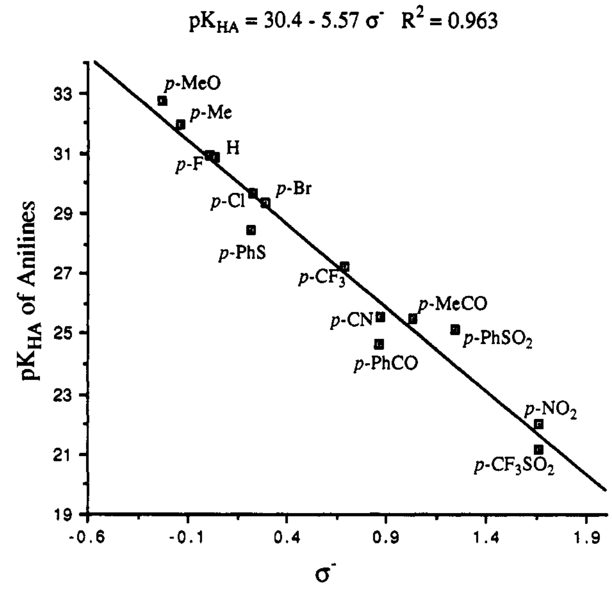

Figure 1. Correlation of the equilibrium acidities of para-substituted anilines measured in DMSO against Hammett σ^- constants (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195).

Three-point σ^+ plots for $E_{ox}(A^-)$ anilines and diphenylamines have ρ^+ values of 5.8 and 3.9 kcal, respectively (Figure 3), compared to $\rho^+ = 8.7$ kcal for the corresponding phenols, suggesting that phenoxyl radicals are more sensitive to stabilization by p-Me and p-MeO substituents than are the radicals derived from anilines and diphenylamines. But extrapolation of Figure 2 to a pK_{HA} value equal to that of phenol ($pK_{HA} = 18$) shows that, at the same basicity, the $E_{ox}(ArNH^-)$ value (−0.258 V) is close to the $E_{ox}(A^-)$ value for phenol (−0.328 V).

Substituent Effects on the BDEs of the N–H Bonds of Anilines. A good correlation with σ^- was found not only with the pK_{HA} values of para-substituted anilines but also with the oxidation potentials of their conjugate bases ($R^2 = 0.994$). These correlations require that an

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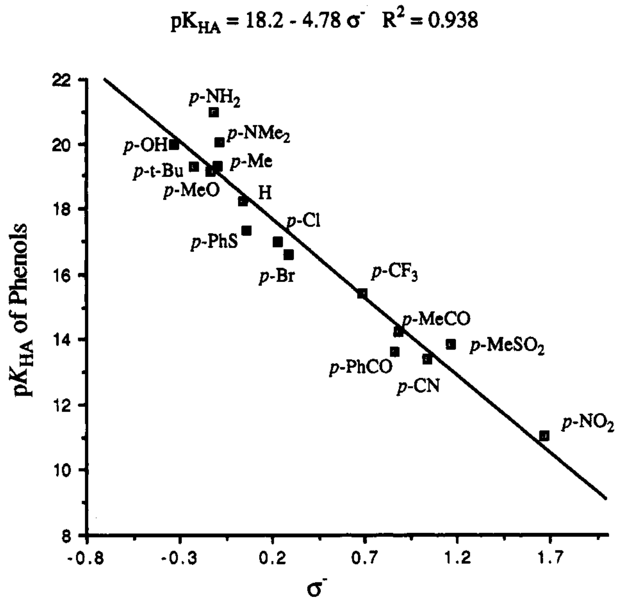


Figure 2. Correlation of the equilibrium acidities of para-substituted phenols measured in DMSO against Hammett σ^- constants (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195).

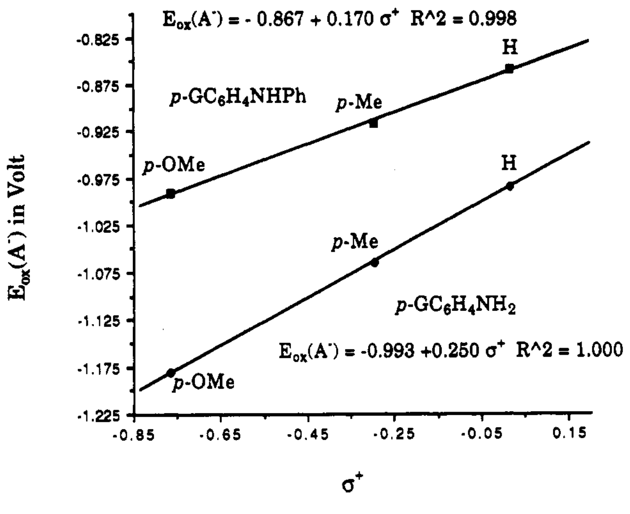


Figure 3. Plots of pK_{HA} values for para-substituted anilines and for para-substituted diphenylamines vs σ^+.

equally good correlation be observed for a plot of $E_{ox}(A^-)$ vs pK_{HA} (Figure 4). It follows from the linearity of Figure 4 that the $E_{ox}(A^-)$ values for anilinide ions are dictated largely by their basicities and are perturbed to only a minor extent by the radical stabilizing or destabilizing effects of substituents. A similar plot was obtained for the corresponding phenoxide ions (Figure 5).

The comparison of substituent effects on radical stabilization energies (RSEs) for phenols and anilines in Table II, as judged by ΔBDEs, shows that there is reasonably good agreement between the RSEs for moderate and strong meta- and para-electron-withdrawing groups, which all appear to be radical destabilizing (negative ΔBDEs), but the stabilizing effects of the donors (*p*-Me and *p*-MeO) are larger for phenoxyl than for anilinyl radicals. The points for *p*-MeO fall off the lines in Figures 4 and 5, but the points for stronger para-donors (*p*-HO, *p*-O⁻, *p*-Me$_2$N, *p*-H$_2$N) would deviate more strongly from Figure 5,[1a] and this would no doubt be true also for these points in Figure 4, if they could be obtained.

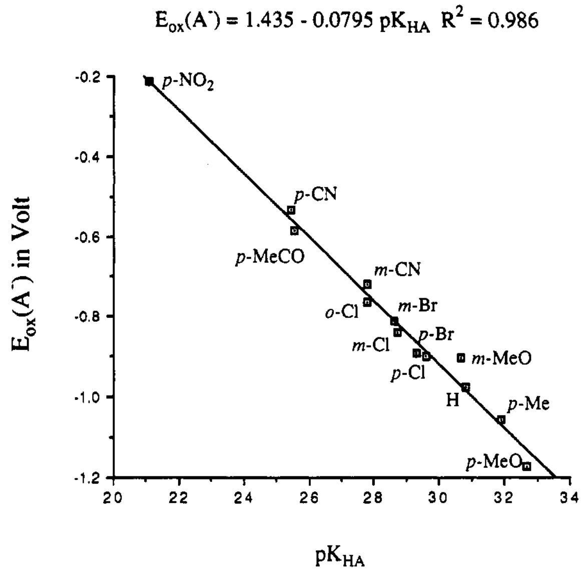


Figure 4. Linear correlation of the oxidation potentials of anilinides anions against their equilibrium acidities in DMSO.

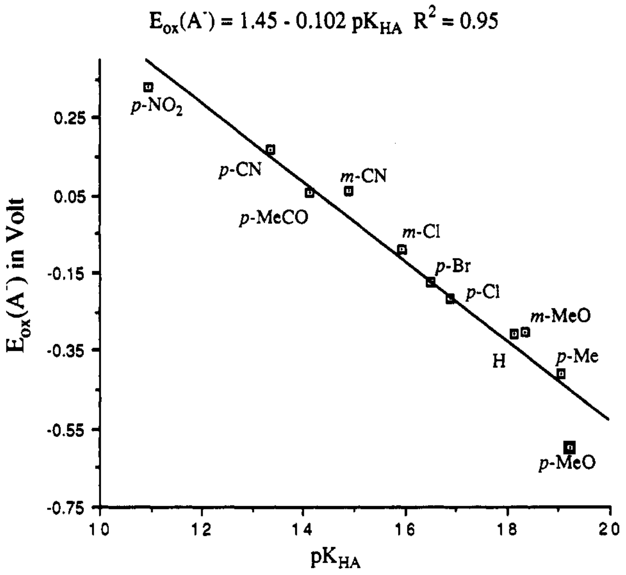


Figure 5. Linear correlation of the oxidation potentials of the phenoxides against their equilibrium acidities in DMSO.

Table II. Comparisons of Apparent Radical Stabilization Energies of Substituted Phenoxyl ($GC_6H_4O^•$) and Anilinyl ($GC_6H_4NH^•$) Radicals

G	RSE (ArO•)[a]	RSE (ArNH•)[a]
p-Me	1.1	0.35
m-MeO	–0.4	-1.5
p-MeO	5.3	1.9
m-Cl	-2.0	-1.1
p-Cl	–0.42	–0.2
p-Br	–0.86	–0.1
p-MeCO	-2.9	-1.8
m-CN	-4.1	-1.8
p-CN	-4.4	-2.9
p-NO$_2$	-4.8	-4.7
m-CF$_3$	-4.0	-4.0
p-CF$_3$	-5.5	-5.0

[a] Calculated in kcal/mol from the equation RSE = ΔBDE = 1.37ΔpK_{HA} + 23.1Δ$E_{ox}(A^-)$.[12a]

The apparent radical destabilizing effects indicated in Table II can be rationalized in terms of electron withdrawal[1a] or possibly in terms of ground-state lowering effects.

Table III. Effects of ΔpK_{HA} and $\Delta E_{ox}(A^-)$ Values on ΔBDEs for Structural Changes in Aniline, Diphenylamines, and Related Compounds[a]

no.	substrate	pK_{HA}[b]	ΔpK_{HA}	$\Delta E_{ox}(A^-)$[c]	ΔBDE[d]
1	$PhNH_2$ (see Table I)	41.9	(0.0)	(0.0)	(0.0)
2	Ph_2NH	34.2	7.7	−2.9	4.8
	Ph_2NH	34.2	(0.0)	(0.0)	(0.0)
3	4-$PhNHC_6H_4NHPh$	35.1	−0.9	9.1	8.2
4	4-$MeOC_6H_4NHPh$	35.3	−1.1	3.1	2.0
5	(4-$MeOC_6H_4)_2NH$	36.6	−2.4	5.7	3.3
6	4-MeC_6H_4NHPh	34.9	−0.7	1.3	0.6
7	3-MeC_6H_4NHPh	34.7	−0.5	0.36	−0.2
8	3-ClC_6H_4NHPh	31.5	2.7	−3.5	−0.80
9	(4-$BrC_6H_4)_2NH$	30.4	3.8	−4.3	−0.56
10	4-$NO_2C_6H_4NHPh$	23.1	11.1	−14	−2.9
11	phenoxazine (1)	29.6	4.6	3.2	7.8
12	phenothiazine (2)	31.1	3.1	2.1	5.2
13	carbazole (5)	27.3	6.9	−12.2	−5.3

[a] Data taken from ref 5. [b] In kcal/mol ($1.37pK_{HA}$). [c] In kcal/mol [$23.1\Delta E_{ox}(A^-)$]. [d] In kcal/mol, $\Delta BDE = \Delta pK_{HA} + \Delta E_{ox}(A^-)$.

The pK_{HA} of *N*-methylaniline is 1.1 units (1.5 kcal) lower than that of aniline, presumably due to the polarizability effect of the methyl group on the highly basic nitranion. This effect is augmented by the 1.4 kcal more negative $E_{ox}(A^-)$ value for the $PhNMe^-$ ion than that for the $PhNH^-$ ion, so the net result for the introduction of a methyl group is to decrease the BDE of the N–H bond by 3 kcal. Methyl substitutions into carbon acids have similar, but larger effects on BDEs. For example, the α-Me group in $PhCOCH_2Me$ decreases the BDE of the acidic C–H bond by 5 kcal.[13]

Equilibrium Acidities and BDEs of the N–H Bonds in Diphenylamines and Related Compounds. Substitution of a phenyl group for a hydrogen atom in NH_3 increases the acidity by about 10.5 pK_{HA} units (14 kcal)[2] and decreases the BDE from about 107 kcal[3] for H_2N–H to about 92 kcal for PhNH–H (Table I). Introduction of a second phenyl group increases the acidity by another 5.6 pK_{HA} units (7.7 kcal) and decreases the BDE by another 4.5 kcal. The BDE that we have estimated for Ph_2N–H of 87.5 kcal by eq 1 is identical to a recent value reported

$$BDE = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \qquad (1)$$

in the gas phase.[13c] If we accept this value, the BDE of 88 kcal for the N–H bond in PhNH–H chosen by McMillen and Golden[3] is obviously too low since the ΔBDE for the second Ph substitution would then be only 0.5 kcal. (The 0.5 kcal value chosen for Me substitution is also too low.) On the other hand, our ΔBDE of 4.5 kcal for the second phenyl substitution fits nicely with the corresponding C–H data, as shown below:

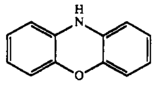
$$\begin{array}{llll} & \mathrm{H_2N{-}H} \xrightarrow{15\ \mathrm{kcal}} & \mathrm{PhNH{-}H} \xrightarrow{4.5\ \mathrm{kcal}} & \mathrm{Ph_2N{-}H} \\ \mathrm{BDE:} & 107\ \mathrm{kcal} & 92\ \mathrm{kcal} & 87.5\ \mathrm{kcal} \\ & \mathrm{H_3C{-}H} \xrightarrow{17\ \mathrm{kcal}} & \mathrm{PhCH_2{-}H} \xrightarrow{6\ \mathrm{kcal}} & \mathrm{Ph_2CH{-}H} \\ \mathrm{BDE:} & 105\ \mathrm{kcal} & 88\ \mathrm{kcal} & 82\ \mathrm{kcal} \end{array}$$

We have gained new insights into the origins of ΔBDE effects recently by a detailed analysis of the ΔpK_{HA} and $\Delta E_{ox}(A^-)$ values used in eq 1, as applied to α-substituent effects on the BDEs of the acidic C–H bonds in acetophenones.[13b] In Table III we have applied this analysis to the ΔBDE values of the N–H bonds in para-substituted diphenylamines and related compounds in order to make comparisons with similar substitutions for para-substituted phenols and α-substituted acetophenones.

We have seen that the structural change from $PhNH_2$ to Ph_2NH causes a 7.7 kcal increase in acidity. Examination of entry 2 in Table III shows, however, that this is accompanied by a 2.9 kcal shift in $E_{ox}(A^-)$ to a more positive potential, which leads to a net 4.8 kcal decrease in the N–H BDE. Similar effects are observed for introducing an α-phenyl group into acetophenone,[13] but here the 9.4 kcal decrease in pK_{HA} is *augmented* by a 0.9 kcal shift of $E_{ox}(A^-)$ to a more negative potential resulting in a 10.3 kcal decrease in the C–H BDE. The smaller Ph effect in Ph_2NH can be attributed to steric inhibition of resonance.

The introduction of PhNH groups into the 4 position of the benzene ring in Ph_2NH (entry 3) has a 8.2 kcal bond weakening effect, which is almost entirely the result of a shift in $E_{ox}(A^-)$ to a more negative potential. This is to be compared with the effects of a 4-Me_2N group in phenol (9.6 kcal[1]) and an α-Me_2N group in $PhCOCH_3$ (21 kcal),[13] which are also caused primarily by negative $E_{ox}(A^-)$ shifts (delocalization effects). Introduction of a 4-MeO group (entry 4) causes a 2.0 kcal decrease in BDE and a (second) 4′-MeO group causes a further 1.3 kcal decrease in BDE; both of these effects are due primarily to negative shifts in $E_{ox}(A^-)$. Negative $E_{ox}(A^-)$ shifts also account primarily for the effect of α-MeO substitution into acetophenone (12.5 kcal).[13] The same is true for the effect of 4-methyl substitution into (a) Ph_2NH (0.6 kcal) or (b) phenol (1.2 kcal)[1a] or (c) the α-Me substitution into $PhCOCH_3$ (4.9 kcal).[13] The small negative ΔBDEs for a 4-Br substituent in Ph_2NH (−0.56 kcal; entry 9) and in 4-BrC_6H_4OH (−0.80 kcal)[1a] and the larger effects for 4-NO_2 in Ph_2NH (−2.9 kcal; entry 10) and 4-$NO_2C_6H_4OH$ (−4.8 kcal)[1a] are due to positive shifts in $E_{ox}(A^-)$. Here the destabilizing effects on radicals caused by substituent electron withdrawal evidently overshadow the radical-stabilizing delocalization effects of these groups.

The effect of introducing an oxygen bridge into diphenylamine to form phenoxazine (1) is to increase the acidity and to shift $E_{ox}(A^-)$ to a more negative potential. These effects, both of which result from bringing the benzene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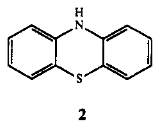
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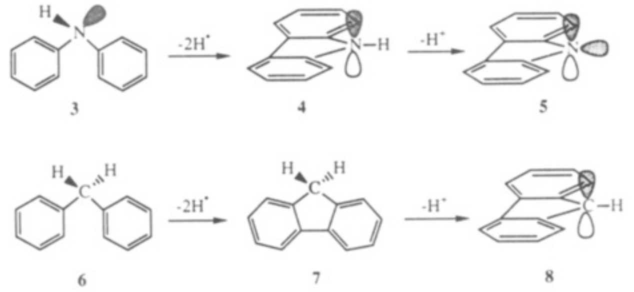
Table IV. Homolytic Bond Dissociation Energies and Radical Cation Acidities for the N–H Bonds in Substituted Diphenylamines and Related Substrates

compd	pK_{HA}[a]	$E_{OX}(HA)$[b]	$E_{ox}(A^-)$[c]	$pK_{HA^{\cdot+}}$[e]	BDE_{HA}[f]
diphenylamine (Ph_2NH)	24.95	0.455	−0.865	2.7	87.5
p-$MeOC_6H_4NHPh$	25.8	0.305	−0.998	3.8	85.6
p-MeC_6H_4NHPh	25.5	0.415	−0.923	2.9	86.9
m-MeC_6H_4NHPh	25.3	0.435	−0.881	3.1	87.6
m-ClC_6H_4NHPh	23.0	0.525	−0.712	2.1	88.4
(*p*-$MeOC_6H_4)_2NH$	26.7	0.195	−1.112	4.7	84.2
4-$PhNHC_6H_4NHPh$	25.6	0.025	−1.257[d]	4.0	79.2
(*p*-$BrC_6H_4)_2NH$	22.2	0.585	−0.676	0.94	88.1
p-$NO_2C_6H_4NHPh$	16.85	0.705	−0.260	0.58	90.4
iminostilbene	26.1	0.235	−1.057	4.3	84.6
iminodibenzyl	25.5	0.385	−0.918	3.5	87.0
carbazole	19.9	0.755	−0.336	1.5	92.8
1,3*H*-dibenzo[*a*,*i*]carbazole	17.7	0.725	−0.207	2.0	92.8
3,6-dibromocarbazole	17.15	0.885	−0.140	−0.13	93.6
2-chlorocarbazole	18.5				

[a] Equilibrium acidities measured in DMSO solution against two indicators or standard acids. [b] In volts; irreversible oxidation potentials of neutral weak acids measured in DMSO solution. [c] In volts; irreversible oxidation potentials of the conjugate anions measured in DMSO solution, unless otherwise indicated. [d] Reversible oxidation potential. [e] Equilibrium acidities of radical cations estimated by using eq 2. [f] In kcal/mol, homolytic bond dissociation energies of the N–H bonds estimated by using eq 1.

Scheme I



rings closer to coplanarity, combine to lower the BDE of the N–H bond in **1** by almost 8 kcal. The sulfur bridge (entry 12) in phenothiazine (**2**), because of its larger size and longer bonds, causes smaller effects, leading to about a 5 kcal decrease of the N–H bond in BDE.

Joining the two benzene rings of diphenylamine (**3**) accompanied by elision of two hydrogen atoms to form carbazole (**4**), as shown in Scheme I, induces coplanarity and results in a 6.9 kcal decrease in pK_{HA}, but the $E_{ox}(A^-)$ value for the conjugate base (**5**) is shifted to a more positive potential by about 12 kcal. It has been suggested that this resistance to oxidation may be caused by removal of the electron from the orbital orthogonal to the π system in order to avoid disruption of its aromaticity.[5,14] The net change of −5.3 kcal in BDE of the N–H bond for the conversion of diphenylamine to carbazole contrasts with the +2 kcal change in the conversion of diphenylmethane (**6**) to fluorene (**7**) in the analogous carbon system. Here there is a 13 kcal positive shift in $E_{ox}(A^-)$ for the conjugate base (**8**) which *must* involve loss of an electron from the π system.

Radical Cation Acidities. Tables I and IV contain a summary of the radical cation acidities for anilines, diphenylamines, and carbazoles estimated by eq 2.[7a] The

$$pK_{HA^{\cdot+}} = pK_{HA} + 16.8[E_{ox}(A^-) - E_{ox}(HA)] \qquad (2)$$

$pK_{HA^{\cdot+}}$ value of 6.4 for the radical cation derived from aniline in DMSO is in good agreement with that of 7 estimated by Land and Porter in H_2O,[10] which is consistent with the observations of Kolthoff that the equilibrium acidities of aminium ions in DMSO are within 0.5–1.5 pK_{HA} units of those in water.[14] The weakly acidic nature of the $PhNH_2^{\cdot+}$ radical cation is in sharp contrast to that of its carbon analogue, the radical cation derived from toluene, $PhCH_3^{\cdot+}$, which is estimated to be in the superacid class ($pK_{HA^{\cdot+}} \approx -12$ in CH_3CN[15]). The difference lies in the relative ease of abstraction of an electron from the lone pair on nitrogen compared to abstraction of an electron from the aromatic π system of the benzene ring in toluene. A similar large difference exists between the acidities of the radical cations derived from carbazole, which has a $pK_{HA^{\cdot+}} = 1.5$ (Table IV), and fluorene, which has $pK_{HA^{\cdot+}} \simeq -17$.[7b]

Earlier studies with carbon-centered radical cations of the type $HA^{\cdot+}$ have shown that substituents affect the acidities primarily by stabilizing or destabilizing the ground-state energy of the radical cation.[7] Donor substituents stabilize the radical cation and lower the acidity, and acceptor groups have the opposite effect. The position of equilibrium (3) is affected also by the substituent effects

$$HA^{\cdot+} \rightleftarrows H^+ + A^{\cdot} \qquad (3)$$

on the stability of the radical $A^{\cdot}$ formed, but these effects are usually small. As a consequence the $E_{ox}(HA)$ values usually correlate linearly with the corresponding $pK_{HA^{\cdot+}}$ values, as is true for the radical cations derived from anilines and diphenylamines as shown in Figures 6 and 7, respectively.

A study of substituent effects on the $pK_{HA^{\cdot+}}$ values of the radical cations derived from fluorene has shown that a 3-MeO (para) group decreased the acidity by about 3.5 $pK_{HA^{\cdot+}}$ units and a 2-MeO (meta) group decreased the acidity by about 7 $pK_{HA^{\cdot+}}$ units. These effects were rationalized by comparing the abilities of the 2- and 3-MeO groups to stabilize the positive charge or odd electrons in the undissociated radical cation by delocalization.[7b] In the radical cation derived by removal of an electron from the nitrogen atom of *m*- or *p*-$MeOC_6H_4NH_2$ the positive charge cannot be delocalized into the benzene ring. The radical cation can be stabilized to some extent by the donor effect of the MeO group, however, which is much greater from the para than the meta position (**9a** ↔ **9b**). Stabi-

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(14) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23–28.

(15) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165–2179.

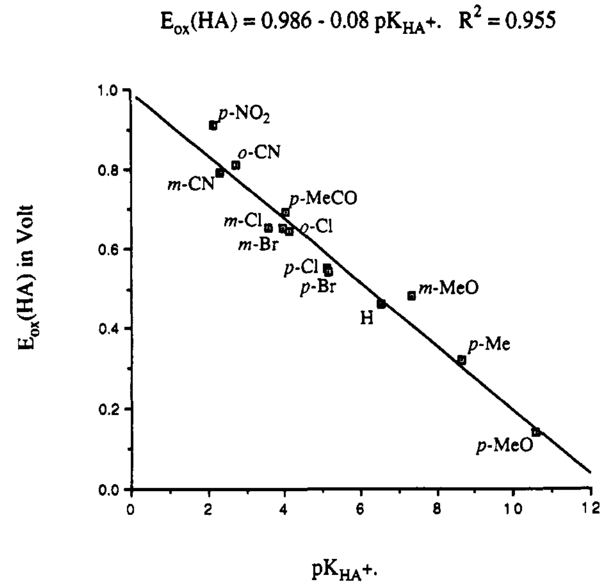


Figure 6. Linear correlation of the oxidation potentials of anilines versus the equilibrium acidities of their radical cations.

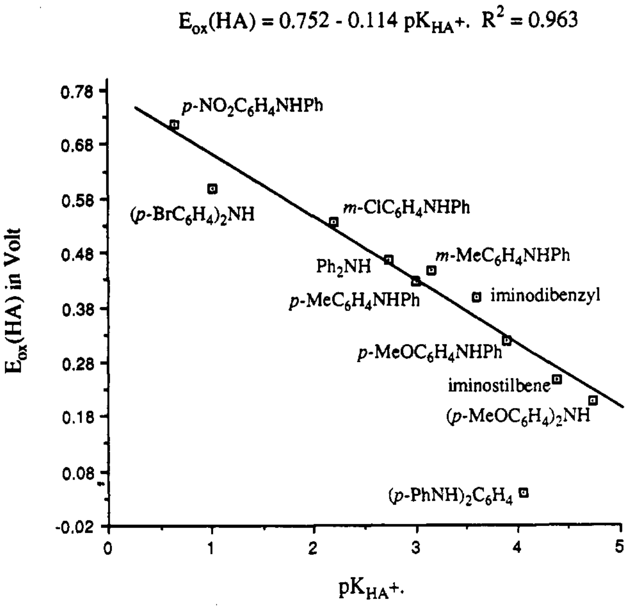
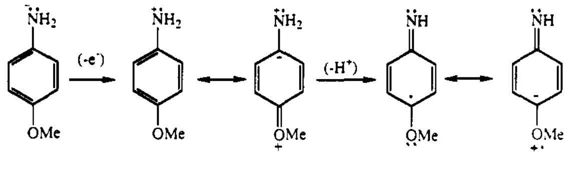


Figure 7. Linear correlation of the oxidation potentials of diphenylamines against the equilibrium acidities of their radical cations (the point for $(p\text{-PhNH})_2C_6H_4$ was not included in the correlation).

Scheme II

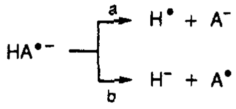


9a 9b 10a 10b

lization of the radical formed on deprotonation is also greater from the para position (**10a** ↔ **10b**), but this is evidently a minor effect compared to the electrostatic effect of stabilizing the positive charge in **9** (Scheme II).

The presence of a second phenyl group in the $Ph_2NH^{\bullet+}$ radical cation leads to an increase in acidity of 3.7 $pK_{HA^{\bullet+}}$ units (5 kcal), relative to that of $PhNH_2^{\bullet+}$. This is probably the result of stabilization of the $Ph_2N^{\bullet}$ radical formed on loss of a proton. On the other hand, the increases in acidity caused by the presence of electron-withdrawing CN or NO_2 groups in $GC_6H_4NH_2^{\bullet+}$ or $GC_6H_4(Ph)NH^{\bullet+}$ radical cations are probably the result of destabilizing the radical cation ground states.

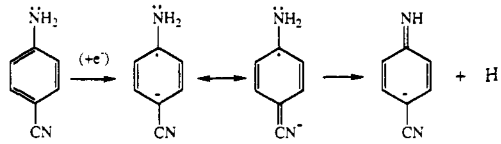
Scheme III



Homolytic Bond Dissociation Energies of the H–N Bonds in Radical Anions Derived from Anilines, Diphenylamines, and Carbazoles. The general method developed for estimating homolytic bond dissociation energies used earlier for the acidic H–A bonds in radical anions derived from carbon acids (eq 3)[11] has now been applied to nitrogen acids (Table V).

$$BDE_{HA^{\bullet-}} = 1.37pK_{HA} + 23.1E_{re}(HA) + 73.3 \qquad (4)$$

In theory, it is possible for the cleavage of the acidic H–A bonds in radical anions of the type $HA^{\bullet-}$ to occur by either path a or b, as shown in Scheme III. The BDEs for both modes of cleavage have been estimated for a variety of radical anions where HA is a carbon acid, and path a has been found to have the lower BDE in most of the instances.[11] We anticipated therefore that path a would also be followed for these nitrogen acids, unless the radical formed by path b is strongly stabilized. The estimates for BDEs for cleavage of the N–H bonds by path a in Table V bear out this expectation, and Borhani and Hawley have found that the N–H bond in the radical anion derived from p-cyanoaniline undergoes cleavage to form hydrogen and the p-cyanoanilinide ion in DMF solution.[16] Molecular hydrogen was apparently formed by dimerization of hydrogen atoms on the electrode surface.



Examination of Table V shows that most of the radical anion $BDE_{HA^{\bullet-}}$ values by path a are in the 30–45 kcal range (38.5 kcal average). The average of the parent N–H BDE_{HA} values is 93.4 kcal. The $BDE_{HA^{\bullet-}}$ values are in the same range as those for the C–H bonds in fluorene radical anions,[11a] which have parent BDE_{HA} values in the 70–80 kcal range compared to the 90s for the parent N–H acids in Table IV. The $BDE_{HA^{\bullet-}}$ value for the N–H bond in carbazole is about 5 kcal smaller than that for the corresponding C–H bond in fluorene even though the BDE_{HA} value for the N–H bond is 14 kcal larger than that for the acidic C–H bond.

The $BDE_{HA^{\bullet-}}$ values estimated by path a for the substrates in Table V bearing nitro groups are unusually high due to the strongly positive reduction potentials (1.55 ± 0.12 V). The $E_{re}(HA)$ value for $p\text{-}NO_2C_6H_4NHPh$ is about 1.5 V (35 kcal) more positive than that for $p\text{-}CNC_6H_4NH_2$. The average reduction potential for the three nitrogen acids containing nitro groups is almost the same as the average reduction potential for 10 nitro triphenylmethanes[11c] and that for 10-nitro-9-methyl-

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[16] Borhani, K. J.; Hawley, M. D. *J. Electroanal. Chem.* **1979**, *101*, 407–417.

Table V. Homolytic Bond Dissociation Energies of the N–H Bonds in Radical Anions Derived from Anilines, Diphenylamines, and Related Compounds

substrates	pK_{HA}[a]	$E_{re}(HA)$[b]	BDE_{HA}[d]	$BDE_{HA^{\bullet -}}$[e]
p-$CNC_6H_4NH_2$	25.26	−3.113	95.2	36.0
m-$CNC_6H_4NH_2$	27.5	−2.855	94.1	45.0
2,4,6-$Cl_3C_6H_2NH_2$	23.5	−2.637	95.5	44.6
m-NO_2-*p*-$ClC_6H_3NH_2$	18.9	−1.436[c]	97.6	66.0
p-$NO_2C_6H_4NH_2$	20.9	−1.684[c]	96.7	63.0
iminostilbene	26.1	−2.501[c]	84.6	51.3
p-$NO_2C_6H_4NHPh$	16.85	−1.525[c]	90.4	61.1
carbazole	19.9	−3.075	93.6	29.5
1,3*H*-dibenzo[*a*,*i*]carbazole	17.7	−2.906	92.8	30.5
3,6-dibromocarbazole	17.15	−2.572	93.6	37.4

[a] Equilibrium acidities measured in DMSO solution against two indicator or two standard acids. [b] In volts; irreversible reduction potentials measured in DMSO solution, unless otherwise indicated. [c] Reversible reduction potentials. [d] In kcal/mol, homolytic bond dissociation energies of the N–H bonds in neutral molecules estimated by using eq 1. [e] In kcal/mol; homolytic bond dissociation energies of the N–H bonds in radical anions estimated by using eq 4.

anthracene.[11b] The rationale here is that the radical anion is formed in these instances by direct addition of the electron to the NO_2 group, from which it can be transferred to other parts of the molecule.

Summary and Conclusions

A plot of $E_{ox}(A^-)$ values for para-substituted anilines vs pK_{HA} was found to be linear, indicating that the $E_{ox}(A^-)$ values are dictated primarily by the basicities of these anilinide ions and are perturbed to only a minor extent by radical-stabilizing or -destabilizing effects. The same was true of comparable para-substituted phenols. There is reason to believe, however, that points for stronger donors, such as *p*-HO, *p*-O^-, *p*-NMe_2, and *p*-NH_2, would deviate from these plots, due to their powerful radical-stabilizing abilities. Substitutions of either a Me or Ph group for an N–H bond in aniline increases the N–H bond acidity and decreases its BDE. The structural change from Ph_2NH to carbazole is accompanied by a 6.8 kcal increase in the N–H acidity compared to a 12.9 kcal increase in C–H acidity for the comparable change from Ph_2CH_2 to fluorene. The smaller change for the N–H acid may be associated with a larger decrease in the ground-state energy due to the formation of a 14 electron π system in carbazole. The N–H acidity of the radical cation derived from carbazole ($pK_{HA^{\bullet +}} = 1.5$) is about 18 $pK_{HA^{\bullet +}}$ units weaker than that of the C–H acidity of that derived from the carbon analogue, fluorene, because the electron is removed from a lone pair on nitrogen rather than from the π system of an aromatic ring. The N–H acidities of the radical cations derived from substituted anilines and diphenylamines correlate linearly with their ground-state energies as measured by $E_{ox}(HA)$ values. The bond dissociation energy for the N–H bond in the radical anion derived from carbazole is 5 kcal smaller than that of the corresponding acidic C–H bond in fluorene radical anion even though the BDE_{HA} value for the N–H bond is 14 kcal larger than that for the acidic C–H bond.

Experimental Section

Materials. The anilines, diphenylamines, iminostilbene, iminodibenzyl, and carbazoles were for the most part commercial samples.[5] The purity (and identity) of each sample was confirmed by spectral analysis.

The equilibrium acidities were determined by the overlapping indicator method as described previously. The redox potentials were measured by cyclic voltammetry. The working electrode (BAS) consists of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal for the measurements of the oxidation potentials of the neutral molecules and their conjugate anions. A carbon-glass electrode (BAS) was used as a working electrode for the measurements of the reduction potentials of the neutrals. It was polished with a 0.05-μm Fisher polishing aluminum or cleaned with an ultrasonic instrument, rinsed with ethanol, and dried before each run. The counter electrode was a platinum wire (BAS). The reference electrode was Ag/AgI, and the reported potentials were referenced to ferrocenium/ferrocene couple ($E_{1/2}$ = 0.875 V vs the Ag/AgI couple).[4] Most electrochemical experiments were conducted in a standard glass cell (BAS). For measurements with highly basic anions ($pK_{HA} > 27$) an air-tight cell was used. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under argon. Although the oxidation potentials for the anions are irreversible, the reversible potentials for the anions derived from iminostilbene, phenoxazine, and phenothiazine obtained by fast scan techniques have been found to be almost identical with the irreversible potentials,[17] and the reversible potentials for 10 other nitranions have been found to differ from the irreversible potentials by less than 50 mV.[18]

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(18) Bordwell, F. G.; Hupp, J. T.; Satish, A. V. Unpublished results.