

Substituent Effects on the Bond Dissociation Enthalpies of Aromatic Amines

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Abstract: Bond dissociation enthalpy differences, $Z-X \Delta BDE = BDE(4-YC_6H_4Z-X) - BDE(C_6H_5Z-X)$, for $Z = CH_2$ and O are largely independent of X and are determined mainly by the stabilization/destabilization effect of Y on the $4-YC_6H_4Z^{\bullet}$ radicals. The effects of Y are small (≤ 2 kcal/mol for all Y) for $Z = CH_2$, but they are large for $Z = O$, where good correlations with $\sigma_p^+(Y)$ yield $\rho^+ = 6.5$ kcal/mol. For $Z = NH$, two sets of electrochemically measured $N-H \Delta BDEs$ correlate with $\sigma_p^+(Y)$, yielding $\rho^+ = 3.9$ and 3.0 kcal/mol. However, in contrast to the situation with phenols, these data indicate that the strengthening effect on $N-H$ BDEs of electron-withdrawing (EW) Y 's is greater than the weakening effect of electron-donating (ED) Y 's. Attempts to measure $N-H \Delta BDEs$ in anilines using two nonelectrochemical techniques were unsuccessful; therefore, we turned to density functional theory. Calculations on 15 $4-YC_6H_4NH_2$ gave $N-H \Delta BDEs$ correlating with σ_p^+ ($\rho^+ = 4.6$ kcal/mol) and indicated that EW and ED Y 's had comparable strengthening and weakening effects, respectively, on the $N-H$ bonds. To validate theory by connecting it to experiment, the $N-H \Delta BDEs$ of four 4,4'-disubstituted diphenylamines and five 3,7-disubstituted phenothiazines were both calculated and measured by the radical equilibration EPR technique. For all compounds, theory and experiment agreed to better than 1 kcal/mol. Dissection of $N-H \Delta BDEs$ in 4-substituted anilines and $O-H \Delta BDEs$ in 4-substituted phenols into interaction enthalpies between Y and NH_2/OH (molecule stabilization/destabilization enthalpy, MSE) and NH^{\bullet}/O^{\bullet} (radical stabilization/destabilization enthalpy, RSE) reveals that for both groups of compounds, ED Y 's destabilize the molecule and stabilize the radical, while the opposite holds true for EW Y 's. However, in the phenols the effects of substituents on the radical are roughly 3 times as great as those in the molecule, whereas in the anilines the two effects are of comparable magnitudes. These differences arise from the stronger ED character of NH_2 vs OH and the weaker EW character of NH^{\bullet} vs O^{\bullet} . The relatively large contributions to $N-H$ BDEs in anilines arising from interactions in the molecules suggested that $N-X \Delta BDEs$ in $4-YC_6H_4NH-X$ would depend on X , in contrast to the lack of effect of X on $O-X$ and $CH_2-X \Delta BDEs$ in $4-YC_6H_4O-X$ and $4-YC_6H_4CH_2-X$. This suggestion was confirmed for $X = CH_3, H, OH,$ and F , for which the calculated $NH-X \Delta BDEs$ yielded $\rho^+ = 5.0, 4.6, 4.0,$ and 3.0 kcal/mol, respectively.

Introduction

We have recently employed a combination of theory and experiment to examine the effects of Y substituents on $C-X$ and $O-X$ bond dissociation enthalpies (BDEs) of $4-YC_6H_4CH_2-X$ ($X = H, F, Cl, Br,$ and OPh)^{4,5} and $4-YC_6H_4O-X$ ($X = H, CH_3,$ and CH_2Ph).⁵ In brief, we found that the effects of Y on the BDE differences, $\Delta BDE(4-YC_6H_4CH_2-X - C_6H_5CH_2-X)$ and $\Delta BDE(4-YC_6H_4O-X - C_6H_5O-X)$, are almost independent of X for all $C-X$ and $O-X$ series of compounds. Both

electron-donating (ED) and electron-withdrawing (EW) Y substituents reduce $C-X$ BDEs relative to the parent compound, but the effects are very small, ≤ 2 kcal/mol. In contrast, ED Y 's reduce and EW Y 's increase $O-X$ BDEs relative to the parent compound, and the effects are substantial; for example, on changing from the strong EW group, $4-NO_2$, to the strong ED group, $4-NH_2$, $O-X \Delta BDEs$ decrease by ca. 14 kcal/mol.⁵ $\Delta BDEs$ for the three series of $O-X$ compounds all gave excellent linear correlations with Brown and Okamoto's⁶ electrophilic substituent constants, $\sigma_p^+(Y)$, with approximately equal slopes, $\rho^+ = 6.5 \pm 0.4$ kcal/mol.⁷

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(7) Early indications that $BDE(YC_6H_4O-H)$ might correlate with $\sigma_p^+(Y)$ ⁸ were confirmed in 1988¹¹ and have been reconfirmed many times subsequently both by experiment¹² ("best" $\rho^+ = 6.9$ kcal/mol)^{12f} and by theory¹³ ("best" $\rho^+ = 6.2$ kcal/mol).^{13d} There was also an early suggestion that $BDE(YC_6H_4CH_2-H)$ might correlate with σ .¹⁴

On the basis of the above facts, one might well expect that the effects of Y substituents on $\Delta\text{BDE}(4\text{-YC}_6\text{H}_4\text{NH-X} - \text{C}_6\text{H}_5\text{-NH-X})$ would be essentially independent of X, of a magnitude intermediate between their effects on C–X and O–X bonds,¹⁵ and would give good correlations with $\sigma_p^+(\text{Y})$. We show herein that these expectations are only partially realized and identify the unique trends in 4-YC₆H₄NH-X BDEs as arising from stabilization/destabilization of these molecules by their Y substituents. That is, C–X BDEs in 4-YC₆H₄CH₂-X and O–X BDEs in 4-YC₆H₄O–X are largely (but not entirely, vide infra) determined by the stabilizing/destabilizing effects of Y on the radicals 4-YC₆H₄CH₂• and 4-YC₆H₄O•. However, N–X BDEs in 4-YC₆H₄NH-X are determined by the stabilizing/destabilizing effects of Y on the parent *molecule* as well as on the derived 4-YC₆H₄NH• radical.

Results

Only three experimental studies on 4-YC₆H₄NH–H BDEs have been published:^{17–20} two employed electrochemical (EC) methods and were quite extensive,^{17,18} while the other used photoacoustic calorimetry (PAC) and was very limited.¹⁹ The results from these three studies are summarized in Table 1, together with the results of our calculations. (The method of calculation is given in the Experimental Section.)

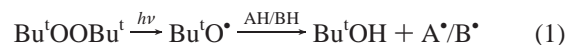
Because of inconsistencies between the two EC studies (cf. Y = CF₃), between the EC and PAC results (cf. Y = CH₃), and between EC results and our calculations (cf. Y = CH₃, OCH₃, and NH₂), we made great efforts to expand the PAC measurements to a wider range of substituents than were originally examined.¹⁹ Unfortunately, we did not succeed because most 4-substituted anilines absorb strongly at 337 nm, the wavelength of the laser light used in PAC experiments.^{11,12e,19} We therefore turned to the radical-equilibrium electron paramagnetic resonance (REqEPR) technique. This has been very

Table 1. Experimental and Calculated N–H ΔBDEs for Para-Substituted Anilines [$\text{BDE}(4\text{-YC}_6\text{H}_4\text{NH-H}) - \text{BDE}(\text{C}_6\text{H}_5\text{NH-H})$] in kcal/mol

substituent (Y)	$\sigma_p^+(\text{Y})^a$	method			
		EC ^{b,c}	EC ^{b,d}	PAC ^e	calcd ^f
(CH ₃) ₂ N	–1.70				–6.1
H ₂ N	–1.30		–3.1		–5.6
HO	–0.78 ^g				–3.8
CH ₃ O	–0.78	–1.9	–1.9		–4.1
CH ₃	–0.31	–0.3	–0.5	–2.2	–1.9
F	–0.07			–0.9	0.3
H	0	0.0 ^h	0.0 ⁱ	0.0 ^j	0.0 ^k
Cl	0.11	0.1			0.1
Br	0.15	0.0			0.5
COOH	0.42				3.3
CHO	(0.47) ^l				2.9
CH ₃ CO	(0.50) ^l	1.9	1.4		2.7
CF ₃	0.61	4.2	2.9		3.1
CN	0.66	2.9	2.6		3.1
NO ₂	0.79	4.4			4.7
ρ^+		3.9 ± 0.6	3.0 ± 0.2		4.6 ± 0.3
R ²		0.860	0.974		0.963

^a From ref 6 unless otherwise noted. ^b Electrochemistry. ^c Reference 17. These data have been derived from Table 1, the primary table in this reference, not from its Table 2 (a secondary table), where the results for some substituents (e.g., 4-CF₃ and 4-NO₂) differ substantially. ^d Reference 18. ^e Photoacoustic calorimetry.¹⁹ ^f This work. Method = (RO)B3LYP/6-311+G(2d,2p)//AM1/AM1. ^g From footnote 25 of ref 5, the value of –0.92 given in ref 6 is almost certainly too large to be applicable with the calculated, gas-phase N–H ΔBDEs and to be applicable with measured N–H ΔBDEs in most nonaqueous solvents; see ref 42. ^h BDE = 92.3. ⁱ BDE = 89.1. ^j BDE = 89.7. ^k BDE = 91.5. ^l There is no σ_p^+ for this group; value given is σ_p .

successfully applied by Pedulli and co-workers to the measurement of O–H ΔBDEs for substituted phenols²¹ and 5-pyrimidinols,²² as well as to the measurement of N–H ΔBDEs in ring-substituted phenothiazines and some related compounds.²³ The measurement of ΔBDEs by this method involves continuous, high-power UV irradiation of di-*tert*-butyl peroxide/benzene solutions in the cavity of an EPR spectrometer, generally at room temperature. Two substrates, AH and BH, are present at known concentrations in the solution. The resulting EPR spectra must permit a measurement of the ratio of the concentrations of the two substrate-derived radicals, A• and B•.



Furthermore, this ratio must be determined under conditions where there is a sufficiently rapid H-atom transfer between the radicals and substrates that the $[\text{A}^\bullet]/[\text{B}^\bullet]$ ratio is determined solely by the equilibrium



With the reasonable assumption (for similar AH and BH) that there is no significant entropy change in reaction 2, $\Delta\text{BDEs}(\text{A-H} - \text{B-H})$ can be calculated from the measured $[\text{A}^\bullet]/[\text{B}^\bullet]$ ratios at known $[\text{AH}]/[\text{BH}]$ ratios.

Unfortunately, under the standard conditions which have worked so well for measuring phenolic O–H ΔBDEs ,²¹ the EPR

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Table 2. Calculated Gas-Phase and REqEPR Measured N–H Δ BDEs for 3,7-Disubstituted Phenothiazines in kcal/mol

substituent (Y)	$\Sigma\sigma_p^+(Y)^a$	N–H Δ BDE	
		calcd ^b	exptl ^c
CH ₃ O	-1.56	-2.8	-3.1 \pm 0.3
(CH ₃) ₃ C	-0.51	-0.9	-1.2 \pm 0.4
H	0	0 ^d	0 (\pm 0.3) ^e
Cl	0.22	-0.2	0.5 \pm 0.4
NO ₂	1.58	2.6	1.7 \pm 1.0
ρ^+		1.7 \pm 0.1	1.6 \pm 0.2
R ²		0.988	0.961

^a $2\sigma_p^+(Y)$; see Table 1. ^b This work. ^c Reference 23. ^d N–H BDE = 73.5, 76.6, and 76.6 kcal/mol by LLM, MLM2, and HLM, respectively. ^e N–H BDE = 79.3 \pm 0.3 kcal/mol by REqEPR²³ and 82.3 kcal/mol by EC.¹⁷

Table 3. Calculated Gas-Phase and Experimental N–H Δ BDEs for 4,4'-Diphenylamines in kcal/mol

substituent (Y)	$\Sigma\sigma_p^+(Y)^a$	N–H Δ BDE			
		calcd ^b	REqEPR ^b	kinetics ^c	other
(CH ₃) ₂ N	-3.40	-7.6	-6.3 \pm 0.5		
CH ₃ O	-1.56	-4.8	-4.0 \pm 0.3	-3.8	-3.3 ^d
CH ₃	-0.62	-1.9	-2.5 \pm 0.6	-1.7	-1.0 ^e
H	0	0 ^f	0.0 (\pm 0.7) ^g	0 ^h	0 ⁱ
CF ₃	1.22	3.3	j		
NO ₂	1.58	4.8	j		
ρ^+		2.5 \pm 0.2			
R ²		0.978			

^a $2\sigma_p^+(Y)$. ^b This work. ^c Based on the kinetics of reaction with 2,4,6-tri-*tert*-butylphenoxyl under “quasiequilibrium” conditions in CCl₄; see ref 25. ^d EC method.¹⁷ ^e PAC method.¹⁹ ^f BDE((C₆H₅)₂N–H) = 83.7, 84.9, and 84.9 kcal/mol by LLM, MLM2, and HLM, respectively. ^g BDE((C₆H₅)₂N–H) = 85.8 \pm 0.7 kcal/mol.²³ ^h BDE((C₆H₅)₂N–H) = 87.0 kcal/mol.²⁵ ⁱ BDE((C₆H₅)₂N–H) = 87.5¹⁷ and 86.2¹⁹ kcal/mol. ^j This measurement could not be made; see text.

spectra of 4-YC₆H₄NH• (Y = H, CH₃, CH₃O, and NH₂) were too weak to be useful,²⁴ probably because 4-YC₆H₄NH• radicals have 6 times as many lines in their spectra as the corresponding 4-YC₆H₄O• radicals.

To validate our calculated N–H Δ BDEs for 4-YC₆H₄NH₂ compounds (Table 1), we turned to calculation and experimental measurements of N–H Δ BDEs by REqEPR in two other series of aromatic amines: 3,7-disubstituted phenothiazines and 4,4-disubstituted diphenylamines.



For the phenothiazines the REqEPR N–H Δ BDEs were already available (Table 2), but for the diphenylamines the REqEPR N–H Δ BDEs had to be measured. They are given in Table 3, together with all data that were available in the literature.^{17,19,25} Unfortunately, the two compounds with EW groups (Y = CF₃ and NO₂) did not yield sufficiently intense EPR spectra for reliable measurements of radical concentrations; consequently, N–H Δ BDEs for these two amines could not be determined.

The good agreement between calculated N–H Δ BDEs and values measured by the REqEPR procedure for both the 3,7-disubstituted phenothiazines (Table 2) and the 4,4'-disubstituted

Table 4. Calculated Gas-Phase N–X Δ BDEs for 4-YC₆H₄NH–X in kcal/mol

substituent (Y)	N–X Δ BDE			
	X = CH ₃	X = H	X = OH	X = F
(CH ₃) ₂ N	-6.4	-6.1	-5.9	-5.0
H ₂ N	-5.9	-5.6	-5.5	-4.8
HO	-3.6	-3.8	-3.2	-3.0
CH ₃ O	-3.6	-4.1	-3.3	-2.9
CH ₃	-1.5	-1.9	-1.6	-1.3
H	0 ^a	0 ^b	0 ^c	0 ^d
COOH	4.0	3.3	2.5	1.6
CHO	3.4	2.9	2.0	0.7
CF ₃	3.7	3.1	2.6	1.5
CN	3.7	3.1	2.3	1.0
NO ₂	5.6	4.7	3.7	2.0
ρ^+e	5.0 \pm 0.3	4.6 \pm 0.3	4.0 \pm 0.2	3.0 \pm 0.2
R ²	0.974	0.967	0.983	0.977

^a N–CH₃ BDE = 66.6 kcal/mol. ^b N–H BDE = 91.5 kcal/mol. ^c N–OH BDE = 43.5 kcal/mol. ^d N–F BDE = 53.6 kcal/mol. ^e For σ_p^+ values, see Table 1.

diphenylamines (Table 3) gave us the confidence to extend our calculations to N–X Δ BDEs in 4-YC₆H₄NH–X compounds (X = CH₃, OH, and F). These results, together with those for X = H from Table 1, are summarized in Table 4.

Discussion

For both the 3,7-disubstituted phenothiazines (Table 2) and the 4,4'-disubstituted diphenylamines (Table 3), our calculated N–H Δ BDEs are in very satisfactory agreement with experimental values determined using the REqEPR technique. This gives us confidence that our calculations reflect reality with reasonable accuracy.

Substituent Effects on N–H Δ BDEs in 4-Substituted Anilines. Examining first the data in Table 1, it is clear that theory and experiment agree about the magnitude of substituent effects on N–H Δ BDEs for 4-YC₆H₄NH–H when Y is a strong EW group, such as NO₂ and CN. However, when Y is a strong ED group, such as NH₂ and CH₃O, the calculated N–H Δ BDEs are roughly twice as large as the EC measured values, which were determined using closed thermodynamic cycles involving either the acidities of the anilines and the one-electron (irreversible) oxidation potentials of the anilide anions¹⁷ or the acidities of the aniline radical cations and one-electron reduction potentials of these cations.¹⁸ Both procedures should provide the same ΔH as for N–H bond homolysis in the EC solvent employed. The EC data for ED Y-substituted anilines derived from the acidities of the anilines and oxidation potentials of the corresponding anilides (which were determined by cyclic voltametry) may well be in error, “because their low acidities make pK_{HA} measurements difficult”,¹⁷ and therefore they are likely to be subject to considerable uncertainties. Indeed, plots of these N–H Δ BDEs vs $\sigma^+(Y)$ show a sharp bend at $\sigma^+(H) = 0$, with a lower slope at negative $\sigma^+(Y)$ than at positive $\sigma^+(Y)$.¹⁷ In the pulse radiolysis experiments of Jonsson et al.,¹⁸ the acidities of the aniline radical cations lie in the normal range (0–14) and could thus be reliably determined. Calculated N–H Δ BDEs give a fairly good correlation with σ_p^+ (solid line in Figure 1, $\rho^+ = 4.6 \pm 0.3$, $R^2 = 0.963$). However, N–H bond-weakening by the strongest ED group, Me₂N ($\sigma_p^+ = -1.70$), is ca. 2 kcal/mol less than would have been predicted from the best straight line through all the other points (dotted line in Figure 1, $\rho^+ = 5.0 \pm 0.2$, $R^2 = 0.974$).

(24) This was also true even in neat di-*tert*-butyl peroxide with the accumulation of several (8–12) EPR spectra.

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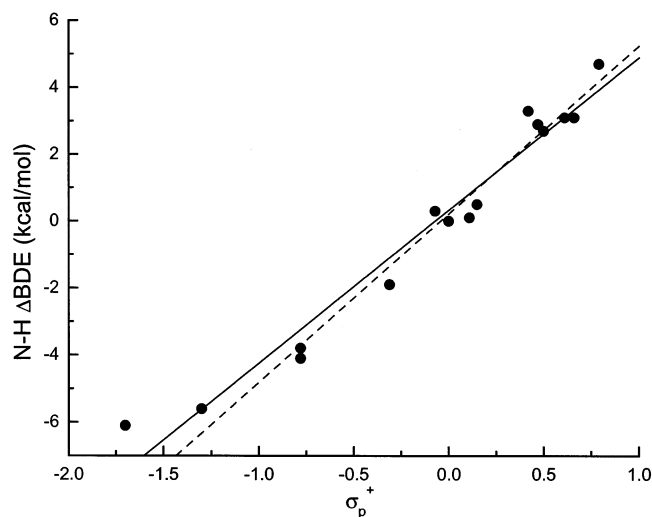
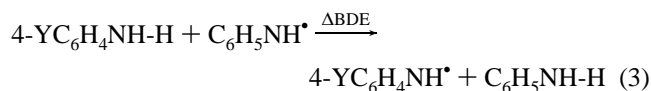
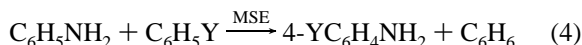


Figure 1. Correlation of calculated aniline N–H Δ BDEs with σ_p^+ . Solid line: Best fit by linear regression analysis. Dashed line: Best fit excluding the data point for Y = $-\text{N}(\text{CH}_3)_2$ ($\sigma_p^+ = -1.7$).

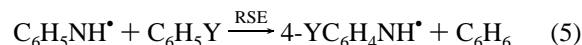
Bordwell et al.¹⁷ appear to have been the first to report that ED Y groups have a smaller effect on 4-YC₆H₄NH–H BDEs than EW Y’s. Among other possibilities, they suggested that this might be a consequence of substituent effects on the stabilities of the parent anilines. A year later, Bordwell^{12d} noted that “para-donor substituents exert effects to decrease BDEs of the acidic H–A bonds primarily by stabilizing the corresponding radicals but also to some extent by raising the ground-state energies in the ArOH, ArSH and ArNH₂ families”. Subsequent investigators, intrigued by the fact that donor substituents “destabilize the undissociated phenol and stabilize the odd electron in the corresponding radical”,^{12d} have concentrated largely on phenolic O–H BDEs^{13b,c} and benzylic C–H BDEs.^{4,26} Following Wu and Lai,^{13b,26} substituent effects on N–H BDEs can be conveniently obtained by calculating the interaction enthalpies between the Y substituents and the NH₂ group in the parent aniline and the NH• group of the aniliny radical using the isodesmic reaction



This procedure yields the N–H BDE for the substituted aniline relative to aniline. This total stabilization effect (TSE) of the substituent is comprised of both an effect on the parent molecule (MSE)²⁷ as well as on the radical (RSE), that is, TSE = RSE – MSE = Δ BDE. We define the *molecule stabilization enthalpy* (MSE) as the stabilization/destabilization arising from the interaction between the substituents and the NH₂ group, calculated from the enthalpy change in the isodesmic reaction



The *radical stabilization enthalpy* (RSE) indicates the effect of the substituent on the stability of the aniliny radical and is calculated from the reaction:



The results of calculations on these isodesmic reactions are summarized in Table 5, together with analogous data calculated at the same level of theory for para-substituted phenols and toluenes.⁴ It is worth noting that our phenol and toluene data are in very satisfactory agreement with all of Wu and Lai’s results^{13b,26} and with the phenol results of Brinck et al.^{13c} for ED Y’s but not for EW Y’s.²⁸

For the EW Y’s, the TSE values are remarkably similar for anilines and phenols, although the MSE/RSE mix differs, with the MSE contributions for the anilines being larger than those for the phenols and the reverse holding for the RSE contributions (see Table 5). Although we will not attempt to completely deconvolute substituent effects on MSEs and RSEs in terms of inductive and resonance contributions, a few major points are worth noting. Thus, the larger MSE contributions for the EW Y’s in the anilines compared with the those in the phenols arise because the NH₂ group is a stronger π electron donor and a weaker σ electron acceptor than the OH group, and hence the NH₂ group interacts more strongly than the OH group with both π - and σ -accepting (EW) Y’s. The EW Y groups’ MSEs for toluenes are the smallest because the CH₃ group is a weak π - (and σ -) donor compared with OH and NH₂. Indeed, plots of MSE versus σ_p^+ yield values of ρ^+ for anilines (-2.3 ± 0.3 kcal/mol), phenols (-1.6 ± 0.2 kcal/mol), and toluenes (-0.8 ± 0.1 kcal/mol) which follow the trend very nicely with σ_p^+ –(NH₂) = -1.3 , σ_p^+ (OH) = -0.78 , and σ_p^+ (CH₃) = -0.31 . For the ED Y’s, the MSE values are similar for anilines and phenols, and, for both classes of compounds, the results imply a limit to substituent effects for the strongest ED Y substituent. This nonadditivity or limiting behavior in substituent effects has been noted previously.²⁹ Thus, in terms of the destabilization of the parent molecule, the law of diminishing returns sets in when the already electron-rich aromatic ring in anilines or phenols is substituted with an ED group. This is clearly apparent since there are essentially no differences in the magnitudes of the MSE of anilines and phenols for Y = CH₃O, HO, H₂N, and (CH₃)₂N, despite the relatively large differences in the electron-donating abilities of these four substituents.

The RSE contributions for the anilines and phenols correlate well with σ_p^+ (see Figure 2)³⁰ but are smaller in the anilines than in the phenols for both EW and ED Y’s. First, the unpaired electron is more localized on the heteroatom and less delocalized into the aromatic ring in aniliny radicals in comparison with phenoxy radicals. This is due to smaller 2p– π orbital overlap

(26) See, e.g.: Wu, Y.-D.; Wong, C. L.; Chan, K. W. K.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746–750. Nau, W. M. *J. Phys. Org. Chem.* **1997**, *10*, 445–455. Bean, G. P. *Tetrahedron* **1998**, *54*, 15445–15456. Pratt, D. A. Unpublished results.

(27) Substituent effects on bond strengths are now generally described in terms of the composite effects on the parent, closed-shell compounds and the daughter, open-shell radicals. The former effect has usually been referred to as a *ground-state effect*. We have changed this established nomenclature in the present paper at the suggestion of a reviewer, who correctly pointed out that in conventional chemical terms the counterpart of *ground-state* is *excited-state* or, sometimes, *transition-state*, and henceforth we use *molecule effect* or *molecule stabilization enthalpy*.

(28) For example, Brinck et al.^{13c} found the CN substituent to have a *stabilizing* effect of 2.1 kcal/mol.

(29) Similar limiting behavior to substituent effects has been observed in other systems. See: (a) Jonsson, M.; Lind, J.; Reitberger, T.; Eriksen, T. E.; Merenyi, G. *J. Phys. Chem.* **1993**, *97*, 11278–11282. (b) DiLabio, G. A.; Pratt, D. A.; Wright, J. S. *J. Org. Chem.* **2000**, *65*, 2195–2203 and references therein. (c) Dubois, J.-E.; Ruasse, M.-F.; Argile, A. *J. Am. Chem. Soc.* **1984**, *106*, 4840–4845.

(30) It is interesting to note that substituent effects on numerous properties of the parent molecules correlate with σ rather than with σ^+ , e.g. $J(^{15}\text{N-H})$ in YC₆H₄NH₂³¹ and ν_{OH} in YC₆H₄OH.³²

Table 5. Calculated Radical Stabilization Enthalpies (RSEs), Molecule Stabilization Enthalpies^a (MSEs), and Total Substituent Effects (TSEs/ Δ BDEs) of Para-Substituents (Y) on N–H BDEs in Anilines, O–H BDEs in Phenols, and C–H BDEs in Toluenes^b

substituent (Y)	anilines			phenols			toluenes		
	RSE	MSE	TSE ^c	RSE	MSE	TSE ^c	RSE	MSE	TSE ^c
(CH ₃) ₂ N	-4.3	1.8	-6.1	-8.1	2.0	-10.1	-1.3	0.7	-2.0
H ₂ N	-4.2	1.4	-5.6	-7.6	1.6	-9.2	-0.9	0.8	-1.7
HO	-1.7	2.2	-3.9	-3.8	2.0	-5.8	-0.3	0.6	-0.9
CH ₃ O	-1.9	2.1	-4.0	-4.3	1.8	-6.1	-0.1	0.6	-0.7
CH ₃	-1.4	0.5	-1.9	-2.3	0.3	-2.6	-0.2	0.3	-0.5
H	0	0	0	0	0	0	0	0	0
COOH	0.5	-2.7	3.2	1.2	-1.5	2.7	-1.4	-0.8	-0.6
CHO	-0.2	-3.1	2.9	0.8	-1.6	2.4	-1.7	-0.8	-0.9
CF ₃	1.3	-1.8	3.1	2.6	-0.7	3.3	-0.3	-0.6	0.3
CN	0.7	-2.4	3.1	1.4	-0.9	2.3	-1.2	-0.8	-0.4
NO ₂	1.4	-3.2	4.6	3.1	-1.4	4.5	-1.2	-0.9	-0.3
ρ^{+d}	2.3 ± 0.1	-2.3 ± 0.3	4.6 ± 0.3	4.5 ± 0.2	-1.6 ± 0.2	6.1 ± 0.2	<i>e</i>	-0.8 ± 0.1	<i>e</i>
R ²	0.952	0.835	0.967	0.982	0.863	0.986		0.908	

^a A number of MSEs can be calculated using NIST data; however, they are of variable quality. ^b Enthalpy differences in kcal/mol; negative values refer to stabilizing interactions. ^c TSE = Δ BDE = RSE - MSE. ^d For σ_p^+ values, see Table 1. ^e Obviously there is no single linear correlation with $\sigma_p^+(Y)$.

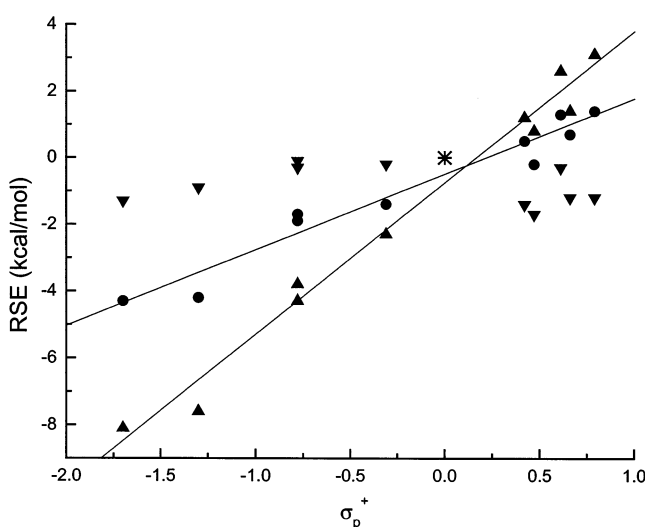


Figure 2. Correlation of calculated effects of 4-Y substituents on the radical stabilization enthalpies for the aniliny radical (●), phenoxyl radical (▲), and benzyl radical (▼) with $\sigma_p^+(Y)$. The asterisk indicates the (0,0) point.

in aniliny radical relative to that in phenoxyl, which arises because the C–N bond in $C_6H_5NH^*$ is longer (1.34 Å) than the C–O bond in $C_6H_5O^*$ (1.25 Å).¹⁶ As a consequence, the unpaired electron in aniliny radicals interacts less strongly with both π -acceptor and π -donor Y's than the unpaired electron in phenoxyls. Second, the NH^* moiety is a weaker π - and σ -acceptor than O^* . Indeed, the ratios of the summed RSE and MSE absolute magnitudes, $\sum|RSE|/\sum|MSE|$, for the phenols and anilines are 2.6 and 0.8, respectively, implying that the O^* group withdraws electrons roughly 2–3 times as strongly as the HO group donates electrons (this corresponds to a σ_p or $\sigma_p^+(O^*)$ value of ca. +2.0), and the NH^* group withdraws electrons only 0.8 times as strongly as the NH_2 group donates electrons (corresponding to $\sigma_p^+(NH^*) \approx +1.0$). The EW nature of O^* has been previously recognized.^{12b,c,13a–c} In contrast, the CH_2^* group in the benzyl radical is neither EW nor ED, and it is stabilized by any group that can delocalize the spin of the unpaired electron. Hence, RSEs in toluene do not correlate with $\sigma_p^+(Y)$.

To conclude this section, the data in Table 5 demonstrate that, for the N–H BDEs of the 4-substituted anilines, substituent effects on the stabilization/destabilization of the molecule and radical are comparable though of opposite sign. This is illustrated

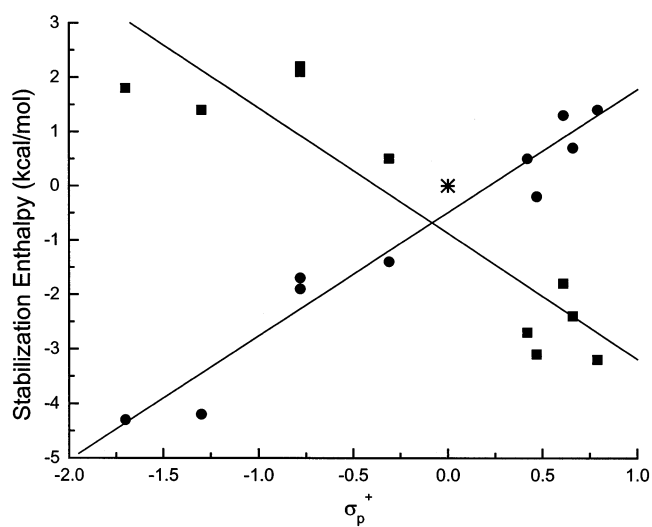


Figure 3. Correlation of calculated stabilization enthalpies in 4-Y-substituted anilines (MSE, ■) and aniliny radicals (RSE, ●) with $\sigma_p^+(Y)$. The asterisk indicates the (0,0) point.

in Figure 3. In contrast, for the O–H BDEs in 4-substituted phenols, substituent effects on the molecule are generally smaller than the effects on the radical. Since all Y's slightly stabilize the benzyl radical and interact weakly with the CH_3 group in toluene (EW Y stabilizing and ED Y destabilizing), effects of Y on benzylic C–H BDEs are small, and hence EW and ED Y's do not give a single linear correlation with $\sigma_p^+(Y)$.

Substituent Effects on N–H Δ BDEs in 3,7-Disubstituted Phenothiazines and in 4,4'-Disubstituted Diphenylamines. For both classes of compounds, the calculated Δ BDEs are within the uncertainties of the experimental values, though it must be admitted that this agreement does not extend to the absolute N–H BDEs.³³ Plots of N–H Δ BDEs vs $\sum\sigma_p^+$ ($=2\sigma_p^+(Y)$) because there are two identical Y substituents para to the N–H moiety) give good linear correlations both experimentally (e.g.,

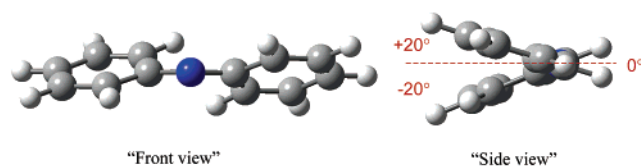
(31) Axenrod, T.; Pregosin, P. S.; Wieder, M. J.; Becker, E. D.; Bradley, R. B.; Miller, G. W. A. *J. Am. Chem. Soc.* **1971**, *93*, 6536–6541.

(32) Ingold, K. U. *Can J. Chem.* **1960**, *38*, 1082–1098.

(33) The calculated N–H BDEs are much lower than the experimental values, but they do get closer to experiment with improvement in the DFT model; see footnotes *d* and *e* to Table 2 and footnotes *f–i* to Table 3. Underestimation of O–H BDEs in phenols and 5-pyrimidinols has been noted previously,²² and the errors become larger the weaker the O–H bond. We are currently exploring the reason(s) for this problem.

for the phenothiazines, $\rho^+ = 1.6 \pm 0.2$ kcal/mol, $R^2 = 0.961$) and by calculation (viz., phenothiazines, $\rho^+ = 1.7 \pm 0.1$ kcal/mol, $R^2 = 0.988$; diphenylamines, $\rho^+ = 2.4 \pm 0.3$ kcal/mol, $R^2 = 0.969$). These ρ^+ values are considerably smaller than the values found for the anilines (see Table 1), most probably because of the limiting electronic effects discussed earlier for MSE in ED-substituted anilines and phenols.

At the AM1 level of theory, geometry optimizations of the structures used in the subsequent DFT electronic energy calculations gave the minimum energy structure of the diphenylaminyl radical, with the two phenyl rings twisted relative to each other by ca. 40° .³⁴ This structure is different from that accepted for the past 15 years, which had the two aromatic rings twisted relative to one another by 90° .³⁵ This “orthogonal” structure was suggested³⁵ because of an “unexpected” long wavelength absorption in the UV–visible spectrum of diphenylaminyl.^{35,36} In this radical, one ring was supposed to be oriented for maximum delocalization of the unpaired electron and the other ring oriented for maximum conjugation with the lone pair on nitrogen.³⁵ However, our calculations indicate that the orthogonal structure is a transition state some 3.5 kcal/mol above the minimum energy structure in which the rings lie about 20° on either side of the N-2p (SOMO) nodal plane; i.e., the two phenyl rings are oriented so they may both interact as strongly as possible with the unpaired electron while relieving steric repulsion between ortho hydrogens on the two aromatic rings. Because our calculations are in excellent agreement with the experimental values for the N–H Δ BDEs in the 4,4'-disubstituted diphenylamines (and for other reasons),³⁴ we believe that diphenylaminyl is less likely to adopt an orthogonal structure than the staggered structure shown below.



Substituent Effects on N–X Δ BDEs in 4-YC₆H₄NH–X.

Upon dissection of the effects of Y on the N–H Δ BDEs in 4-YC₆H₄NH–H, it becomes apparent that the strong ED character of the NH₂ group and the weak EW character of the NH• group cause the effects of Y on the stabilities of the parent molecules to be of comparable magnitude to their effects on the radicals. This contrasts with the role of Y on O–X and C–X Δ BDEs in 4-YC₆H₄O–X (X = H, CH₃, and PhCH₂)⁵ and 4-YC₆H₄CH₂–X (X = H, F, Cl, Br, and PhCH₂)⁵. In these two families of molecules, the effects of Y on the stability of the molecule are relatively small, radical effects dominate, and the effects of Y on O–X Δ BDEs are essentially independent of X, and similarly for the effects of Y on C–X Δ BDEs. It is obvious that the ED character of the NH₂ group will be modified by substitution of one of its hydrogen atoms by a different atom or group, NHX, and this must influence the magnitude of the

effect of Y on the molecule, and thus the N–X Δ BDEs in 4-YC₆H₄NH–X.³⁷ That is, our original proposal⁴ that the effect of Y on Z–X Δ BDEs in 4-YC₆H₄Z–X would be independent of X, while true for Z = O and CH₂, now seems unlikely to be true for Z = NH. We have explored this matter by calculating N–X Δ BDEs for 4-YC₆H₄NH–X with X = CH₃, OH, and F (and, of course, X = H). These results are given in Table 4. Since dissociation of the N–X bond gives the same aniliny radical in all cases, the differences in the magnitudes of the substituents effects on N–X Δ BDEs reflect differences in effects on the parent molecules. These differences can be substantial, particularly for EW Y substituents where, as the NHX group becomes less electron-rich, stabilization of the parent molecule and hence Δ BDEs decline dramatically; for example, for Y = NO₂, N–X Δ BDEs = 5.6, 4.7, 3.7, and 2.0 kcal/mol for X = CH₃, H, OH, and F, respectively. For ED Y's, the parent molecule is less destabilized for X = F than for X = CH₃; hence, N–F Δ BDEs are somewhat smaller than N–CH₃ Δ BDEs.

The correlation of N–X Δ BDEs with $\sigma_p^+(Y)$ yields ρ^+ values which decrease from 5.0 ± 0.3 to 4.6 ± 0.3 , 4.0 ± 0.2 , and 3.0 ± 0.2 kcal/mol for X = CH₃, H, OH, and F, respectively. Despite large changes in the magnitude and direction of bond polarity (as given by differences in Pauling electronegativities, viz., N ^{δ^-} –C ^{δ^+} ($\Delta\chi = 0.6$), N ^{δ^-} –H ^{δ^+} ($\Delta\chi = 1.0$), N ^{δ^+} –O ^{δ^-} ($\Delta\chi = -0.4$), N ^{δ^+} –F ^{δ^-} ($\Delta\chi = -0.9$)), the signs of ρ^+ remain the same, and the magnitudes remain between the values found for 4-YC₆H₄O–X (ca. 6–7 kcal/mol)⁵ and 4-YC₆H₄CH₂–X (very small, or no correlation with σ_p^+).^{4,5}

Summary

Our DFT model successfully reproduces the experimentally determined effects of substituents on N–H Δ BDEs in 4,4'-disubstituted diphenylamines (Table 3), 3,7-disubstituted phenothiazines (Table 2), and 4-substituted anilines, provided the substituent is electron-withdrawing (Table 1). We are therefore led to suggest that the lack of agreement between theory and experiment for anilines substituted with electron-donating groups (Table 1) is due to errors in the measured BDEs for this particular group of anilines.

By analogy with the effects of Y substituents on Z–X Δ BDEs in 4-YC₆H₄Z–X for Z = CH₂ and O, we had expected that substituent effects for Z = NH would have the three following properties (see Introduction):

1. NH–X Δ BDEs would be essentially independent of X, an expectation that is not fulfilled (see Table 4) because effects of Y on the stability of 4-YC₆H₄NHX are comparable in magnitude to effects of Y on the stability of 4-YC₆H₄NH• (see, e.g., Figure 3).

2. For the same Y substituents, NH–X Δ BDEs would be lower than O–X Δ BDEs but greater than CH₂–X Δ BDEs, an expectation which is fulfilled (see Table 5).

3. NH–X Δ BDEs should correlate well with $\sigma_p^+(Y)$, an expectation that is fulfilled but, in contrast to the situation with phenols, the MSEs and RSEs for 4-YC₆H₄NH₂ are of comparable magnitude (see Table 5).

In conclusion, the effects of Y substituents on N–X Δ BDEs in 4-YC₆H₄NH–X are determined by the competing effects of Y in stabilizing (EW Y's)/destabilizing (ED Y's) the parent

(34) It should be noted that the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory also predict similar minimum energy structures. AM1 finds the twist angle as 39.5° for diphenylaminyl, 39.6° for 4,4'-(NO₂)₂-diphenylaminyl and 37.5° for 4,4'-(N(CH₃)₂)-diphenylaminyl. Other computational and experimental work regarding the structure of diphenylaminyls will be presented elsewhere.

(35) Leyva, E.; Platz, M. S.; Niu, B.; Wirz, J. *J. Phys. Chem.* **1987**, *91*, 2293–2298.

(36) Shida, T.; Kira, A. *J. Phys. Chem.* **1969**, *73*, 4315–4320.

(37) This matter is further explored for the even more electron-rich 4-YC₆H₄N(CH₃)₂ and 4-YC₆H₄N⁺CH₃ in the Supporting Information.

molecule and in destabilizing (EW Y's)/stabilizing (ED Y's) 4-YC₆H₄NH•. The effects on the parent molecule are larger than the effects on the radical for all but very strong ED Y's, and thus they play a very critical role in determining the magnitude of the N–X BDE. This contrasts with 4-YC₆H₄CH₂-X and 4-YC₆H₄O-X, where the effects of Y on the stability of the radical largely determine the magnitudes of the CH₂-X and O-X ΔBDEs.

Experimental Section

Method of Calculation. This has been described elsewhere. In short, all calculations were done with the low-level model (LLM) described by DiLabio et al.^{13d} unless otherwise indicated. This DFT model calls for geometries to be optimized and vibrational frequencies to be calculated using the semiempirical AM1 approach.³⁸ This is followed by a single-point calculation at the AM1 minimum energy geometry with the (RO)B3LYP exchange-correlation functional³⁹ and a 6-311+G-(2d,2p) basis set. The bond dissociation enthalpies (BDEs) were then obtained by taking the difference between molecule and radical enthalpies using the standard enthalpic corrections along with the scaled⁴⁰ AM1-calculated vibrational contributions to the enthalpy. The electronic energy of the hydrogen atom was set to its exact value of -0.500 000 hartree.

To examine the suitability of AM1 for calculating geometries and vibrational frequencies for these systems, the N–H BDE calculations were repeated, where indicated, with the medium-level model (MLM) and high-level model (HLM) of ref 13d. The MLM calls for a HF/6-31G(d) geometry optimization and frequency calculation, followed by reoptimization at the MP2(full)/6-31G(d) level of theory and then single-point calculation with (RO)B3LYP/6-311+G(2d,2p). The HLM is simply the full (RO)B3LYP/6-311+G(2d,2p) calculation. In both cases, the electronic energy of the hydrogen atom is again set to -0.500 000 hartree.

The interaction enthalpies presented in Table 5 (X = NH, O, CH₂) were obtained by calculating the enthalpy differences for the isodesmic reactions



where the enthalpy of each species was calculated with LLM.⁴³

Synthesis of 4,4'-Disubstituted Diphenylamines. The 4,4'-symmetrically disubstituted diarylamines were prepared using the method

described by Hartwig and co-workers for the palladium-catalyzed amination of aromatic amines.⁴¹ Briefly:

N,N-Di(4-methylphenyl)amine. Amounts of 5.0 g (29.2 mmol, 1 equiv) of 4-bromotoluene (Aldrich), 1.13 g (1.46 mmol, 0.05 equiv) of [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ((DP-PF)PdCl₂, Aldrich), and 2.43 g (4.38 mmol, 0.15 equiv) of 1,1'-bis(diphenylphosphino)ferrocene (DPPF, Aldrich) were suspended in 50 mL of dry dioxane in a flame-dried round-bottom flask kept under argon. To the mixture was added 4.07 g (38.0 mmol, 1.3 equiv) of *p*-toluidine (*p*-methylaniline, Aldrich) and 4.26 g (38.0 mmol, 1.3 equiv) of potassium *tert*-butoxide, and the contents were stirred under argon for 3 h at 80–100 °C. The orange-brown suspension was then allowed to cool to room temperature, after which water (5 mL) was added and the mixture extracted with ethyl acetate. The organic solution was filtered, washed with water (2 × 15 mL), and dried over Na₂SO₄, and the solvent was removed under vacuum. The dry solid was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate 9:1, to yield the diphenylamine in >99% purity by GC/MS (yield 92%). *m/z* (EI⁺) (relative intensity): 197 (M⁺, 100), 182 (5), 181 (11), 180 (16), 167 (5), 106 (3) 91 (20), 90 (5). ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.20 (s, 6H), 6.90 (d, 4H, *J* = 8.5 Hz), 6.99 (d, 4H, *J* = 8.5 Hz), 7.83 (s, 1H, exchanges with D₂O).

N,N-Di(4-methoxyphenyl)amine. Amounts of 5.0 g (26.7 mmol, 1 equiv) of 4-bromoanisole (Aldrich), 1.03 g (1.34 mmol, 0.05 equiv) of (DPPF)PdCl₂, and 2.23 g (4.02 mmol, 0.15 equiv) of DPPF were reacted as described above with 4.27 g (34.7 mmol, 1.3 equiv) of *p*-anisidine (*p*-methoxyaniline, Aldrich) and 3.89 g (34.7 mmol, 1.3 equiv) of potassium *tert*-butoxide. The reaction mixture was treated as described above to yield 23.8 mmol (89%) of the diphenylamine product in >99% purity by GC/MS. *m/z* (EI⁺) (relative intensity): 229 (M⁺, 60), 214 (100), 199 (10), 154 (6), 143 (9), 115 (5). ¹H NMR (DMSO-*d*₆, 200 MHz): δ 3.67 (s, 6H), 6.78 (d, 4H, *J* = 9.0 Hz), 6.90 (d, 4H, *J* = 9.0 Hz), 7.51 (s, 1H, exchanges with D₂O).

N,N-Di(4-*N,N*-dimethylaminophenyl)amine. Amounts of 5.0 g (25.0 mmol, 1 equiv) of 4-bromo-*N,N*-dimethylaniline (Aldrich), 0.96 g (1.25 mmol, 0.05 equiv) of (DPPF)PdCl₂, and 2.08 g (3.75 mmol, 0.15 equiv) of DPPF were reacted as described above with 4.43 g (32.5 mmol, 1.3 equiv) of 4-(dimethylamino)aniline (Aldrich) and 3.65 g (32.5 mmol, 1.3 equiv) of potassium *tert*-butoxide for 8 h. After the usual workup, the crude reaction product was purified twice by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate/triethylamine 7:2.96:0.05, to yield the diphenylamine in >99% purity by GC/MS (yield 80%). *m/z* (EI⁺) (relative intensity): 255 (M⁺, 100), 240 (36), 239 (34), 224 (10), 167 (7), 119 (4). ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.76 (s, 12H), 6.65 (d, 4H, *J* = 8.0 Hz), 6.83 (d, 4H, *J* = 8.0 Hz), 7.15 (s, 1H, exchanges with D₂O).

Measurement of N–H ΔBDEs of 4,4'-Disubstituted Diphenylamines by the REqEPR Technique. A deoxygenated benzene solution containing the diarylamine under investigation (1 × 10⁻²–1 × 10⁻³ M), an appropriate reference phenol (1 × 10⁻²–1 × 10⁻³ M), and di-*tert*-butyl peroxide (0.1 M) was sealed under nitrogen in a Suprasil quartz EPR tube placed inside the thermostated cavity of an EPR spectrometer. Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity. The temperature was controlled with a standard variable-temperature accessory and monitored before and after each run with a copper–constantan thermocouple. The molar ratio of the two equilibrating radicals [Ar₂N•]/[ArO•] was obtained from the EPR spectra and used to determine the equilibrium constant *K* = [Ar₂N•][ArOH]₀/[Ar₂NH]₀[ArO•], where the subscript zero refers to the initial concentrations of the reference phenol and diphenylamine under investigation. Initial concentrations were employed, and only one EPR spectrum was recorded from each sample to avoid significant reagent consumption. Since the concentrations of all equilibrating species had to be kept as low as possible, the intensity of irradiation was modulated by means of metal sectors of different diameters in order to prevent the dynamic

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exchange of the hydrogen atom (reaction 2) from occurring on the same time scale as the EPR experiment. Accumulation of several spectra from different samples (to increase the signal/noise ratio) was achieved by driving the EPR scan with a field-frequency lock accessory. To confirm that the two radicals were at their equilibrium concentrations under the experimental conditions, different initial absolute concentrations of the phenol and diarylamine and different light intensities were investigated.

EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with a Bruker ER 033M FF lock and a Hewlett-Packard 5350B microwave frequency counter for the determination of the g -factors, which were corrected with respect to that of the perylene radical cation in concentrated H_2SO_4 ($g = 2.0025_8$). Relative radical concentrations were determined by comparison of the digitized experimental spectra with computer simulated spectra. An iterative, least-squares fitting procedure based on the systematic application of the Monte Carlo method was performed in order to obtain the experimental spectral parameters of the two species including their relative intensities. The BDEs were calculated from the measured equilibrium constants using the equation

$$\text{BDE}(\text{Ar}_2\text{N}-\text{H}) = \text{BDE}(\text{ArO}-\text{H}) + \Delta H^\circ \approx \text{BDE}(\text{ArO}-\text{H}) - RT \ln K$$

This equation assumes that the entropy change ΔS° for the hydrogen-

transfer reaction is negligible. This assumption has been shown previously to be correct with phenols²¹ and phenothiazines.²³ The reference phenols employed were 2,4,6-trimethylphenol (BDE = 82.73 ± 0.18 kcal/mol) for N,N -di(4-methylphenyl)amine and N,N -di(4-methoxyphenyl)amine, and 2,4,6-trimethoxyphenol (BDE = 80.00 ± 0.12 kcal/mol) for N,N -di(4- N,N -dimethylaminophenyl)amine.

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Supporting Information Available: Substituent effects on 4- $\text{YC}_6\text{H}_4\text{N}(\text{CH}_3)_2$ and 4- $\text{YC}_6\text{H}_4\text{N}^\bullet\text{CH}_3$, text and Table S1; Cartesian coordinates and electronic energies of all computed structures in Tables 1–5 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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