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Remote Substituent Effects on N−X (X = H, F, Cl, CH_3, Li) Bond Dissociation Energies in *Para*-Substituted Anilines

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Received June 17, 2002

UB3LYP/6-311++g**//UB3LYP/6-31+g* and ROMP2/6-311++g**//UB3LYP/6-31+g* methods were used to calculate (i) N−X bond dissociation energies (BDE) in 4-YC_6H_4NH−X and (ii) N−H BDEs in 4-YC_6H_4NU−H, where Y = H, Me, OCH_3, SMe, NH_2, NMe_2, $SiMe_3$, F, Cl, CN, COOH, CF_3, and NO_2, X = H, CH_3, F, Cl, and Li, and U = H, F, and CH_3. It was found that N−H BDEs of 4-YC_6H_4-NH_2 have a positive correlation with the substituent $\sigma_p{}^+$ constants. The slope (ρ^+) is about 3.0−4.3 kcal/mol, which is in good agreement with the experimental results. It was also found that the substituent effects on N−X BDEs of 4-YC_6H_4NH−X change considerably when X changes. ρ^+ values for N−CH_3, N−F, N−Cl, and N−Li BDEs were calculated to be 3.1−4.6, 1.3−1.9, 1.8−2.6, and 4.9−6.8 kcal/mol, respectively. The reason for the variation of substituent effects was proposed to be the ground-state effect, i.e., the interaction between the intact NH−X moiety and the *para* substituents. Finally, α-substitution was found to be able to significantly change the substituent effects. ρ^+ values for N−H BDEs of 4-$C_6H_4NCH_{3-}$H and 4-C_6H_4NF−H are 2.5−4.0 and 1.7−1.9 kcal/mol, respectively.

1. Introduction

Bond dissociation energy (BDE), defined as the gas-phase enthalpy change for the reaction X−Y → X• + Y•, is important in understanding the stability and reactivity of radicals. BDE has been intensively studied for many years, and so far BDEs have been successfully measured for many relatively simple compounds.[1] However, it remains hard to obtain the gas-phase BDEs of relatively large nonvolatile molecules or compounds with several labile chemical bonds.

An alternative way to determine BDEs is to do measurements in solution. Either the electrochemical[2] or photoacoustic[3] technique can be used. The data obtained in this way can be extrapolated to the standard state conditions (i.e. 298 K in the gas phase). Remarkably, using the solution-phase methods it is fairly easy to estimate the BDEs of relatively large compounds such as phenols, anilines, and thiophenols.[4,5] However, because of the solvent effect, sometimes we cannot reliably extrapolate gas-phase BDEs from BDEs measured in solution.[6]

The third way to determine BDEs is to use theories. Presently, there are many quantum chemistry methods that can be used for this purpose. Nevertheless, unrestricted Hartree−Fock (UHF) and perturbation theory methods (e.g. UMP2) are not recommended for BDE calculation, as they suffer acutely from spin contamination.[7] Higher levels of ab initio methods such as QCISD and CCSD are reliable for many radicals, but they still cannot reach an accuracy of 1−2 kcal/mol in predicting BDEs. At present, the best way to calculate BDEs is to use the composite ab initio methods such as G3[8] and CBS.[9] Unfortunately, the cost of such computation for molecules with over eight heavy atoms is too expensive.

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10.1021/jo0204146 CCC: $25.00

A practical solution to the above problem has been proposed. According to it, one does not need to directly calculate the BDE of a large molecule (**L**) using a sophisticated method. Instead, one can calculate the BDE of a much simpler analogue (or model compound, **M**) of the large molecule using a high level of method. Then one can calculate BDEs of **L** and **M** using a low level method. A good estimation for the BDE of **L** can be obtained as[10]

$$\mathrm{BDE}(\mathbf{L})^{\text{high level}} = \mathrm{BDE}(\mathbf{M})^{\text{high level}} + \mathrm{BDE}(\mathbf{L})^{\text{low level}} - \mathrm{BDE}(\mathbf{M})^{\text{low level}} \quad (1)$$

The success of eq 1 in predicting BDEs demands the relative BDE of the large molecule vs its analogue, i.e., the term BDE(**L**) − BDE(**M**), to be insensitive to methods. Luckily, such insensitivity has been found to be true for many systems.[11] In fact, recently Radom et al found that B3LYP (either restricted or unrestricted) and ROMP2 methods are often good enough for the calculation of BDE(**L**) − BDE(**M**).[12] Thus, using a combination of B3LYP, ROMP2, and G3 methods we should be able to calculate the BDEs of relatively large molecules with a reasonable precision.

In this study we take advantage of eq 1 to determine the BDEs of substituted anilines. Experimental studies on the same subject have been conducted before using electrochemical measurement (EM) in DMSO, pulse radiolysis (PR) in water, and photoacoustic calorimetry (PC) in benzene.[5] However, these experimental results are not completely consistent with each other. For example, from EM the N−H BDE of aniline was predicted to be 92.3 kcal/mol, whereas from PR and PC the same BDE was predicted to be 89.1 and 89.7 kcal/ mol.

The substituent effect on aniline BDEs is another target of this study. The same topic has been addressed in the previous experimental studies.[5] However, the origin of the substituent effects on aniline BDEs, i.e., whether the substituent effects come from the stabilization/destabilization of neutral anilines by the substituents (ground-state effect) or from the stabilization/ destabilization of aniline radicals by the substituents (radical state effect), remains unclear. In fact, for some time it was assumed that the direction and magnitude of the effects of Y-substituents on Z−X BDEs in compounds having the general formula $4\text{-}YC_6H_4Z{-}X$ could be correlated with the polarity of the Z−X bond undergoing homolysis.[13] However, recently it was proposed that when Y have significant effects on Z−X BDEs it must be due to their stabilization or destabilization of the radicals instead of the neutral compounds regardless of the nature of X, Y, and Z.[14] In other words, it was proposed that

$$\mathrm{BDE}(4\text{-}YC_6H_4Z{-}X_a) - \mathrm{BDE}(C_6H_5Z{-}X_a) \approx \mathrm{BDE}(4\text{-}YC_6H_4Z{-}X_b) - \mathrm{BDE}(C_6H_5Z{-}X_b) \quad (2)$$

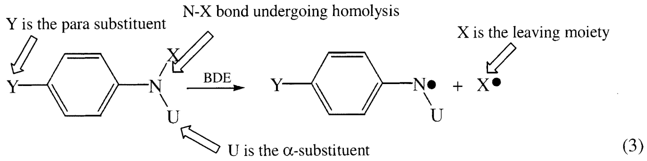
Equation 2 was thought to be supported by the fact that the effects of Y on C−X BDEs in $4\text{-}YC_6H_4CH_2{-}X$ (X = H, F, Cl, and Br) are roughly equal for each X, despite large changes in C−X bond polarity.[14] Equation 2 was also thought to be supported by the fact that changes in O−X BDEs induced by changing Y in $4\text{-}YC_6H_4O{-}X$ (X = H, CH_3, and CH_2Ph) are large and essentially identical for each X.[14]

Our recent studies on P−X (X = H, F, and Cl) BDEs of $4\text{-}YC_6H_4PH{-}X$ and Si−X (X = H, Li, F, and Cl) BDEs of $4\text{-}YC_6H_4SiH_2{-}X$, however, gave contradictory results against the above proposal.[15] Not only the magnitude of the substituent effects vary significantly when X changes but also the direction of the substituent effects may change when X changes from an electronegative atom (i.e. F or Cl) to an electropositive one (i.e. Li). It was found that the ground-state effect plays a very important role for the substituent effects. Therefore, eq 2 was found to be invalid.[15]

It is interesting to test if the same behaviors of substituent effects can be observed with anilines. Therefore, we conducted calculations on N−X BDEs of $4\text{-}YC_6H_4\text{-}NH{-}X$ (X = H, F, Cl, CH_3, and Li). Furthermore, to see if α-substitution can also change the substituent effects, we calculated the N−H BDEs of $4\text{-}YC_6H_4NCH_3{-}H$ and $4\text{-}YC_6H_4NF{-}H$.

2. Method

All the calculations were done using Gaussian 98.[16] BDE was calculated as the enthalpy change of the following reaction in the gas phase at 298 K using UB3LYP/ 6-311++g**// UB3LYP/6-31+g* and ROMP2/6-311++g**//UB3LYP/6-31+g* methods.[12]



(3)

In detail, the geometry was optimized at UB3LYP/6-31+g* level and the single-point energy was calculated at UB3LYP/ 6-311++g** or ROMP2/6-311++g** level. The results were corrected with zero point energies, temperature corrections, and the pressure−volume work term obtained at the UB3LYP/

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TABLE 1. N−X Bond Dissociation Energies (kcal/mol) Calculated Using the G3 Method

N−X	BDE	N−X	BDE
C_6H_5NH-H	91.4	C_6H_5NH-Li	67.6
$C_6H_5NH-CH_3$	71.8	$C_6H_5NCH_3-H$	89.1
C_6H_5NH-F	56.9	C_6H_5NF-H	76.8
C_6H_5NH-Cl	47.4		

6-31+g* level (unscaled), as the enthalpy of a species was evaluated using

$$H_{298} = E + \text{ZPE} + \Delta H_{298-0} + RT \tag{4}$$

It should be mentioned that all the final structures were confirmed by UB3LYP/ 6-31+g* frequency calculations to be real minima without any imaginary frequency.

3. Results and Discussion

3.1. N−X BDEs of C_6H_5NU-X. In Table 1 are summarized the N−X BDEs calculated using G3 method. According to the previous studies,[12] these BDEs should have accuracy of 1−2 kcal/mol.

According to Table 1, N−H BDE of Ph−NH_2 is 91.4 kcal/mol. This value is larger than that estimated from pulse radiolysis (89.1 kcal/mol) and photoacoustic calorimetry (89.7 kcal/mol) but smaller than that estimated from electronchemical measurement (92.3 kcal/mol).[5]

When X changes in C_6H_5NH−X, the N−X BDE decreases in the order N−H > N−CH_3 > N−Li > N−F > N−Cl. The variation is over 40 kcal/mol. The α-substituent U also affects the N−H BDE in C_6H_5NU−X. From C_6H_5NH−H to C_6H_5NF−H, the N−H BDE decreases by about 15 kcal/mol.

3.2. N−H BDEs of 4-YC_6H_4NH−H. According to eq 1, we can predict the N−X BDEs of substituted anilines using

$$\text{BDE}(YC_6H_4NU-X)^{\text{predicted}} = \text{BDE}(C_6H_5NU-X)^{G3} + [\text{BDE}(YC_6H_4NU-X)^{\text{low level}} - \text{BDE}(C_6H_5NU-X)^{\text{low level}}] \tag{5}$$

We define

$$\Delta\text{BDE} = \text{BDE}(YC_6H_4NU-X) - \text{BDE}(C_6H_5NU-X) \tag{6}$$

Then the accuracy of eq 5 depends on how well we can calculate ΔBDE.

For N−H BDEs of *para*-substituted anilines, experimental ΔBDEs are available. Therefore, we compared the experimental ΔBDEs with the ΔBDEs calculated using UB3LYP/6-311++g**//UB3LYP/6-31+g* and ROMP2/6-311++g**//UB3LYP/6-31+g* methods in Table 2.

TABLE 2. Theoretical (UB3LYP/6-311++g//UB3LYP/6-31+g* and ROMP2/6-311++g**//UB3LYP/6-31+g*) and Experimental ΔBDEs of *Para*-Substituted Anilines (kcal/mol)**

substituent	ΔBDE(B3LYP)[a]	ΔBDE(MP2)	ΔBDE(expt)
H	0.0	0.0	0.0
F	−1.2	−0.9	−0.9[b]
Cl	−0.5	0.0	0.1[c]
NH_2	−6.0	−4.4	−3.1[d]
COMe	2.0	1.8	1.5,[d] 1.9[c]
CN	2.4	2.4	2.7,[d] 2.9[c]
CH_3	−0.5	−1.0	−0.4,[d] −0.3,[c] −2.2[b]
OCH_3	−3.9	−3.2	−1.9,[d] −1.9[c]
NO_2	4.1	2.6	4.4[c]

[a] ΔBDE is defined as ΔBDE = BDE(Y−C_6H_4−NH_2) − BDE(C_6H_5−NH_2). [b] Taken from ref 5c. [c] Taken from ref 5a. [d] Taken from ref 5b.

According to Table 2, good to excellent agreement between the theory and experiment is found for the ΔBDEs of F, Cl, CH_3, COMe, CN, CF_3, and NO_2 substituents. Nevertheless, for NH_2 the theoretical ΔBDE is about 1.3−2.9 kcal/mol lower than the experimental value. For OCH_3, the theoretical ΔBDE is about 1.3−2.0 kcal/mol lower than the experimental value.

Hammett regression between UB3LYP/6-311++g** ΔBDEs and substituent σ_p^+ constants gives a slope (ρ^+) of 4.5 kcal/mol. ρ^+ for ROMP2/6-311++g** results is 3.5 kcal/mol. ρ^+ for the average experimental ΔBDEs is 3.5 kcal/mol. It appears that ROMP2 method gives a better prediction.

3.3. Substituent Effects on N−X BDEs. The above results demonstrate that it is acceptable to use UB3LYP and ROMP2 methods to calculate ΔBDEs. Thus, we used the same strategy and calculated the ΔBDEs associated with the N−X BDEs in different Y−C_6H_4NU−X systems. The results are summarized in Table 3. On the basis of Tables 1 and 3, one can use eq 5 to obtain the N−X BDEs of a large number of substituted anilines.

The results from Hammett regressions between the calculated ΔBDEs and substituent σ_p^+ constants are also shown in Table 3. In general, the correlations are good to excellent as the correlation coefficients (r) are always higher than 0.90. ρ^+ values from ROMP2 are usually slightly lower than ρ^+ from UB3LYP except for the NH−F and NH−Cl cases. As discussed above, it is likely that the real ρ^+ should be closer to ROMP2 predictions.

According to Table 3, ρ^+ for NH−H is 3.0−4.3 kcal/mol. This value is slightly smaller than the number obtained in section 3.2 because more substituents are included in the regression. It should be mentioned that Pratt et al. gave a value of 4.6 kcal/mol for the same bond homolysis.[14c]

ρ^+ for NH−CH_3 BDEs is 3.1−4.6 kcal/mol, which is slightly larger than that for NH−H BDEs. Pratt et al. reported a value of 5.0 kcal/mol for the same bond homolysis.[14c]

ρ^+ for NH−F BDEs is 1.3−1.9 kcal/mol, which is significantly smaller than that for NH−H. Pratt et al. reported a value of 3.0 kcal/mol for the same bond homolysis.[14c]

ρ^+ for NH−Cl BDEs is 1.8−2.6 kcal/mol, which is also significantly smaller than that for NH−H. On the other

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TABLE 3. Relative N−X BDEs[a] (kcal/mol) of Substituted Anilines Calculated Using UB3LYP/6-311++G//UB3LYP/6-31+g* and ROMP2/6-311++G**//UB3LYP/6-31+g* Methods**

	YC$_6$H$_4$NH−H		YC$_6$H$_4$NH−CH$_3$		YC$_6$H$_4$N H−F		YC$_6$H$_4$NH−Cl		YC$_6$H$_4$NH−Li		YC$_6$H$_4$NCH$_3$−H		YC$_6$H$_4$NF−H	
substituent	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Me	−0.5	−1.0	−0.5	−1.0	−1.3	−1.2	−1.3	−1.7	0.0	−0.5	−1.4	−1.0	−0.8	−0.8
OMe	−3.9	−3.2	−4.1	−3.3	−1.4	−1.9	−1.9	−2.1	−5.7	−4.4	−3.6	−2.8	−1.4	−1.4
SMe	−2.2	−0.8	−2.0	−0.8	−2.0	−1.9	−2.2	−1.7	−0.8	0.2	−1.7	−0.5	−2.0	−1.4
NH$_2$	−6.0	−4.4	−6.1	−4.4	−2.1	−2.9	−2.8	−3.4	−7.2	−5.1	−5.5	−3.7	−2.4	−2.2
NMe$_2$	−6.6	−4.7	−6.8	−4.7	−2.2	−3.3	−2.9	−3.9	−7.7	−4.4	−6.0	−3.7	−2.7	−2.6
SiMe$_3$	0.7	−1.8	0.0	−0.6	−0.1	−0.6	−0.1	0.6	0.7	0.7	0.1	−0.5	−0.2	0.0
F	−1.2	−0.9	−1.0	−0.8	−0.7	−0.7	−0.8	−0.5	−0.7	−0.6	−1.2	−0.9	−0.3	−0.3
Cl	−0.5	0.0	−0.3	−0.1	−0.9	−0.5	−0.8	0.0	0.8	0.7	−0.4	−0.3	−0.4	−0.2
CN	2.4	2.4	3.0	2.2	0.1	0.7	0.5	1.4	6.7	5.9	2.5	2.1	1.2	1.3
COOH	2.6	1.7	3.1	1.8	0.7	0.9	1.0	1.5	6.3	5.0	2.6	1.4	1.2	1.1
NO$_2$	4.1	2.6	4.9	2.7	1.1	1.2	1.6	2.4	9.9	7.2	4.2	1.9	2.3	1.6
ρ^+	4.3	3.0	4.6	3.1	1.3	1.9	1.8	2.6	6.8	4.9	4.0	2.5	1.9	1.7
r	0.98	0.95	0.98	0.97	0.90	0.98	0.95	0.98	0.95	0.92	0.98	0.96	0.95	0.98

[a] ΔBDE is defined as ΔBDE = BDE(Y−C$_6$H$_4$−NU−X) − BDE(C$_6$H$_5$−NU−X).

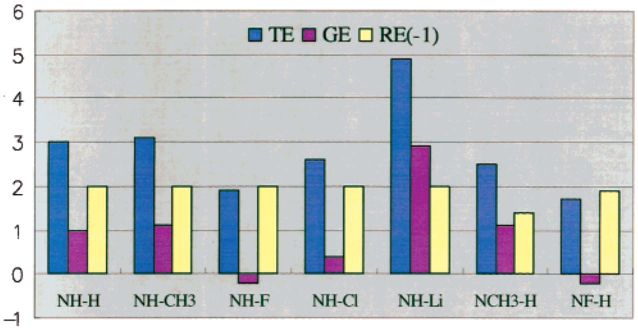

FIGURE 1. ρ^+ values for the total substituent effects (TE), ground-state effect (GE), and radical-state effect × −1 (RE) on N−X BDEs of Y−C$_6$H$_4$−NU−X. Notice the significant variation of TE, GE, and RE. Also notice the following relationship: TE = GE − RE.

hand, ρ^+ for NH−Li BDEs is 4.9−6.8 kcal/mol, which is significantly larger than that for NH−H.

The above ρ^+ values indicate that the Y-substituent effects on the Z−X BDEs of 4-YC$_6$H$_4$Z−X should have some dependence on the nature of X (Figure 1). Therefore, the recent theory[14] about the remote substituent effects on BDEs (i.e. eq 2) is wrong.

Interestingly, α-substitution can also change the remote substituent effects. According to Table 3, ρ^+ for NCH$_3$-H BDEs is 2.5−4.0 kcal/mol, which is slightly smaller than that for NH−H. On the other hand, ρ^+ for NF−H BDEs is 1.7−1.9 kcal/mol, which is much smaller than that for NH−H.

3.4. Origin of the Substituent Effects. To explain the observed substituent effects on BDEs, we define the ground-state and the radical-state effects using the enthalpy changes of the following isodesmic reactions.

$$\text{ground-state effect: } Y{-}C_6H_4{-}NUX + C_6H_6 \rightarrow Y{-}C_6H_5 + C_6H_5{-}NUX \quad (7)$$

$$\text{radical-state effect: } Y{-}C_6H_4{-}NU\bullet + C_6H_6 \rightarrow Y{-}C_6H_5 + C_6H_5{-}NU\bullet \quad (8)$$

According to above equations, the ground-state effect reflects the energy affect to separate the NUX moiety from the substituent Y. The radical-state effect reflects the energy effect to separate the NU• moiety from the substituent Y.[19] The detailed results for the ground-state and radical-state effects can be found in the Supporting Information. The Hammett regression results are shown in Table 4.

TABLE 4. Slopes and the Correlation Coefficients of Hammett Regressions of the Ground-State or Radical-State Effect[a] against Substituent $\sigma_p{}^+$ Constants

	UB3LYP/6-311++g**		ROMP2/6-311++g**	
species	ρ^+	r	ρ^+	r
Y−C$_6$H$_4$NH−H	2.3	0.90	1.0	0.76
Y−C$_6$H$_4$NH−CH$_3$	2.6	0.90	1.1	0.77
Y−C$_6$H$_4$NH−F	−0.7	0.70	−0.2	0.28
Y−C$_6$H$_4$NH−Cl	−0.2	0.40	0.4	0.00
Y−C$_6$H$_4$NH−Li	4.8	0.88	2.9	0.80
Y−C$_6$H$_4$NH•	−2.0	0.94	−2.0	0.97
Y−C$_6$H$_4$NCH$_3$•	−1.4	0.94	−1.4	0.95
YC$_6$H$_4$NF•	−2.6	0.98	−1.9	0.97

[a] For Y−C$_6$H$_4$−NU−X, the ground-state effect is calculated as the enthalpy change of the following reaction at 298 K: Y−C$_6$H$_4$−NU−X + C$_6$H$_6$ → Y−C$_6$H$_5$ + C$_6$H$_5$−NU−X. For the Y−C$_6$H$_4$−NU· radical, the radical-state effect is calculated as the enthalpy change of the following reaction at 298 K: Y−C$_6$H$_4$−NU·+ C$_6$H$_6$ → Y−C$_6$H$_5$ + C$_6$H$_5$−NU·.

According to Table 4, the ground-state effects mostly do not have good correlation with substituent $\sigma_p{}^+$ constants. Nevertheless, ρ^+ for NH−H is positive. Therefore, separating the NH−H moiety from an electron-withdrawing *para*-substituent is an energy-uphill process, whereas separating NH−H from an electron-donating *para*-substituent is energy-downhill. The reason for these behav-

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(17) Dilabio, G. A.; Pratt, D. A.; LoFaro, A. D.; Wright. J. S. *J. Phy. Chem. A* **1999**, *103*, 1653.

(18) *CRC Handbook of Chemistry and Physics*, 82nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2001−2002.

(19) It should be mentioned that Nau has proposed another separation method for the substituent effects. (See: (a) Nau, W. M. *J. Org. Chem.* **1996**, *61*, 8312. (b) Nau, W. M. *J. Phys. Org. Chem.* **1997**, *10*, 445.) According to his proposal, the radical-state effect should be calculated using the following isodesmic equation: Y−C$_6$H$_4$−NU−NU−C$_6$H$_4$−Y + 2C$_6$H$_5$−NU−X → C$_6$H$_5$−NU−NU−C$_6$H$_5$ + 2Y−C$_6$H$_4$−NU−X. The advantage of using the above isodesmic equation is that the radical-state effect would be free from the polar effect in Y−C$_6$H$_4$−NU•, because Y−C$_6$H$_4$−NU−NU−C$_6$H$_4$−Y contains a nonpolar N−N bond. Thus, all the polar effect involved in the bond homolysis is allocated to the ground-state effect. However, we consider that there is no necessity to believe that all the radical-state effect is nonpolar as most radicals (like Y−C$_6$H$_4$−NU•) are polar species.

iors is clear. That is, an electron-withdrawing group (e.g. NO_2), which has a low-lying unoccupied molecular orbital to receive the lone-pair electrons from NH_2, is harder to separate from the NH−H moiety than the H substituted case. On the other hand, an electron-donating substituent (e.g. NH_2), whose high-lying occupied orbitals repel the lone-pair electrons of NH_2, is easier to separate from the NH−H moiety than the H-substituted case.

The ground-state effect for $NH-CH_3$ shows a slightly higher ρ^+ than NH−H. This should be caused by the fact that $NH-CH_3$ is a better electron donor than NH−H. Indeed, the HOMO energy of H−NH−H is −0.430 68 hartree (ROMP2/6-311++g**), lower than that for $H-NCH_3-H$ (−0.392 58 hartree, ROMP2/6-311++g**). Similarly, as the HOMO energy of H−NH−Li is −0.285 60 hartree, the ground-state effect for NH−Li shows the highest ρ^+.

On the other hand, the HOMO energy of H−NH−F is −0.475 81 hartree, which is lower than that for H−NH−H. Therefore, ρ^+ for the ground-state effect of NH−F is lower than that for NH−H. The HOMO of H−NCl−H is −0.417 10 hartree. Although it is higher than that for H−NH−H, ρ^+ for the ground-state effect of NCl−H is lower than that for NH−H. The reason for this behavior remains to be clarified.

It should be noted that subtraction of eq 7 by eq 8 gives the following equation:

$$Y-C_6H_4-NUX + C_6H_5-NU\bullet \rightarrow C_6H_5-NUX + Y-C_6H_4-NU\bullet \quad (9)$$

Thus, subtraction of ρ^+ for the ground-state effect of NU−X by ρ^+ for radical-state effect of NU• should give a value equal to ρ^+ for the substituent effects on NU−X BDEs (see Figure 1). For example, ρ^+(B3LYP) for the ground-state effect of NH−H is 2.3 kcal/mol. ρ^+(B3LYP) for the radical-state effect of NH• is −2.0 kcal/mol. Therefore, ρ^+(B3LYP) for the substituent effects on NH−H BDEs is 4.3 kcal/mol.

Because all the NH−X homolysis provides the same radical ($YC_6H_4-NH\bullet$), the different ρ^+ observed for NH−X BDEs must be caused by the unequal ground-state effect. Since the ground-state effects change from $\rho^+ = -0.7$ kcal/mol for NH−F to $\rho^+ = 4.8$ kcal/mol for NH−Li, the contribution from the ground-state effects to the total substituent effects on BDEs is large. As a result, eq 2 is wrong.

3.5. α-Substitution Effects. According to Table 4, the radical-state effect for NH• has a negative ρ^+ of −2.0 kcal/mol. This means that NH• is electron withdrawing, obviously because NH• has a singly occupied molecular orbital (SOMO) capable of accepting more electron density.

The SOMO energy for $NCH_3\bullet$ is −0.009 95 hartree (ROMP2/6-311++g**), which is slightly higher than that for NH•, −0.115 53 hartree. Therefore, $NCH_3\bullet$ is less electron withdrawing than NH•, reflected by the higher ρ^+ found for $NCH_3\bullet$, −1.4 kcal/mol.

The SOMO energy for NF• is −0.132 59 hartree, lower than that for NH•. Therefore, NF• is more electron withdrawing than NH•. As a result, ρ^+(B3LYP) for NF• (−2.6 kcal/mol) is lower than that for NH•. However, it is surprising that ρ^+(MP2) for NF• (−1.9 kcal/mol) is slightly higher than that for NH•.

Because CH_3 reduces ρ^+ for the ground-state effect of NCH_3-H almost to the same extent as it reduces ρ^+ for the radical-state effect of $NCH_3\bullet$, ρ^+ for the substituent effect on NCH_3-H BDEs is quite close to that for NH−H BDEs.

However, because F reduces ρ^+ for the ground-state effect of NF−H to a larger extent than it reduces ρ^+ for the radical-state effect of NF•, ρ^+ for the substituent effect on NF−H BDEs is significantly lower than that for NH−H BDEs.

4. Conclusion

In the study we used UB3LYP/6-311++g**//UB3LYP/6-31+g* and ROMP2/6-311++g**//UB3LYP/6-31+g* methods to study the N−X BDEs of substituted anilines. In addition to the collection of a large number of BDE data, we found that the substituent effects on the N−X BDEs of $4-YC_6H_4NH-X$ changes considerably when X changes. ρ^+ values for N−H, $N-CH_3$, N−F, N−Cl, and N−Li BDEs are 3.0−4.3, 3.1−4.6, 1.3−1.9, 1.8−2.6, and 4.9−6.8 kcal/mol, respectively. The reason for the large variation of the substituent effects on different N−X BDEs was found to be the ground-state effect, i.e., the interaction between the intact NH-X moiety and the *para* substituents. In addition, it was found that α-substitution can also significantly change the substituent effects. ρ^+ values for the N−H BDEs of $4-C_6H_4NCH_3-H$ and $4-C_6H_4-NF-H$ are 2.5−4.0 and 1.7−1.9 kcal/mol, respectively.

Acknowledgment. We are grateful to the NSFC for financial support.

Supporting Information Available: Tables listing bond dissociation energies, ground and radical state effects, and detailed descriptions of the optimized geometry for each of the molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0204146