A theoretical study on the homolytic dissociation energies of H–N$^+$ bonds†

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Various levels of theoretical calculations were performed to study the N$^+$–H bond dissociation energies (BDEs) of protonated amines in order to check the experimental results and to investigate the substituent effects. It was found that the reported experimental N$^+$–H BDEs in the gas phase are possibly not accurate. Our best predictions on the basis of CBS-Q and G3 calculations for the N$^+$–H BDEs of NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $PhNH_3^+$, and pyridinium are 125 ± 1, 110 ± 1, 107 ± 1, 95 ± 1, 75 ± 2, and 124 ± 1 kcal mol^{-1}, respectively. In agreement with a previous study, it was also found that the solvent effects on the N$^+$–H homolysis in acetonitrile are large, which significantly increases the N$^+$–H BDEs compared to the gas phase. Further studies on the N$^+$–H BDEs of protonated *para*-substituted anilines indicated that the substituent effects should have a slope of about 8.7 kcal mol^{-1} against the substituent σ_p^+ constants. This value is larger than that for the O–H BDEs of phenols (6.7–6.9 kcal mol^{-1}) and N–H BDEs of neutral anilines (3.0 kcal mol^{-1}). The pattern of substituent effects is also completely different from that for the C–H BDEs of toluenes, as the C–H BDEs of toluenes are reduced by both the electron-withdrawing and -donating groups. Thus, we concluded that it is the electron demand of the system that dictates the substituent effects on BDEs. For the protonated aniline case, the origin of the substituent effects was found to be that an electron-withdrawing group destabilizes $X–C_6H_4–NH_2^{+\bullet}$ more than $X–C_6H_4–NH_3^+$, whereas an electron-donating group stabilizes $X–C_6H_4–NH_2^{+\bullet}$ more than $X–C_6H_4–NH_3^+$.

1. Introduction

Remote substituent effects on the homolytic bond dissociation energies (BDEs) have been of interest for years.[1] Studies have been conducted on systems including substituted toluenes, phenols, and anilines. In general, it has been found that remote substituent effects on C–H BDEs are small,[2] whereas remote substituent effects on the O–H (ρ^+ = 6.7–6.9 kcal mol^{-1})[3] and N–H ($\rho^+ \approx$ 3.0 kcal mol^{-1})[4] BDEs are significant. It is usually believed that the magnitude and direction of the substituent effects are related to the electron demand of the chemical bond undergoing homolysis. However, not all the details about such a relationship between the electron demand and radical substituent effects have been fully understood.[1]

For example, it is known that the C–H BDEs are usually lowered by both electron-donating and electron-withdrawing substituents.[2] In comparison, the O–H and N–H BDEs are often lowered by electron-donating substituents but raised by electron-withdrawing ones.[3,4] The difference was initially explained in terms of the non-bonding lone-pair electrons of heteroatoms,[5] which are not available for the carbon case. However, in recent studies on highly polarized toluenes, the "apparent" electronegativity was proposed to govern the pattern of the substituent effects.[1a,6]

Further examination of the above problem is probably necessary. For this purpose, we consider the *para*-substituted protonated anilines to be a good system to study because they are isoelectronic with toluenes. Since the nitrogen radical cation does not carry any non-bonding lone-pair electrons, any difference between the substituent effects on the C–H BDEs in toluenes and those on the N$^+$–H BDEs in protonated anilines can only come from the different electron demands of the two systems.

It should be mentioned that the gas-phase N$^+$–H BDEs of protonated amines actually have been estimated before from the gas-phase proton affinities (PAs) and adiabatic ionization potentials (IPs). However, because PAs and IPs from different sources may have discrepancies larger than 4 kcal mol^{-1}, one has to be cautious about the experimental gas-phase N–H BDEs of protonated amines.

Reexamination of the gas-phase N$^+$–H BDEs clearly is necessary. Therefore, Bordwell *et al.* recently used the solution-phase electrochemical method and measured the homolytic H–N BDEs of a number of protonated amines.[7] However, it was found that a large solvent effect is involved in the solution-phase N$^+$–H homolysis and thereby, the solution-phase BDEs are significantly larger than the gas-phase values. As a result, the solution-phase method cannot be used to check the gas-phase BDEs.

In the present study we performed high-level theoretical calculations to reexamine the N$^+$–H BDEs of various protonated amines and to study the remote substituent effects on the N$^+$–H BDEs of protonated anilines. The questions which interest us include: 1. What are reasonable theoretical methods to be used for the study of N$^+$–H BDEs of protonated amines? 2. What are reasonable values for the N$^+$–H BDEs of protonated amines in the gas phase? 3. What are the remote substituent effects on the N$^+$–H BDEs of protonated anilines? 4. What are the sources of the remote substituent effects on the N$^+$–H BDEs of $4-X–C_6H_4–NH_3^+$?

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† Electronic supplementary information (ESI) available: RMP2 input files and geometries of all the optimized species. See http://www.rsc.org/suppdata/p2/b2/b204417j/

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2. Methods

All the calculations were performed with GAUSSIAN 98.[8] The geometry was optimized at UB3LYP/6-31g(d), UB3LYP/6-311++g(d,p), RMP2/6-311++g(d,p), QCISD(T)/6-31g(d), and UCCSD(T)/6-31g(d) levels. All the optimized structures were confirmed by frequency calculations at the corresponding level of theory to be real minima.

Single-point energy calculations were performed at UB3LYP/6-31g(d), UB3LYP/6-311++g(d,p), UB3LYP/6-311++g-(2df,p), RMP2/6-311++g(d,p), QCISD(T)/6-31g(d), QCISD-(T)/6-311++g(d,p), UCCSD(T)/6-31g(d) and UCCSD(T)/6-311++g(d,p) levels. In addition, composite *ab initio* methods including G3, CBS-Q, and CBS-4M were used in the study.

The BDE was calculated as the enthalpy change of the following reaction in the gas phase at 298 K.

$$X–NH_3^+ \longrightarrow X–NH_2^{+\bullet} + H^\bullet \qquad (1)$$

The result was corrected with zero point energies, temperature corrections, and a pressure–volume work term obtained at UB3LYP/6-31g(d) level scaled by a factor of 0.9806 (*i.e.* $H_{298} = E + ZPE + \Delta H_{298-0} + RT$). The electronic energy of the H atom was set at its exact value, 0.500000 hartree.

The solvent effects of acetonitrile on the N$^+$–H BDEs were studied using a continuum description of the solvent based on an SCRF method at RMP2/6-311++g** level. The polarized continuum model (PCM) with the cavity definition given by the UAHF of Tomasi and coworkers[9] was employed. In the UAHF model the atomic radii of the spheres used to build the molecular cavity were adjusted by introducing chemical considerations such as hybridization, formal charge and first neighbor inductive effect. In addition, the effect of the escaped electronic charge outside the cavity was corrected with an additional set of charges on the cavity surface distributed according to the solute electronic density in each point of the surface. With this method the mean error with respect to the experimental absolute solvation energies was about 0.2 and 1 kcal mol^{-1} for neutral molecules and ions, respectively.

3. Results and discussion

3.1 Bond dissociation energies of protonated ammonia

In Table 1 are summarized the N$^+$–H BDEs of NH_4^+ calculated at different levels of theory. The corresponding experimental values are 123.6 and 127.9 kcal mol^{-1}.[7]

From Table 1, it can be seen that the UB3LYP, RMP2, UQCISD(T) and UCCSD(T) BDEs are about 1–5, 3–8, 10, and 10 kcal mol^{-1} smaller than the experimental values. Therefore, none of these methods could accurately predict N$^+$–H BDEs. In comparison, G3, CBS-Q, and CBS-4M give values of about 125 kcal mol^{-1}. This indicates that the composite *ab initio* methods could be employed to predict the absolute N$^+$–H BDEs.

From Table 1, it can also be seen that energy calculations using the same method always give similar results for BDEs, despite the fact that different methods are used in the geometry optimization. Therefore, it is reasonable to use a relatively low-level method to do geometry optimization. This strategy has been widely used before.[10] In the following we will use the UB3LYP/6-31g(d) method for the geometry optimization.

3.2 N$^+$–H Bond dissociation energies of protonated amines

In Table 2 are summarized the N$^+$–H BDEs of a number of protonated amines calculated at various levels of methods. The experimental results are also listed for comparison.

From Table 2, it is clear again that the UB3LYP, RMP2, UQCISD(T), and UCCSD(T) methods systematically underestimate the N–H BDEs. In comparison, the G3, CBS-Q, and CBS-4M methods always give BDE values fairly close to experimental results. Interestingly, from Table 2 it can be seen that one set of experimental N$^+$–H BDEs are always about 2–4 kcal mol^{-1} smaller than the theoretical values from the composite *ab initio* methods, whereas the other set of experimental values are always about 2–4 kcal mol^{-1} larger than the theoretical ones. Given the fact that the composite *ab initio* method could often achieve an accuracy of 1–2 kcal mol^{-1} in the calculation and the fact that predictions from the three composite methods are very close to each other, it is very likely that neither of the two sets of experimental BDEs are accurate. As a result, it is reasonable to use G3, CBS-Q, or CBS-4M as the benchmark methods for the calculation of N$^+$–H BDEs.

Table 1 N$^+$–H bond dissociation energy of NH_4^+ calculated at different levels of theory (kcal mol^{-1})

Method[a]	BDE
UB3LYP/6-31g(d)//UB3LYP/6-31g(d)	122.4
UB3LYP/6-311++g(d,p)//UB3LYP/6-311++g(d,p)	122.8
UB3LYP/6-311++g(d,p)//UB3LYP/6-31g(d)	122.9
RMP2/6-311++g(d,p)//RMP2/6-311++g(d,p)	120.4
RMP2/6-311++g(d,p)//UB3LYP/6-31g(d)	120.5
UQCISD(T)/6-31g(d)//UQCISD(T)/6-31g(d)	113.7
UQCISD(T)/6-31g(d)//UB3LYP/6-31g(d)	112.6
UCCSD(T)/6-31g(d)//UCCSD(T)/6-31g(d)	113.7
UCCSD(T)/6-31g(d)//UB3LYP/6-31g(d)	112.5
G3	124.1
CBS-Q	125.0
CBS-4M	125.6

[a] Except for the composite *ab initio* methods, zero-point energy correction using B3LYP/6-31g(d) vibration frequencies (scaled by 0.9806) was conducted for all the calculations of BDEs. The method depicted by, for example, RMP2/6-311++g(d,p)//UB3LYP/6-31g(d) means that the geometry optimization is done at UB3LYP/6-31g(d) level and the energy calculation is done at RMP2/6-311++g(d,p) level.

Nevertheless, once we calculate the relative N$^+$–H BDEs (Table 3) all the theoretical and experimental results become fairly consistent with each other except for the UB3LYP/6-311++g(2df,p) method.[11] Herein, the relative N$^+$–H BDE for a protonated and substituted amine is defined as the difference between its N$^+$–H BDE and that of NH_4^+. The above observation indicates that the errors of the UB3LYP, RMP2, UQCISD(T), and UCCSD(T) methods in predicting BDEs are highly systematic. As a result, it is reliable to use a relatively low-level method to calculate the relative BDEs.

According to Table 3, the N$^+$–H BDE of $CH_3NH_3^+$ is about 12–17 kcal mol^{-1} smaller than that for NH_4^+. In comparison, the N–H BDE of CH_3NH_2 is only about 7 kcal mol^{-1} smaller than that for NH_3,[12] and the C–H BDE of CH_3CH_3 is only about 4 kcal mol^{-1} smaller than that for CH_4.[10]

An additional methyl group causes about another 10 kcal mol^{-1} of decrease for the N$^+$–H BDE from $CH_3NH_3^+$ to $(CH_3)_2NH_2^+$. The third methyl group causes about 6–7 kcal mol^{-1} of decrease for the N$^+$–H BDE from $(CH_3)_2NH_2^+$ to $(CH_3)_3NH^+$. *sec*-Butyl substitution leads to about 13–17 kcal mol^{-1} of reduction in the N$^+$–H BDE. *tert*-Butyl substitution leads to about 12–16 kcal mol^{-1} of reduction in the N$^+$–H BDE.

Phenyl group shows a large effect on the N$^+$–H BDE. The difference in the N$^+$–H BDE between Ph–NH_3^+ and NH_4^+ is about 50 kcal mol^{-1}. In comparison, the N–H BDE of Ph–NH_2 is about 18 kcal mol^{-1} smaller than that for NH_3.[12] In addition, the C–H BDE of Ph–CH_3 is only about 15 kcal mol^{-1} smaller than that for CH_4.[10]

Interestingly, the N$^+$–H BDE of $PhNHMe_2^+$ is almost the same as that for $PhNH_3^+$, which means that the two methyl groups in this compound do not show any radical-stabilization effect. The reason for this behavior is possibly the steric effect in the $PhNMe_2^{+\bullet}$ radical, which makes the conjugation between the phenyl ring and the radical center not as good as that in

Table 2 N^+–H bond dissociation energies of different protonated amines calculated at various levels of theory[a] (kcal mol^{-1})

Amine	UB3LYP/6-311++g(2df,p)	RMP2/6-311++g(d,p)	UQCISD(T)/6-311++g(d,p)	UCCSD(T)/6-311++g(d,p)	G3	CBS-Q	CBS-4M	Exp.[b]	Exp.[b]
NH_3	122.6	120.5	119.6	119.6	124.1	125.0	125.6	123.6	127.9
CH_3NH_2	104.7	108.2	106.4	106.5	110.3	110.6	112.8	106.9	112.4
Me_2NH	94.3	99.8	97.9	98.0	100.7	100.7	103.5	96.4	103.6
NMe_3	85.4	91.9	89.9	90.0	95.1	94.9	96.5	91.4	99.0
s-$BuNH_2$	100.2	107.4	—	—	107.8	107.7	111.9	107.1	113.1
t-$BuNH_2$	102.9	108.4	—	—	109.3	109.1	112.9	106.0	114.4
$PhNH_2$	68.3	72.6	—	—	75.9	73.8	75.8	73.5	78.8
$PhNMe_2$	71.0	74.5	—	—	—	—	77.2	73.6	81.1
Pyridine	116.8	120.3	118.4	118.7	124.0	124.3	124.9	120.1	126.9

[a] Geometry optimized at UB3LYP/6-31g(d) was used except for the composite *ab initio* methods. [b] Data from ref. 7. There are two sets of experimental BDE values, because two sets of experimental gas phase proton affinities were used by Bordwell to calculate the BDEs. For details, see: J. E. Szelejko and T. B. McMahon, *J. Am. Chem. Soc.*, 1993, **115**, 7839; B. J. Smith and L. Radom, *J. Am. Chem. Soc.*, 1994, **115**, 4885; and M. Mautner and L. W. Sieck, *J. Am. Chem. Soc.*, 1991, **113**, 4448.

Table 3 Relative N^+–H bond dissociation energies of different protonated amines calculated at various levels of theory[a] (kcal mol^{-1})

Amine	UB3LYP/6-311++g(2df,p)	RMP2/6-311++g(d,p)	UQCISD(T)/6-311++g(d,p)	UCCSD(T)/6-311++g(d,p)	G3	CBS-Q	CBS-4M	Exp.[b]	Exp.[b]
NH_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_3NH_2	−17.9	−12.3	−13.2	−13.1	−13.8	−14.4	−12.8	−16.7	−15.5
Me_2NH	−28.3	−20.7	−21.7	−21.6	−23.4	−24.3	−22.1	−27.2	−24.3
NMe_3	−37.2	−28.6	−29.7	−29.6	−29.0	−30.1	−29.1	−32.2	−28.9
s-$BuNH_2$	−22.4	−13.1	—	—	−16.3	−17.3	−13.7	−16.5	−14.8
t-$BuNH_2$	−19.7	−12.1	—	—	−14.8	−15.9	−12.7	−17.6	−13.5
$PhNH_2$	−54.3	−47.9	—	—	−48.2	−51.2	−49.8	−50.1	−49.1
$PhNMe_2$	−51.6	−46.0	—	—	—	—	−48.4	−50.0	−46.8
Pyridine	−5.8	−0.2	−1.2	−0.9	−0.1	−0.7	−0.7	−3.5	−1.0

[a] Geometry optimized at UB3LYP/6-31g(d) was used except for the composite *ab initio* methods. [b] Data from ref. 7. There are two sets of experimental BDE values, because two sets of experimental gas phase proton affinities were used by Bordwell to calculate the BDEs.

$PhNH_2^{+\bullet}$. In fact, although the $PhNH_2^{+\bullet}$ radical is completely planar, the dihedral angle between the CH_3–N–CH_3 plane and the phenyl plane is 10.3°. The better conjugation in $PhNH_2^{+\bullet}$ than in $PhNMe_2^{+\bullet}$ can also be seen from the shorter C–N bond length in $PhNH_2^{+\bullet}$ (1.336 Å) than in $PhNMe_2^{+\bullet}$ (1.359 Å) (Fig. 1).

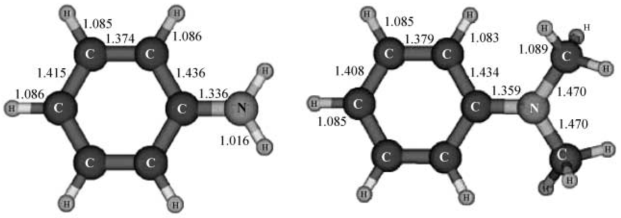


Fig. 1 Structures of C_6H_5–$NH_2^{+\bullet}$ and C_6H_5–$NMe_2^{+\bullet}$.

Finally, the N^+–H BDE of protonated pyridine is only about 1 kcal mol^{-1} smaller than that for NH_4^+. This clearly relates to the fact that the π electrons of the pyridine ring cannot interact with the singly-occupied orbital of the radical cation.

3.3 Solvent effects on the N^+–H BDEs of protonated amines

Using the PCM model we are able to estimate the N^+–H BDEs of the protonated amines in acetonitrile at RMP2/6-311++g** level. The results and the corresponding experimental values measured by Bordwell *et al.*[4] are listed in Table 4.

Because the gas-phase N^+–H BDEs calculated by the RMP2/6-311++g** method are about 3–5 kcal mol^{-1} smaller than those calculated by the composite *ab initio* methods, we cannot consider the solution-phase N^+–H BDEs calculated by the RMP2/6-311++g** PCM method to be accurate. However, from Table 4 one may notice that the RMP2/6-311++g** BDEs in acetonitrile actually agree fairly well with the values reported by Bordwell *et al.* Therefore, we conclude that either the Bordwell method[13] or the PCM model may have systematic errors. The same conclusion can also be drawn if one compares the experimental and theoretical solvent effect on the BDE, which is defined as the difference between the BDE in solution and the BDE *in vacuum*.

Table 4 Theoretical and experimental N^+–H bond dissociation energies of different protonated amines in acetonitrile[a] (kcal mol^{-1})

	Exp.[b]		RMP2/6-311++g(d,p)	
Amine	BDE	Solvent effect[c]	BDE	Solvent effect[d]
NH_3	—	—	129.5	9.0
CH_3NH_2	114.6	4.3	111.4	3.2
Me_2NH	101.5	0.8	107.6	7.8
NMe_3	96.1	1.0	102.7	10.8
s-$BuNH_2$	113.6	5.8	116.6	9.2
t-$BuNH_2$	114.3	5.0	115.6	7.2
$PhNH_2$	84.9	9.0	87.6	15.0
$PhNMe_2$	82.0	—	87.6	13.1
Pyridine	127.5	3.5	127.5	7.2

[a] Geometry optimized at UB3LYP/6-31g(d) was used. [b] Data from ref. 7. [c] This solvent effect is defined as the difference between the experimental BDEs in acetonitrile and theoretical BDEs at G3 level *in vacuum*. [d] This solvent effect is defined as the difference between the RMP2/6-311++g(d,p) BDEs in acetonitrile and *in vacuum*.

Nevertheless, one thing is certain if we compare the RMP2 BDEs in the gas phase and in acetonitrile, *i.e.* the N–H BDEs in acetonitrile are usually significantly larger than those in the gas phase. This observation was also reported by Bordwell.[7] His explanation for it was that the solvation energy for HB^+ is larger than that for $B^{+\bullet}$. Clearly, this means that one must be cautious when trying to use the solution-phase experimental results to interpret the gas-phase events.

Table 5 N^+–H bond dissociation energies of protonated *para*-substituted anilines calculated at various levels of theory[a] (kcal mol^{-1})

Substituent	σ_p^+	UB3LYP/6-311++g(2df,p)	RMP2/6-311++g(d,p)	CBS-4M	UQCISD(T)/6-31g(d)
H	0.0	68.3	72.6	75.8	65.8
CH_3	−0.31	64.3	69.1	71.2	62.6
NO_2	0.79	71.4	74.1	78.3	69.5
CN	0.66	67.9	73.2	72.5	66.8
NH_2	−1.30	53.2	56.2	59.9	50.2
$N(CH_3)_2$	−1.70	52.3	52.7	54.4	50.0
F	−0.07	66.0	69.5	73.4	64.2
Cl	0.11	64.1	68.7	72.4	63.5
$COCH_3$	—	67.7	108.3	75.2	65.6
OCH_3	−0.78	58.5	62.0	65.8	56.6
$CONH_2$	—	66.3	106.7	73.5	65.6
CF_3	0.61	70.4	74.8	77.1	68.1

[a] Geometry optimized at UB3LYP/6-31g(d) was used except for the CBS-4M method.

A slightly less certain conclusion from the comparison between the gas-phase and solution-phase RMP2 BDEs is that for the protonated alkylamines the solvent effects increase the N^+–H BDEs by about 7–10 kcal mol^{-1}. Bordwell claimed an increase of 5–7 kcal mol^{-1} for the same compounds in his study.[7] In comparison, for the protonated anilines the solvent effects increase the N^+–H BDEs by about 13–15 kcal mol^{-1}, which is larger than that for protonated alkylamines. Bordwell also observed this difference and his estimation of BDE increase for protonated anilines in acetonitrile was about 10 kcal mol^{-1}.[7] He claimed that the difference between HB^+ and $B^{+\bullet}$ solvation energies was somewhat greater for the aromatic amines than for the alkylamines.

3.4 Remote substituent effects on N^+–H BDEs of protonated anilines

In Table 5 are summarized the N^+–H BDEs of a number of protonated *para*-substituted anilines calculated using UB3LYP/6-311++g(2df,p), RMP2/6-311++g(d,p), CBS-4M, and UQCISD(T)/6-31g(d) methods.

From Table 5, it can again be seen that UB3LYP, RMP2, and UQCISD(T) methods underestimate N^+–H BDEs compared to the benchmark CBS-4M method. However, the relative BDEs (results not shown here) calculated using different methods are fairly close to each other. The only exceptions are the RMP2 results on the CH_3CO and NH_2CO substitution cases.

The problem of the RMP2 method in the BDE calculation was noticed by us in an earlier study.[14] We found that the RMP2 method could lead to an unrealistic spin distribution in a radical species. Herein, we show in Table 6 the spin density distributions of 4-CH_3CO–C_6H_4–$NH_2^{+\bullet}$ and 4-NH_2CO–C_6H_4–$NH_2^{+\bullet}$ predicted by different theoretical methods. From Table 6, it is clear that the UB3LYP, CBS-4M, and UQCISD(T) methods predict the 4-CH_3CO–C_6H_4–$NH_2^{+\bullet}$ and 4-NH_2CO–C_6H_4–$NH_2^{+\bullet}$ radicals to be nitrogen-centered ones, although the delocalization of the spin to other carbon and oxygen atoms is significant. However, the RMP2 method predicts the two radicals to be predominantly oxygen-centered ones, where the remaining atoms including nitrogens carry almost no spin. The wrong distribution of the spin clearly is the cause of the erratic N^+–H BDEs from RMP2 calculations.

Nevertheless, it appears that the spin-distribution problem only occurs for the carbonyl substituents. Therefore, for all the carbonyl-free groups, different theoretical methods predict very similar substituent effects, as shown in the following Hammett-type regressions.

$$\text{BDE (UB3LYP)} = 65.2 + 7.8\,\sigma_p^+\ (r = 0.97) \qquad (2)$$

$$\text{BDE (RMP2)} = 69.1 + 8.9\,\sigma_p^+\ (r = 0.97) \qquad (3)$$

$$\text{BDE (CBS-4M)} = 71.8 + 8.7\,\sigma_p^+\ (r = 0.94) \qquad (4)$$

$$\text{BDE (QCISD)} = 63.4 + 8.2\,\sigma_p^+\ (r = 0.97) \qquad (5)$$

The high correlation coefficients (r) in the above equations indicate the presence of well-defined substituent effects. If we take the CBS-4M results as the benchmark, one may suggest from the above results that the RMP2 could predict the substituent effects fairly well. In comparison, UB3LYP tends to give less accurate predictions about the substituent effects. Similar conclusions were drawn before by Radom *et al.* recently.[10]

The slope of the regression (~8.7 kcal mol^{-1}) is obviously much larger than that (6.7–6.9 kcal mol^{-1}) for the O–H BDEs of *para*-substituted phenols and that (~3.0 kcal mol^{-1}) for the N–H BDEs of *para*-substituted anilines. The positive sign means that electron-withdrawing groups increase the N^+–H BDE of 4-X–C_6H_4–NH_3^+ whereas electron-donating ones decrease it. This pattern of the substituent effects is completely different from that for 4-X–C_6H_4–CH_3, according to which both the donor and acceptor substituents should decrease the C–H BDEs. Clearly, the presence or absence of non-bonded lone-pair electrons on the center atom does not matter. The dominant cause of the substituent effects must be the electron demand of the system.

3.5 Origin of the remote substituent effects

In order to understand the substituent effects on N^+–H BDEs, we define the ground-state (GE) and radical-state (RE) effects as the enthalpy changes of the following gas-phase chemical reactions at 298 K.

$$\text{GE: X–}C_6H_4\text{–}NH_3^+ + C_6H_6 \longrightarrow C_6H_5\text{–}NH_3^+ + \text{X–}C_6H_5 \qquad (6)$$

$$\text{RE: X–}C_6H_4\text{–}NH_2^{+\bullet} + C_6H_6 \longrightarrow C_6H_5\text{–}NH_2^{+\bullet} + \text{X–}C_6H_5 \qquad (7)$$

Clearly, these two equations reflect the energy effects of connecting the NH_3^+ (or $NH_2^{+\bullet}$) moiety to the *para* substituents. The gap between the two effects is the total effect (TE), which actually equals the relative BDE using BDE(C_6H_5–NH_3^+) as the reference, *i.e.*

$$\text{TE: X–}C_6H_4\text{–}NH_3^+ + C_6H_5\text{–}NH_2^{+\bullet} \longrightarrow \text{X–}C_6H_4\text{–}NH_2^{+\bullet} + C_6H_5\text{–}NH_3^+ \qquad (8)$$

The results are summarized in Table 7.

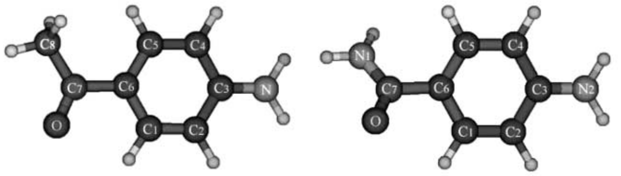
Hammett analyses of the GEs, REs, and TEs give the following equations (see also Fig. 2):

$$\text{GE} = -3.2 - 7.9\,\sigma_p^+\ (r = 0.96) \qquad (9)$$

$$\text{RE} = -0.1 - 15.7\,\sigma_p^+\ (r = 0.99) \qquad (10)$$

$$\text{TE} = -3.1 + 7.8\,\sigma_p^+\ (r = 0.97) \qquad (11)$$

Table 6 The spin distributions of the 4-CH$_3$CO–C$_6$H$_4$-NH$_2^{+\bullet}$ and 4-NH$_2$CO–C$_6$H$_4$-NH$_2^{+\bullet}$ radicals



Atom	UB3LYP/6-311++g(2df,p)	RMP2/6-311++g(d,p)	UQCISD(T)/6-31g(d)	CBS-4M
4-CH$_3$CO–C$_6$H$_4$–NH$_2^{+\bullet}$				
C$_1$	−0.051	−0.015	−0.698	−0.524
C$_2$	0.123	0.010	0.656	0.470
C$_3$	0.133	−0.003	−0.226	−0.047
C$_4$	0.169	0.001	0.722	0.554
C$_5$	−0.053	0.004	−0.734	−0.542
C$_6$	0.338	0.037	0.937	0.704
C$_7$	−0.067	0.096	−0.499	−0.556
C$_8$	0.005	−0.023	0.050	0.068
N	0.322	−0.000	0.453	0.382
O	0.123	0.888	0.441	0.591
4-NH$_2$CO–C$_6$H$_4$–NH$_2^{+\bullet}$				
C$_1$	−0.029	0.010	−0.686	−0.517
C$_2$	0.098	0.007	0.651	0.506
C$_3$	0.128	0.005	−0.222	−0.038
C$_4$	0.160	0.010	0.718	0.573
C$_5$	−0.061	0.007	−0.714	−0.537
C$_6$	0.316	0.039	0.897	0.673
C$_7$	−0.039	0.032	−0.165	−0.154
N$_1$	−0.004	0.015	−0.014	−0.015
N$_2$	0.296	0.003	0.466	0.412
O	0.170	0.874	0.140	0.161

Table 7 The ground-state and radical-state effects on the N$^+$–H bond dissociation energies of protonated *para*-substituted anilines calculated using the UB3LYP/6-311++g(2df,p) method (kcal mol^{-1})

Substituent	GE	RE	TE
H	0.0	0.0	0.0
CH$_3$	2.3	6.3	−4.0
NO$_2$	−11.4	−14.6	3.2
CN	−10.2	−9.8	−0.4
NH$_2$	6.3	21.4	−15.1
N(CH$_3$)$_2$	8.9	24.9	−16.0
F	−3.8	−1.6	−2.3
Cl	−4.1	0.1	−4.2
COCH$_3$	−3.7	−3.1	−0.6
OCH$_3$	3.2	13.0	−9.8
CONH$_2$	−3.1	−1.1	−2.0
CF$_3$	−7.4	−9.5	2.2

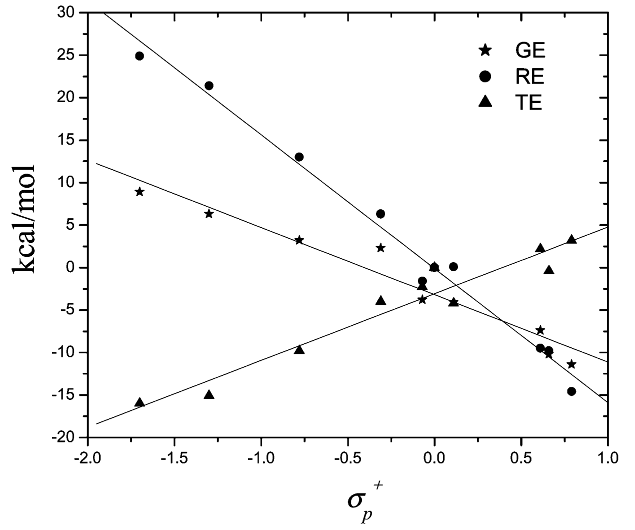


Fig. 2 The correlations between GE, RE, TE and the substituent σ_p^+ constants.

Therefore, separation of the NH$_3^+$ moiety from an electron-withdrawing substituent (GE) is an energy-downhill reaction, which clearly is true. In comparison, separation of the NH$_2^{+\bullet}$ moiety from an electron-withdrawing substituent (RE) should also be an energy-downhill process, but its slope against the σ_p^+ constants must be more negative than that for NH$_3^+$ as the radical is normally more electron-deficient. A better conjugation between the substituent and the NH$_2^{+\bullet}$ moiety than NH$_3^+$ can also be used to explain the same observation.

The total effect on the BDEs is then a positive correlation with the σ_p^+ constants. The reason is that an electron-withdrawing group should destabilize X–C$_6$H$_4$–NH$_2^{+\bullet}$ more than X–C$_6$H$_4$–NH$_3^+$, whereas an electron-donating group should stabilize X–C$_6$H$_4$–NH$_2^{+\bullet}$ more than X–C$_6$H$_4$–NH$_3^+$. Indeed, the observed slope of the N–H BDE of protonated anilines is 7.8 kcal mol^{-1} according to the UB3LYP/6-311++g(2df,p) theory, which is exactly the difference between the slope for GE (−7.9 kcal mol^{-1}) and the slope for RE (−15.7 kcal mol^{-1}).

4. Conclusion

Various levels of theoretical calculations are performed to study the N$^+$–H bond dissociation energies of protonated amines. It is found that the experimental N$^+$–H BDEs in the gas phase are possibly not accurate. It is also found that the solvent effects on the N$^+$–H BDEs in solution are large. Further studies on the N$^+$–H BDEs of protonated *para*-substituted anilines indicate that the substituent effects should have a slope of about 8.7 kcal mol^{-1} against the substituent σ_p^+ constants. This value is larger than that for the O–H BDEs of phenols and N–H BDEs of neutral anilines. The pattern of substituent effects is also completely different from that for the C–H BDEs of toluenes. Therefore, it is the electron demand of the system that dictates the substituent effects on BDEs.

Acknowledgements

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References

1 For recent examples, see: (*a*) J.-P. Cheng, B. Liu, Y.-Y. Zhao, Z. Wen and Y.-K. Sun, *J. Am. Chem. Soc.*, 2000, **122**, 9987; (*b*) D. A. Pratt, M. I. de Heer, P. Mulder and K. U. Ingold, *J. Am. Chem. Soc.*, 2001, **123**, 5518.

2 (*a*) Y.-D. Wu, C.-L. Wong, K. W. K. Chan, G.-Z. Ji and X.-K. Jiang, *J. Org. Chem.*, 1996, **61**, 746; (*b*) D. A. Pratt, J. S. Wright and K. U. Ingold, *J. Am. Chem. Soc.*, 1999, **121**, 4877.

3 (*a*) D. D. M. Wayner, E. Lusztyk and K. U. Ingold, *J. Org. Chem.*, 1996, **61**, 6430; (*b*) Y.-D. Wu and D. K. W. Lai, *J. Org. Chem.*, 1996, **61**, 7904; (*c*) T. Brinck, M. Haeberlein and M. Jonsson, *J. Am. Chem. Soc.*, 1997, **119**, 4239.

4 (*a*) F. G. Bordwell, X.-M. Zhang and J.-P. Cheng, *J. Org. Chem.*, 1993, **58**, 6410; (*b*) M. Jonsson, J. Lind, T. E. Eriksen and G. Merenyi, *J. Am. Chem. Soc.*, 1994, **116**, 1423.

5 (*a*) R. I. Walter, *J. Am. Chem. Soc.*, 1966, **88**, 1923; (*b*) R. I. Walter, *J. Am. Chem. Soc.*, 1966, **88**, 1930.

6 W. Zhong, Z.-C. Li, Z.-F. Shang and J.-P. Cheng, *J. Org. Chem.*, 2001, **66**, 1466.

7 W.-Z. Liu and F. G. Bordwell, *J. Org. Chem.*, 1996, **61**, 4778.

8 GAUSSIAN 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

9 (*a*) M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327; (*b*) V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3210; (*c*) B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151; (*d*) The solvation energy of $H^{\bullet}$ cannot be calculated using the PCM model. So we chose the SCI-PCM model to calculate this particular case. For the SCI-PCM model, see: J. B. Foresman, T. A. Keith, K. B. Wiberg, J. Snoonian and M. J. Frisch, *J. Phys. Chem.*, 1996, **100**, 16098.

10 (*a*) C. J. Parkinson, P. M. Mayer and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2305; (*b*) D. J. Henry, C. J. Parkinson, P. M. Mayer and L. Radom, *J. Phys. Chem. A*, 2001, **105**, 6750.

11 The tendency of the UB3LYP method to overestimate the relative BDEs has been shown for some systems previously. See ref. 10 for more details.

12 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.

13 In Bordwell's experiment, they used the empirical equation BDE $(HB^+) = 1.37\,pK(HB^+) + 23.1\,E_{ox}(HB^+) + C$ to determine the N–H BDEs of protonated amines in acetonitrile. C is an empirical constant and they chose $C = 59.5$ kcal mol^{-1} for acetonitrile. This C value was obtained from Bordwell's previous studies on the other types of BDEs and is probably not accurate for the protonated amine systems. Clearly, an inaccurate C value should result in a set of N–H BDEs with systematic errors.

14 K.-S. Song, Y.-H. Cheng, Y. Fu, L. Liu, X.-S. Li and Q.-X. Guo, *J. Phys. Chem. A*, 2002, in the press.