J. Phys. Chem. A **2002,** *106,* 6651−6658

Radical Stabilization Energies of Substituted XNH• Radicals

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Received: March 1, 2002; In Final Form: May 13, 2002

The performances of a number of theoretical methods in the calculation of N−H bond dissociation energies and radical stabilization energies associated with the X−NH$^•$ radicals were examined. It was found that the UHF, UMP2, and UMP4 methods were not reliable for the nitrogen radicals because of the spin contamination suffered by them. Surprisingly, the ROHF, ROMP2, and ROB3LYP methods were not found to be reliable for the nitrogen radicals either, because they could lead to unrealistic spin-localization of the radical. This unrealistic spin-localization was even seen with the UCCSD(T) method. The only credible modest-level method for the nitrogen radical was found to be UB3LYP, which could provide at least qualitatively correct radical stabilization energies for the nitrogen radicals. The basis set effect on the UB3LYP calculation was also found to be very small. Nevertheless, G3 and CBS-Q methods were found to be able to provide fairly accurate bond dissociation energies and radical stabilization energies for the substituted nitrogen radicals. According to G3 and CBS-Q results, CH_3, NH_2, OH, F, Cl, and CN were assigned to be stabilizing substituents for the nitrogen radical, as these groups could effectively delocalize the odd electron on the nitrogen radical. By contrast, $COCH_3$, $CONH_2$, COOH, and CHO were assigned to be destabilizing substituents for the nitrogen radical, although these groups could also delocalize the odd electron on the nitrogen radical. The origin of the destabilization effect was found to be the loss of the conjugation between the NH_2 lone-pair electrons and the substituent from the neutral X−NH_2 molecule to the X−NH$^•$ radical.

1. Introduction

The homolytic bond dissociation energy (BDE) of a chemical bond X−Y, defined as the enthalpy change of the following reaction in the gas phase,

$$X{-}Y \rightarrow X^{\bullet} + Y^{\bullet} \qquad (1)$$

is important to chemistry as well as diverse fields from material engineering to biomedical science.[1] So far, although a number of experimental methods have been developed to measure BDEs,[2] to obtain a single BDE datum still requires considerably sophisticated lab work. For those compounds hard to vaporize or having several labile chemical bonds, direct measurement of the BDEs is even more difficult. Therefore, except for the BDEs of some relatively small and simple chemical species, BDEs of many important compounds remain unknown.

Theoretical computation offers an alternative approach to obtain BDEs.[3] Indeed, since the early studies in computational chemistry, a lot of researchers in various fields have used the theoretical method either to support their experimental results or to estimate an unknown BDE value. Nevertheless, it must be emphasized that because such computation has to deal with the open-shell system with an odd number of electrons, one must be very cautious about the calculation results.

Errors in the theoretical estimation of the BDEs may result from a change in the electron correlation energy in proceeding from the reactants to the radical products. Such a change, unlike that in a closed-shell to closed-shell reaction, is often not simple to describe with low-level perturbation theories. A further source of error results from the so-called spin contamination,[4] from which the unrestricted Hartree−Fock (UHF) method and those methods using UHF wave functions as the reference states suffer acutely. The origin of this effect is that UHF wave functions for open-shell systems are not eigenfunctions of the operator $\mathbf{S}^2$.

Theoretically, a method to circumvent the above two problems has been developed that requires one to use a multiconfiguration self-consistent-field (MCSCF) wave function as the reference state. However, this method is known to be computationally too expensive for general application. Moreover, it is usually difficult to find a good multiconfiguration reference. Therefore, currently it is more interesting to know whether there are some single-reference methods being able to make up for the spin contamination of the UHF reference.[5−11]

Another pragmatic method to circumvent the BDE computation problems is to calculate the relative bond dissociation energy of a compound versus its simpler analogue rather than to calculate the absolute BDE of the compound. For this purpose, the concept of radical stabilization energy (RSE) is introduced by many researchers, which is only meaningful when a reference compound is specified. For example, the RSE for the substituted XNH$^•$ radicals can be defined as

$$\mathrm{RSE(XNH^{\bullet}) = BDE(NH_3) - BDE(XNH_2)} \qquad (2)$$

Clearly, this RSE is equivalent to the enthalpy change of the following isodesmic reaction

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10.1021/jp020610g CCC: $22.00

$$NH_3 + XNH^{\bullet} \rightarrow XNH_2 + NH_2^{\bullet} \qquad (3)$$

According to this isodesmic reaction, the RSE actually reflects the effect of a substituent on the stability of a free radical.

The advantage of using RSE is that the error of a theoretical method in the calculation of absolute BDEs is often highly systematic and, therefore, could be considerably cancelled if we calculate the energy change of an isodesmic reaction. As a result, the estimated RSEs would be expected to be much more accurate than the calculated BDEs. This means that one can use an accurate experimental BDE of a simpler molecule and calculate the RSE for a relatively more complicated compound. Using the definition of RSE as depicted in eq 2, one could then easily obtain a fairly accurate BDE value for a relatively large molecule.

The large error cancellation in RSE calculations indicates that we could use relatively cheap theoretical methods to calculate RSEs. Indeed, very recently Radom et al. assessed the performance of a series of theoretical methods for the calculation of RSEs associated with the substituted methyl radicals.[3,12] They found that, except for UMP2 or PMP2, which involved considerable spin contamination, all the methods from B3LYP and RMP2 to G3 and CBS performed satisfactorily (or at least the corresponding results were qualitatively correct) for RSEs. In particular, they suggested that RMP2 single-point calculation on B3LYP geometry with reasonable basis sets should represent a very efficient and reliable procedure to estimate RSEs.

In the present study, we would like to know if Radom's conclusion is also valid for the RSE calculation on the substituted $XNH^{\bullet}$ radicals. Thus, we used a number of theoretical methods to calculate the geometries, BDEs, and RSEs of various substituted $XNH^{\bullet}$ radicals and compare them with each other systematically. After establishing a reasonable theoretical procedure to calculate the RSEs, we would also like to look into the α-substituent effects on the stability of a nitrogen-centered radical with a focus on their magnitudes, pattern, and origin. It should be mentioned that none of the above questions about the nitrogen-centered radicals has been adequately addressed before.

2. Method

All the calculations were done with Gaussian 98.[13] Geometry optimization was performed with various levels of theoretical methods including UHF, ROHF, UB3LYP, ROB3LYP, UMP2, ROMP2, and UQCISD(T) using the 6-31+g* basis set. After the geometry optimization on a compound was done with a certain method, a frequency calculation was performed at the same level of method on the optimized structure. This frequency calculation confirmed that the optimized structure was a real minimum without any imaginary vibration frequency.

Single-point energies were calculated with the UHF, ROHF, UB3LYP, ROB3LYP, UMP2, ROMP2, UMP4, and UCCSD(T) methods using the basis sets including 6-31+g*, 6-311++g(2df, p), and 6-311++g(2d,2p). BDE at 0 K for a substituted ammonia was calculated as the enthalpy change of the following reaction at 0 K

$$XNH_2 \rightarrow XNH^{\bullet} + H^{\bullet} \qquad (4)$$

This enthalpy change was correct with the zero-point energy (ZPE) calculated at the UB3LYP/6-31+g* level (unscaled). The RSE was then calculated as defined in eq 2.

In addition, BDEs and RSEs associated with various substituted XNH• radicals were also calculated with the standard G3, CBS-4M, and CBS-Q methods. Herein, it should be mentioned that the standard G3 (Gaussian-3, G3/MP2) theory[14] is a composite ab initio method with geometry optimization at the MP2(full)/6-31g(d) level. It uses a scaled HF/6-31g(d) ZPE. A base energy calculated at the MP4/6-31g(d) level of theory is corrected to the QCISD(T)(full)/G3Large level using several additivity approximations at the MP2 and MP4 levels, to take account of more complete incorporation of electron correlation, core correlation, and the effect of a large basis set.

CBS-4M is another high-level composite method.[15] It involves a series of calculations that are designed to recover the errors that result from the truncation of both the one-electron basis set and the number of configurations used for treating correlation energies. The original CBS-4 method uses a single-point HF calculation with a very large basis set (6-311+g(3d2f, 2df, p)) at the HF/3-21g* optimized geometry, followed by correction for electron correlation using MP2 and MP4(SDQ) calculations with much smaller basis sets and an extrapolation to the complete basis set. CBS-4M, in contrast to the CBS-4 model, includes the minimal population localization procedure and improved empirical parameters.

Similarly, the CBS-Q method[15] starts with HF/6-31g* geometry optimization and frequency calculation, which is then followed by the MP2(FC)/6-31g* optimization. The single-point energy is calculated at the MP2/6-311+g(3d2f, 2df, 2p), MP4(SDQ)/6-31+g(d(f),p), and QCISD(T)/6-31+g* levels. This energy is then extrapolated to the complete basis set limit.

3. Results and Discussion

3.1. Geometry Optimization of Nitrogen-Center Radicals. In Tables 1−3 are summarized the N−H bond lengths, N−X bond lengths, and H−N−X bond angles in the XNH• radicals optimized by different theoretical methods. Clearly, these three structural parameters are the most important for the nitrogen radicals.

According to Table 1, the ROHF and UHF methods systematically underestimate the N−H bond lengths as normally expected. Nevertheless, all the other methods that take the electron correlation effects into consideration agree fairly well with each other and predict the N−H bond lengths to be around 1.020−1.030 Å.

In comparison, the agreement on the N−X bond length is less satisfactory between different theoretical methods. First, ROHF and UHF tend to underestimate the N−X bond lengths again. Second, the UMP2, ROMP2, UB3LYP, and ROB3LYP methods usually provide N−X bond lengths quite close to each other (difference < 0.02 Å). However, one may notice that the UMP2 method predicts the N−C bond length in HCO−NH• radical to be 1.276 Å, which is about 0.12 Å smaller than that from any other method. Third, the QCISD(T)/6-31+g* N−X bond lengths sometimes are about 0.01−0.07 Å longer than the corresponding values from UMP2, ROMP2, UB3LYP, or ROB3LYP. Finally, although the N−X bond lengths predicted by the G3 (actually MP2(full)/6-31g(d)) and CBS-Q (actually MP2(FC)/6-31g*) methods are fairly close to the values from UMP2, ROMP2, UB3LYP, or ROB3LYP, N−X bond lengths from the CBS-4M method are either too large or too small compared to the results from any other method. Presumably, the relatively low method (HF/3-21g*) used by CBS-4M in geometry optimization leads to such results.

According to Table 3, The H−N−X bond angles calculated by different methods are in reasonable agreement with each other. In fact, all the H−N−X angles are found to be about 100−110°. The largest angle is seen in the NC−NH• radical,

TABLE 1: N−H Bond Lengths (Å) in the XNH• Radicals Optimized by Different Theoretical Methods

method	CH_3	Cl	CN	$COCH_3$	COOH	F	H	NH_2	NO_2	OCH_3	OH	$CONH_2$	CHO	CF_3
UHF/6-31+g*	1.010	1.011	1.008	1.009	1.009	1.013	1.012	1.008	1.010	1.009	1.009	1.009	1.010	1.010
ROHF/6-31+g*	1.009	1.011	1.007	1.006	1.008	1.012	1.011	1.007	1.012	1.008	1.007	1.002	1.009	0.994
UMP2/6-31+g*	1.028	1.032	1.025	1.027	1.027	1.033	1.028	1.025	1.033	1.028	1.027	1.027	1.027	1.028
ROMP2/6-31+g*	1.028	1.032	*a*	1.028	1.027	1.033	1.028	1.027	1.033	1.031	1.027	*a*	1.030	1.029
UB3LYP/6-31+g*	1.031	1.035	1.025	1.028	1.026	1.038	1.033	1.027	1.033	1.031	1.031	1.027	1.030	1.030
ROB3LYP/6-31+g*	1.031	1.035	1.025	1.027	1.026	1.038	1.033	1.027	1.033	1.031	1.031	1.027	1.030	1.033
UQCISD(T)/6-31+g*	1.035	1.038	*b*	*b*	*b*	1.041	1.035	1.032	*b*	1.035	1.034	*b*	*b*	*b*
G3[c]	1.028	1.032	1.024	1.027	1.026	1.033	1.028	1.026	1.032	1.029	1.028	1.027	1.031	1.027
CBS-4M[d]	1.023	1.027	1.018	1.008	1.016	1.028	1.026	1.023	1.023	1.024	1.023	1.018	1.019	1.018
CBS-Q[e]	1.026	1.030	1.023	1.025	1.024	1.032	1.026	1.024	1.030	1.027	1.026	1.025	1.029	1.025

[a] Optimization failed to converge. [b] Too CPU-consuming for the computer resources. [c] Actually equivalent to the MP2(full)/6-31g(d) optimization. [d] Equivalent to the HF/3-21g* optimization. [e] Actually equivalent to the MP2(FC)/6-31g* optimization.

TABLE 2: N−X Bond Lengths (Å) in the XNH• Radicals Optimized by Different Theoretical Methods

method	CH_3	Cl	CN	$COCH_3$	COOH	F	H	NH_2	NO_2	OCH_3	OH	$CONH_2$	CHO	CF_3
UHF/6-31+g*	1.444	1.696	1.289	1.375	1.400	1.348	1.012	1.351	1.348	1.338	1.349	1.413	1.353	1.415
ROHF/6-31+g*	1.445	1.696	1.304	1.250	1.381	1.349	1.011	1.354	1.397	1.339	1.356	1.235	1.399	1.385
UMP2/6-31+g*	1.449	1.691	1.296	1.413	1.404	1.391	1.028	1.352	1.426	1.364	1.378	1.425	1.276	1.422
ROMP2/6-31+g*	1.444	1.712	*a*	1.371	1.404	1.391	1.028	1.356	1.428	1.363	1.374	*a*	1.399	1.422
UB3LYP/6-31+g*	1.444	1.712	1.280	1.371	1.381	1.384	1.033	1.356	1.401	1.363	1.375	1.397	1.364	1.421
ROB3LYP/6-31+g*	1.444	1.712	1.279	1.382	1.385	1.384	1.033	1.356	1.406	1.363	1.375	1.403	1.376	1.409
UQCISD(T)/6-31+g*	1.456	1.716	*b*	*b*	*b*	1.402	1.035	1.370	*b*	1.433	1.391	*b*	*b*	*b*
G3[c]	1.448	1.693	1.293	1.414	1.404	1.378	1.028	1.352	1.426	1.363	1.374	1.429	1.427	1.422
CBS-4M[d]	1.490	1.751	1.295	1.243	1.375	1.422	1.026	1.402	1.402	1.426	1.432	1.414	1.337	1.426
CBS-Q[e]	1.450	1.694	1.296	1.418	1.408	1.361	1.026	1.348	1.429	1.353	1.363	1.432	1.432	1.426

[a] Optimization failed to converge. [b] Too CPU-consuming for the computer resources. [c] Actually equivalent to the MP2(full)/6-31g(d) optimization. [d] Equivalent to the HF/3-21g* optimization. [e] Actually equivalent to the MP2(FC)/6-31g* optimization.

TABLE 3: H−N−X Bond Angles (deg) in the XNH• Radicals Optimized by Different Theoretical Methods

method	CH_3	Cl	CN	$COCH_3$	COOH	F	H	NH_2	NO_2	OCH_3	OH	$CONH_2$	CHO	CF_3
UHF/6-31+g*	108.0	104.2	111.7	107.5	110.0	100.9	105.3	106.5	104.5	102.1	102.0	106.8	108.2	106.9
ROHF/6-31+g*	108.0	104.2	112.6	112.9	109.9	100.9	105.2	106.4	104.7	102.2	101.9	110.2	110.9	119.0
UMP2/6-31+g*	107.1	103.7	111.9	110.3	108.5	99.5	104.6	105.7	103.2	100.5	100.4	106.0	111.4	105.5
ROMP2/6-31+g*	107.1	103.7	*a*	109.8	108.0	99.5	104.4	105.7	103.1	100.6	100.4	*a*	107.6	105.5
UB3LYP/6-31+g*	106.9	102.7	113.0	109.8	109.0	99.6	103.5	105.7	104.4	100.6	100.5	106.9	108.6	105.8
ROB3LYP/6-31+g*	106.9	102.7	113.0	110.0	109.1	99.6	103.5	105.7	104.3	100.6	100.5	106.7	109.4	106.1
UQCISD(T)/6-31+g*	106.7	103.0	*b*	*b*	*b*	99.2	104.1	105.2	*b*	100.2	100.1	*b*	*b*	*b*
G3[c]	106.4	103.3	111.7	109.8	108.0	99.9	103.3	105.2	102.9	100.2	100.2	105.2	107.4	105.5
CBS-4M[d]	108.0	103.8	115.3	116.4	109.3	99.9	106.0	105.7	103.2	100.2	100.1	108.5	111.7	110.2
CBS-Q[e]	106.2	103.5	111.3	109.6	107.8	100.6	103.8	105.4	103.0	100.6	100.6	105.0	104.3	105.7

[a] Optimization failed to converge. [b] Too CPU-consuming for the computer resources. [c] Actually equivalent to the MP2(full)/6-31g(d) optimization. [d] Equivalent to the HF/3-21g* optimization. [e] Actually equivalent to the MP2(FC)/6-31g* optimization.

whereas the smallest is seen in the FNH• radical. Noticeably, the UB3LYP/6-31+g* X−N−H bond angles are in the best agreement with the corresponding values predicted by UQCISD(T)/6-31+g*, as their difference is never larger than 0.6°.

From the above results it is clear that geometry optimization of the nitrogen-centered radical is not very sensitive to the theoretical methods as long as the electron correlation effects are taken into consideration. Needless to say, this means that the UB3LYP method is the most efficient in doing such optimization.

3.2. BDEs Calculated with Different Methods. In Table 4 are summarized the N−H bond dissociation energies of the XNH_2 molecules calculated at different levels of methods. The UB3LYP/6-31+g* geometries are used throughout these calculations, except for the composite ab initio methods.

According to Table 4, it is clear that BDEs calculated at different levels of theories are very different from each other. Compared to the only available experimental BDEs,[16] i.e., 107.3 ± 0.3 kcal/mol for $H-NH_2$, 99.1 ± 2.5 kcal/mol for $H-NHCH_3$, and 86.6 kcal/mol for $H-NHNH_2$, it appears that the CBS-4M method gives the most accurate estimations (107.7, 101.3, and 81.1 kcal/mol for the above three compounds). Estimations from the other composite ab initio methods, G3 (105.3, 98.1, and 78.4 kcal/mol, respectively) and CBS-Q (106.1, 98.6, and 78.3 kcal/mol, respectively), are slightly less close to the experimental values.

All the remaining theoretical methods significantly underestimate the N−H BDEs. In fact, even UCCSD(T)/6-311++g(2d,2p) results (100.5, 93.7, and 75.9 kcal/mol for $H-NH_2$, $H-NHCH_3$, and $H-NHNH_2$) are about 6−8 kcal/mol smaller than the corresponding experimental values. Using BDEs calculated by CBS-4M method as the references, it is clear that methods including UMP2, ROMP2, UMP4, and UCCSD(T) with the 6-31+g* basis set underestimate the N−H BDEs by as much as 10−20 kcal/mol. The underestimation by UHF and ROHF methods with the 6-31+g* basis set can even be over 30 kcal/mol.

Nevertheless, it is interesting to notice that UB3LYP and ROB3LYP methods can estimate the magnitude of BDEs almost as well as the UCCSD(T)/6-311++g(2d,2p) method. For example, the UB3LYP/6-31+g* BDE for NH_3 is 101.9 kcal/mol, compared to 93.7 kcal/mol by UCCSD(T)/6-31+g*, 100.5 kcal/mol by UCCSD(T)/6-311++g (2d,2p), and 108.2 kcal/mol by experimental measurement. In addition, it can be seen that

TABLE 4: N−H Bond Dissociation Energies of the X−NH_2 Molecules Calculated at Different Levels of Methods (kcal/mol)

X	UHF/ 6-31+g*	ROHF/ 6-31+g*	UB3LYP/ 6-31+g*	UB3LYP/ 6-311++ g(2df,p)	ROB3LYP/ 6-31+g*	UMP2/ 6-31+g*	ROMP2/ 6-31+g*	UMP4/ 6-31+g*	G3	CBS-4M	CBS-Q	UCCSD(T)/ 6-31+g*	UCCSD(T)/ 6-311++ g(2d,2p)
CH_3	66.2	69.3	93.1	95.5	94.2	89.3	89.2	87.6	98.1	101.3	98.6	86.8	93.7
Cl	62.3	65.8	86.4	88.1	87.4	83.2	82.8	76.6	90.1	93.7	90.6	80.0	87.3
CN	63.7	80.2	88.0	90.2	90.6	97.7	86.3	90.7	93.5	92.9	92.7	84.1	91.2
COCH3	79.2	111.5	105.5	108.2	107.3	110.1	123.4	105.3	111.2	128.8	111.7	98.9	106.3
COOH	83.3	86.8	107.9	110.3	109.2	105.9	105.6	103.0	112.4	114.1	113.2	101.6	108.3
F	58.5	61.9	84.7	87.1	85.8	80.0	79.8	78.9	88.6	91.3	88.6	78.3	85.4
H	72.1	74.9	101.9	104.3	102.8	95.9	95.9	94.3	105.3	107.7	106.1	93.7	100.5
NH_2	51.9	55.8	73.4	74.9	74.5	70.4	69.8	70.1	78.4	81.1	78.3	69.1	75.9
NO_2	74.0	80.2	100.7	102.7	101.9	118.9	98.1	111.7	104.3	123	104.8	95.3	101.8
OCH_3	50.7	54.3	73.9	77.2	75.0	70.0	69.7	68.8	79.1	82.7	79.2	67.7	76.4
OH	49.8	53.4	73.1	76.8	74.2	68.8	68.5	67.6	78.7	82.1	78.8	66.8	76.1
$CONH_2$	77.1	123.3	101.2	104.2	102.6	99.8	115.7	97.4	106.9	107.2	107.2	95.7	103.1
CHO	106.1	88.5	108.1	113.6	110.2	128.4	105.8	122.9	113.5	116.3	114.1	116.0	125.6
CF_3	75.7	125.5	103.5	106.0	147.2	99.9	145.3	82.4	108.1	105.0	108.8	97.2	

TABLE 5: Basis Set Effects on the Calculation of N−H Bond Dissociation Energy for NH_3 (kcal/mol)

method	UB3LYP	ROMP2	UCCSD(T)
3-21g	100.5	89.7	89.2
3-21+g(d)	103.2	92.7	91.6
631g	101.5	91.4	90.4
6-31+g(d)	102.8	95.9	93.7
6-311++g(d,p)	104.2	102.0	100.4
6-311++g(2d,2p)	104.3	103.5	101.7
6-311++g(3df,3p)	104.3	104.5	
aug-cc-pvdz	102.9	101.2	99.5
aug-cc-pvtz	104.3	105.5	
aug-cc-pvqz	104.1	106.7	

the difference between the UB3LYP/6-31+g* BDE and the UB3LYP/6-311++g(2df,p) BDE is usually small (1−4 kcal/mol), which means that the basis set effects on B3LYP calculation of BDEs are not significant.

The different basis effects on BDE calculations are also shown in Table 5. From this table, it is clear that changing from a very small basis set (3-21g) to a considerably extended one (aug-cc-pvqz) only causes a variation of 3.6 kcal/mol for the UB3LYP BDE calculation. In comparison, the same change of basis set results in variations of as large as 17.0 and 12.5 kcal/mol for the ROMP2 and UCCSD(T) BDE calculations. Therefore, the B3LYP method is fairly insensitive toward the basis sets in the calculation of BDEs.

From the above results it is clear that unless some composite ab initio method is used, the calculated N−H BDEs are always significantly smaller than the real values, even though the electron correlation is treated in a fairly sophisticated way and a considerably flexible basis set is employed. This means that currently (or even soon) it will be very hard to accurately estimate the absolute BDEs of a relatively large molecule (with over eight heavy atoms) in an ab initio fashion. Nevertheless, if the underestimation of BDEs by a relatively low level of theoretical method is systematic, we could use this method to predict the relative BDEs of a series of compounds in a fairly accurate manner. Then, by measuring the experimental BDEs of any one of the compounds in the series we would be able to know the absolute BDEs of the whole series. Clearly, this is one of the reasons that we need to introduce the concept of the radical stabilization energy.

3.3. RSEs of the Nitrogen-Centered Radicals. In Table 6 are summarized the radical stabilization energies of the nitrogen-centered radicals calculated from the corresponding BDEs according to eq 2.

From Table 6, it can be seen that the RSEs calculated by different methods are usually fairly close to each other, which is in sharp contrast to the large variation between the absolute BDEs calculated by different theoretical methods. This means that indeed the underestimation of the BDEs is mostly systematic, and therefore, simple use of a modest level of theoretical method for BDEs of large molecules is possible. However, a more detailed examination of Table 6 reveals lots of problems that argue against such a simple use.

First, comparing the RSEs calculated by different theoretical methods, it is clear that the UHF and UMP2 results for radicals such as NC−NH• and NO_2−NH• are odd. Not only can the predicted RSE be about 20 kcal/mol different from those estimated by other methods, but also the sign of the predicted RSE appears wrong. Similar peculiar results were found before, for example, for cyanovinyl radical,[12] and it was proposed that the spin contamination caused such behaviors. In accordance with this proposal, we find that the calculated $\langle S^2 \rangle$ values at the UHF/6-31+g* level for NC−NH• and NO_2−NH• radicals are 0.960 and 1.191, respectively (see Table 7). Therefore, use of UHF and UMP2 for RSEs is not reliable. It is known that PMP2 is not going to make the situation significantly better, although it annihilates the spin contamination to some extent.[12] In addition, from Table 4 it can be seen that UMP4 gives odd results, too.

In a former study, it was found that RMP2 (which actually was ROMP2) was a particularly good theoretical method for RSE.[12] Therefore, we carefully compare the RSEs calculated by the ROMP2/6-31+g* method with those calculated by the G3, CBS-4M, and UCCSD(T) methods. To our surprise, we find that although usually the agreement is good, there are three radicals, i.e., CH_3CO−NH•, NH_2CO−NH•, and CF_3−NH•, whose ROMP2 RSEs are peculiar.

The ROMP2/6-31+g* RSE for CH_3CO−NH• radical is −27.5 kcal/mol, which is about 22 kcal/mol more negative than the corresponding G3, CBS-Q, and UCCSD(T) results. This peculiar RSE should not be caused by any basis set effects, because our calculations using the ROMP2 method with various basis sets give similar magnitudes of RSEs (see Table 8). On the other hand, when we examine the spin distribution of the ROMP2/6-31+g* wave function, we find that the ROMP2 method actually regards the CH_3CO−NH• radical as an oxygen-centered radical (see Figure 1). In comparison, according to the spin distribution of the UB3LYP/6-31+g* and UCCSD(T)/6-31+g* wave functions, the CH_3CO−NH• radical is certainly a nitrogen-centered one. This means that ROMP2 wrongly assigns the position of the radical. Such an invalid treatment clearly means that the ROMP2 method is not always reliable for RSE calculations. This conclusion is in contrast to the previous proposal that ROMP2 is remarkably good for RSE calculations.[3,12] It should be mentioned that this behavior, i.e., the

TABLE 6: Radical Stabilization Energies Associated with the X−NH• Radicals Calculated at Different Levels of Methods (kcal/mol)

X	UHF/ 6-31+g*	ROHF/ 6-31+g*	UB3LYP/ 6-31+g*	UB3LYP/ 6-311++ g(2df,p)	ROB3LYP/ 6-31+g*	UMP2/ 6-31+g*	ROMP2/ 6-31+g*	UMP4/ 6-31+g*	G3	CBS-4M	CBS-Q	UCCSD(T)/ 6-31+g*	UCCSD(T)/ 6-311++ g(2d,2p)
CH_3	5.9	5.6	8.7	8.8	8.7	6.6	6.7	6.7	7.2	6.4	7.5	7.0	6.8
Cl	9.8	9.1	15.5	16.2	15.4	12.7	13.1	17.7	15.2	14.0	15.4	13.8	13.3
CN	8.5	−5.3	13.8	14.1	12.2	−1.8	9.6	3.6	11.8	14.8	13.4	9.6	9.4
$COCH_3$	−7.1	−36.6	−3.6	−3.9	−4.5	−14.2	−27.5	−11.0	−5.9	−21.1	−5.6	−5.2	−5.8
COOH	−11.2	−11.9	−6.0	−6.0	−6.4	−9.9	−9.7	−8.7	−7.1	−6.3	−7.2	−7.8	−7.8
F	13.7	13.0	17.1	17.2	17.0	15.9	16.1	15.5	16.7	16.4	17.5	15.5	15.1
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
NH_2	20.2	19.1	28.4	29.4	28.3	25.6	26.1	24.3	26.9	26.6	27.8	24.7	24.7
NO_2	−1.9	−5.3	1.1	1.6	0.9	−23.0	−2.2	−17.4	1.1	−15.3	1.2	−1.6	−1.2
OCH_3	21.5	20.6	27.9	27.1	27.8	25.9	26.2	25.5	26.3	25.0	26.9	26.1	24.1
OH	22.4	21.5	28.7	27.5	28.6	27.1	27.4	26.7	26.6	25.6	27.3	26.9	24.5
CONH2	−4.9	−48.4	0.6	0.1	0.2	−3.9	−19.8	−3.1	−1.6	0.5	−1.1	−2.0	−2.6
CHO	−34.0	−13.6	−6.2	−9.3	−7.4	−32.5	−9.9	−28.6	−8.2	−8.6	−8.0	−22.3	−25.0
CF_3	−3.5	−50.6	−1.7	−1.7	−44.3	−4.0	−49.4	11.9	−2.8	2.7	−2.7	−3.5	

TABLE 7: Calculated $\langle S^2 \rangle$ Values for Various Substituted-Amino Radicals by the UHF/6-31+g* Method (au)

X	$\langle S^2 \rangle$	X	$\langle S^2 \rangle$
CH_3	0.761	NH_2	0.765
Cl	0.767	NO_2	1.191
CN	0.960	OCH_3	0.763
$COCH_3$	0.919	OH	0.763
COOH	0.775	$CONH_2$	0.784
F	0.762	CHO	0.765
H	0.759	CF_3	0.759

TABLE 8: Basis Set Effects on the Calculation of Bond Dissociation Energy and Radical Stabilization Energy for NH_2COCH_3 (kcal/mol)

	UB3LYP		ROMP2		UCCSD(T)	
method	BDE	RSE	BDE	RSE	BDE	RSE
3-21g	110.8	−10.3	125.7	−36.0	98.8	−9.6
3-21+g(d)	112.9	−9.7	124.9	−32.1	101.2	−9.5
6-31g	111.1	−9.6	123.8	−32.3	99.4	−9.0
6-31+g(d)	107.3	−4.5	123.4	−27.5	98.9	−5.2
6-311++g(d,p)	108.8	−4.7	129.1	−27.2	105.3	−4.9
6-311++g(2d,2p)	108.7	−4.4	131.2	−27.7	107.1	−5.4
6-311++g(3df,3p)	109.2	−4.8	132.9	−28.5		
aug-cc-pvdz	107.7	−4.7	129.1	−27.9	105.2	−5.7
aug-cc-pvtz	108.2	−3.9	133.9	−28.4		
aug-cc-pvqz	111.8	−7.7	135.3	−28.6		

unrealistic spin-localization in a radical by the spin-restricted wave functions, has been noticed before.[17] However, the possible bad effects of such a behavior have not been recognized in the studies of BDEs and RSEs.

The ROMP2/6-31+g* RSE for NH_2CO−NH• radical is −19.8 kcal/mol, which is about 17 kcal/mol more negative than the corresponding G3, CBS-4M, CBS-Q, and UCCSD(T) results. From Figure 1, it is clear that this peculiar RSE is also caused by the wrong spin-localization. Again, such a wrong spin-localization is not a simple quantitative error. It means that the ROMP2 method can be qualitatively wrong for RSE.

The ROMP2/6-31+g* RSE for F_3C−NH• radical is −49.4 kcal/mol, which is about 46 kcal/mol more negative than the corresponding G3, CBS-4M, CBS-Q, and UCCSD(T) results. Comparing the spin distribution of the ROMP2 wave function and UCCSD(T) (or UB3LYP) wave function of the radical does not reveal any significant difference (see Figure 1). Therefore, the reason for this peculiar result remains to be clarified.

From the above results, we have to conclude that use of the ROMP2 method in the calculation of radicals is not always reliable. This conclusion is in disagreement with the former opinion,[12] but it justifies many people's suspicion that use of the spin-restricted wave function method is not always safe. In fact, from Table 6 it can be seen that the ROHF/6-31+g* method also has trouble in its treatment of CH_3CO−NH•, NH_2-CO−NH•, and CF_3−NH• radicals. Interestingly, although the ROB3LYP/6-31+g* method does not predict peculiar RSEs for CH_3CO−NH• and NH_2CO−NH• radicals, it predicts an odd RSE for the CF_3−NH• radical. This may suggest that the reason for the failure of the spin-restricted method in dealing with the former two radicals is different from that with the CF_3−NH• radical.

Comparing the results from the most credible methods in our study including G3, CBS-4M, CBS-Q, and UCCSD(T) reveals that they are mostly in good agreement with each other. Nevertheless, one may notice that the CBS-4M RSE for CH_3-CO−NH• radical is about 15 kcal/mol more negative than that from G3, CBS-Q, or UCCSD(T). Also, CBS-4M predicts that NO_2−NH• radical has a RSE of −15.3 kcal/mol, which is about 14 kcal/mol more negative than the value predicted by G3, CBS-Q, or UCCSD(T). As the CBS-4M method basically involves a series of HF and MPn calculations, it is conceivable that the wrong treatment of radicals by HF and MPn methods would occur for CBS-4M too.

G3 and CBS-Q appear to be able to predict at least qualitatively correct RSEs for all the radicals. This conclusion is drawn on the basis of the fact that prediction from G3 fully agrees with that from CBS-Q. This conclusion is also drawn on the basis of the fact that predictions from G3 and CBS-Q methods agree at least with one of the CBS-4M and UCCSD-(T) results.

In comparison, UCCSD(T) appears to be able to deal with most of the radicals in this study, as normally expected. In addition, the basis set effects on the RSE calculations by the UCCSD(T) method are small, because the difference between the UCCSD(T)/6-31+g* and UCCSD(T)/6-311++g(2d,2p) RSEs is usually smaller than 1 kcal/mol. The only problem with the UCCSD(T) method is found for the HCO−NH• radical, where UCCSD(T) predicts a RSE value about 14 kcal/mol more negative than the CBS-4M, CBS-Q, and G3 results. The origin of this erratic prediction is found to be associated with the wrong assignment of spin distribution again. As shown in Figure 1d, UB3LYP/6-31+g* and ROMP2/6-31+g* clearly indicate that the HCO−NH• radical is a nitrogen-centered one. In contrast, according to the UCCSD(T)/6-31+g* wave function, this radical should be oxygen-centered instead. Therefore, UCCSD(T) may also wrongly assign of the position of a radical, which means that we even need to be cautious with the UCCSD(T) results on the open-shell systems.

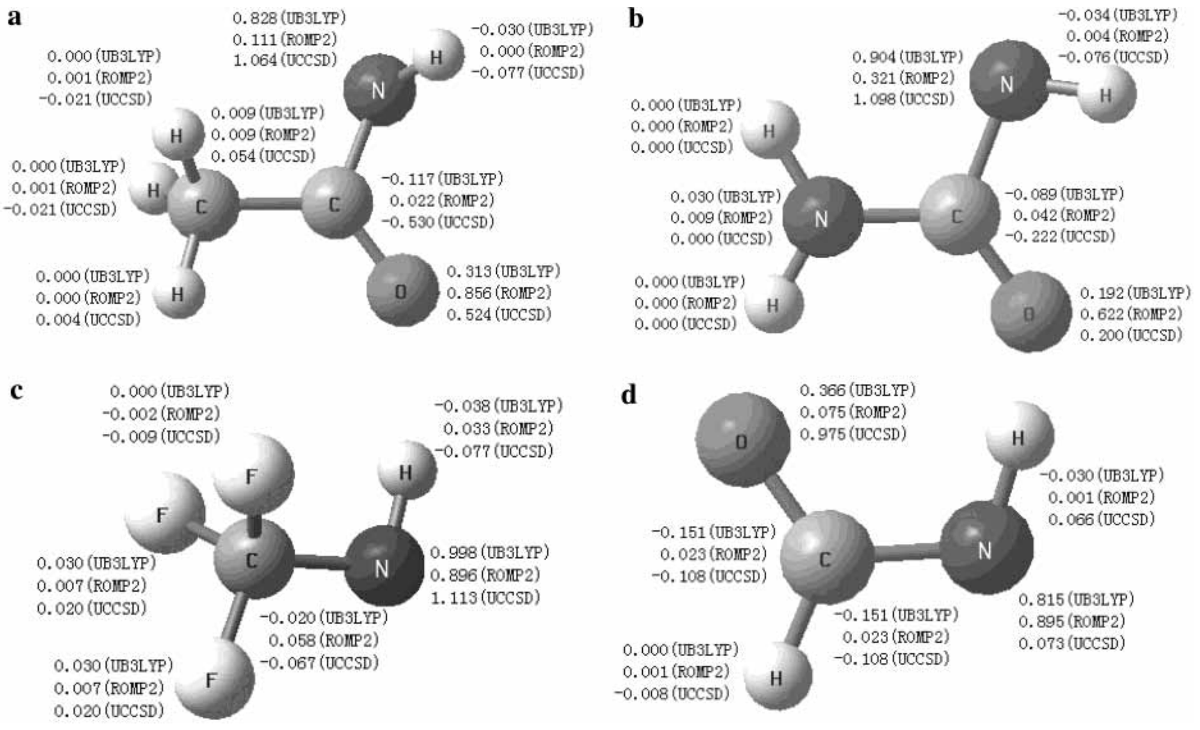

Figure 1. The spin distributions of (a) $CH_3CO{-}NH\bullet$, (b) $NH_2CO{-}NH\bullet$, (c) $CF_3{-}NH\bullet$, and (d) $HCO{-}NH\bullet$ radicals calculated by the UB3LYP/6-31+g*, ROMP2/6-31+g* and UCCSD(T)/6-31+g* methods.

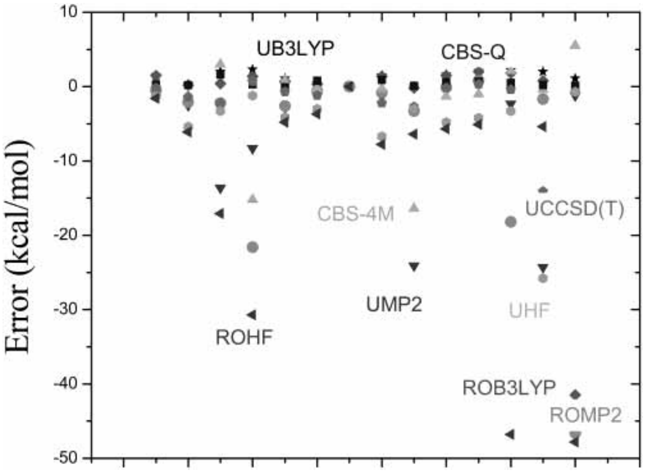

Figure 2. The errors of different theoretical methods in predicting the radical stabilization energies using the G3 method as the benchmark.

Nevertheless, it is interesting to notice from Table 6 that UB3LYP is the only method that can predict RSEs always in agreement with G3 and CBS-Q (Figure 2). In fact, the difference between the UB3LYP and G3 (or CBS-Q) RSEs is never larger than 2.5 kcal/mol. The basis set effects on the UB3LYP RSEs are also found to be very small if one compares the UB3LYP/6-31+g* results with the UB3LYP/6-311++g(2df,p) ones. Given the fact that B3LYP is a considerably cheaper method than MP2 and UCCSD(T) in computation, such a good agreement between the UB3LYP and G3 or CBS-Q results is really remarkable. Nevertheless, it should be mentioned that it was found before that for some radicals such as cyanovinyl radical, B3LYP could significantly overestimate the substituent stabilization effect.[12]

TABLE 9: Recommended Radical Stabilization Energies Associated with the $X{-}NH\bullet$ and $X{-}CH_2\bullet$ Radicals (kcal/mol)

X	XNH radical (G3)	XCH_2 radical (G3-RAD)[a]	X	XNH radical (G3)	XCH_2 radical (G3-RAD)[a]
CH_3	7.2	3.4	NH_2	26.9	10.6
Cl	15.2	5.0	NO_2	1.1	2.8
CN	11.8	7.6	OCH_3	26.3	7.4
$COCH_3$	−5.9		OH	26.6	7.6
COOH	−7.1	5.1	$CONH_2$	−1.6	
F	16.7	3.0	CHO	−8.2	8.3
H	0.0	0.0	CF_3	−2.8	−1.8

[a] Taken from ref 3.

3.4. α-Substituent Effects on the Stability of Nitrogen-Centered Radicals. In Table 9 are summarized the radical stabilization energies associated with the $X{-}NH\bullet$ radicals calculated at the G3 level. For comparison, the radical stabilization energies obtained before for the $X{-}CH_2\bullet$ radicals[3] are also listed in Table 9. To understand the substituent effects on the stability of nitrogen-centered radicals, we also show the Mulliken charge and spin density distributions associated with these radicals in Table 10.

According to Table 9, it is clear that the pattern of substituent effects on the stability of nitrogen-centered radicals is remarkably different from that for carbon-centered radicals. For the carbon cases, only CF_3 destabilizes a carbon-centered radical. Other substituent groups stabilize the carbon radical to various extents depending on the ability of the substituents to delocalize the spin of the carbon radical.[18] By contrast, for the nitrogen radicals, in addition to CF_3, the $COCH_3$, COOH, $CONH_2$, and CHO substituents are found to destabilize the radical, too. Such an observation appears to be against the intuition that $COCH_3$, COOH, $CONH_2$, and CHO should be good substituents to delocalize the spin of a radical species.

Detailed examination of the nitrogen-centered radicals reveals that the substituents could be divided into several classes. For example, H should apparently be placed in an independent class, because no conjugation effect is expected in either NH_3 or $NH_2\bullet$. Removal of one hydrogen atom from NH_3 results in a decrease

TABLE 10: Mulliken Charge and Spin Density at the N Atom in the Substituted XNH_2 Molecules and XNH_2• Radicals Calculated by G3 Method (au)

	Mulliken charges		
X	in XNH_2	in XNH	spin
CH_3	−0.339 454	−0.211 121	1.068 115
Cl	−0.159 106	−0.078 828	1.051 391
CN	−0.295 643	−0.216 818	0.882 916
$COCH_3$	−0.341 036	−0.148 586	1.077 522
COOH	−0.388 810	−0.163 950	1.061 408
F	−0.323 319	−0.075 669	1.057 903
H	−0.468 191	−0.294 384	1.110 860
NH_2	−0.303 993	−0.213 832	0.928 274
NO_2	−0.227 355	−0.057 576	1.076 458
OCH_3	−0.429 761	−0.240 634	1.006 665
OH	−0.333 824	−0.246 019	1.012 314
$CONH_2$	−0.394 845	−0.219 492	1.048 360
CHO	−0.318 846	−0.214 408	1.009 111
CF_3	−0.326 129	−0.196 489	1.060 739

of negative charge carried by nitrogen from −0.468 to −0.294. The spin of the NH_2• radical is mostly populated on the nitrogen atom.

CH_3, NH_2, OH, OCH_3, F, and Cl constitute the second class. In the corresponding neutral compounds X−NH_2 in this class, the lone pair electrons on NH_2 should not conjugate with the substituents. By contrast, in the corresponding radicals X−NH• in this class, the spin carried by the nitrogen atom is smaller than that found for NH_2•. Also, the X−N bond length is significantly shortened from X−NH_2 to X−NH• (for example, N−N in NH_2NH_2 is shortened from 1.484 to 1.352 Å in NH_2-NH•), Therefore, in the radicals the odd electron on NH• should be conjugated with the substituents. Such a conjugation (or hyperconjugation) effect clearly is the driving force for the stabilization of the nitrogen radical by 7−27 kcal/mol observed for the class.

CN substituent is a special case, because in the neutral compound NC−NH_2 the NH_2 group is already conjugated to the CN group using its lone pair electrons. Nevertheless, as seen from Table 10, the nitrogen atom in NC−NH• radical carries significant less spin than that in NH_2•. The C−N bond is shortened from 1.347 Å in NC−NH_2 to 1.293 Å in NC−NH•, whereas the N≡C bond is elongated from 1.166 Å in NC−NH_2 to 1.174 Å in NC−NH•. All of these observations indicate that the conjugation between the NH• and CN group in the NC−NH• radical is stronger than the conjugation between NH_2 and CN in NC−NH_2. The reason for this enhanced conjugation effect relies on the fact that CN is linear and has two sets of π orbitals perpendicular to each other. As a result, both the odd electron and lone pair electrons on NH• can be conjugated to the CN group simultaneously. Clearly, the additional conjugation between the CN group and the odd electron compared to the situation in NC−NH_2 makes CN a stabilizing substituent for the nitrogen-centered radical.

$COCH_3$, COOH, $CONH_2$, and CHO represent another classes of substituents. Unlike the CN group, the substituents in this class have only one set of π orbitals. As a result, in the neutral compounds X−NH_2, the lone pair electrons are readily conjugated to the substituent. This conjugation effect can be seen from the HOMO (highest occupied molecular orbital) of the neutral compounds (e.g. HOOC−NH_2 in Figure 3), where it is clear that the lone pair electrons on nitrogen are delocalized to the antibonding π^* orbital of the C=O double bond. However, in the X−NH• radical the lone pair electrons and odd electron on NH• cannot be both conjugated to the substituent. Detailed analyses indicate that it is the odd electron on NH• involved in the conjugation, because the SOMO (singly occupied molecular orbital) of the radicals (e.g. HOOC−NH• in Figure 3) is perpendicular to the N−C−O plane and contains significant contribution from the C=O antibonding π^* orbital. Therefore, from the neutral compound to the radical the conjugation between one odd electron and the substituent is gained, but at the same time the conjugation between the two lone pair electrons and the substituent is lost. Presumably, the gained conjugation effect is not as strong as the lost one, which is indicated by the elongation of the C−N bond during the N−H homolysis, for example from 1.399 Å in HOOC−NH_2 to 1.426 Å in HOOC−NH•. As a result, the $COCH_3$, COOH, $CONH_2$, and CHO substituents increase the N−H BDEs. It should be mentioned that the same effect is not observed with the carbon radicals, because in the carbon case (X−CH_3) there is no conjugation between X and CH_3 to lose.

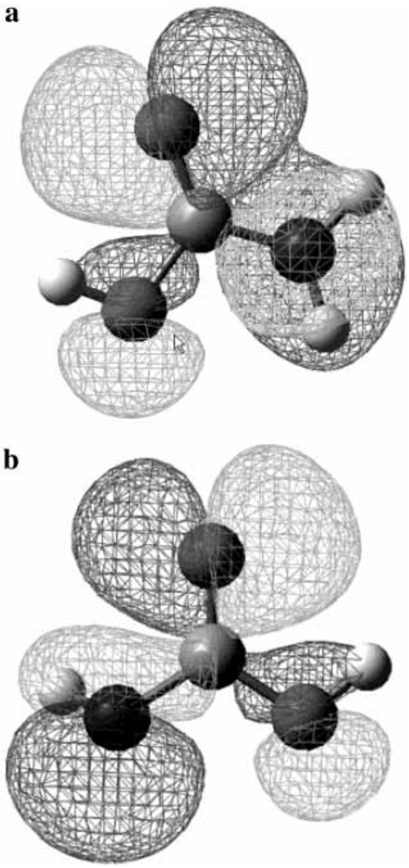

Figure 3. The HOMO of HOOC−NH_2 molecule and the SOMO of HOOC−NH• radical according to the ROB3LYP/6-31+g* method.

NO_2 is isoelectronic to $COCH_3$, $CONH_2$, and COOH. However, it turns out that NO_2 can slightly stabilize a nitrogen radical as the RSE associated with NO_2 is 1.1 kcal/mol. Nevertheless, it should be noticed that the RSE associated with $CONH_2$ is −1.6 kcal/mol, which is not very different from that of NO_2. Therefore, the loss of the conjugation between the lone pair electrons and NO_2 during the N−H homolysis makes the NO_2 group not an effective radical stabilization substituent for a nitrogen radical. It should be mentioned that the weakening of the conjugation effect during the N−H homolysis can also be indicated by the N−N bond elongation from 1.363 Å in NO_2−NH_2 to 1.404 Å in NO_2−NH•.

CF_3 is a destabilization substituent for the nitrogen radical, as its corresponding RSE is −2.8 kcal/mol. The origin of the destabilization could be attributed to the strong electron-withdrawing effect of this group.[19] Nevertheless, it should be mentioned that there is a little hyperconjugation effect between NH• and CF_3, which can be seen from the C−F bond contraction from 1.467 Å in CF_3-NH_2 to 1.422 Å in CF_3−NH•.

4. Conclusion

In the present study we systematically examine the performances of a number of theoretical methods in the calculation of N−H bond dissociation energies. The major results of the study include the following.

(1) UHF, UMP2, and UMP4 are not reliable methods for the nitrogen radicals because of the spin contamination suffered by these methods. Unfortunately, ROHF, ROMP2, and ROB3LYP are not reliable either for the nitrogen radicals because they could lead to unrealistic spin-localization of the radical. This unrealistic spin-localization is even seen with the UCCSD(T) method.

(2) The only credible modest-level method for the nitrogen radical is UB3LYP, which can provide at least qualitatively valid radical stabilization energies for the nitrogen radicals. The basis set effect on the UB3LYP calculation is also very small.

(3) The G3 and CBS-Q methods can provide considerably accurate bond dissociation energies and radical stabilization energies for the substituted nitrogen radicals. CBS-4M, on the other hand, gives qualitatively wrong predictions sometimes.

(4) CH_3, NH_2, OH, F, Cl, and CN are stabilization substituents for the nitrogen radical, as these groups can effectively delocalize the odd electron on the nitrogen radical. By contrast, $COCH_3$, $CONH_2$, COOH, and CHO are destabilization substituents for the nitrogen radical, although these groups also delocalize the odd electron on the nitrogen radical. The origin of the destabilization effect is the loss of the conjugation between the NH_2 lone-pair electrons and the substituents from the neutral $X-NH_2$ molecules to the X−NH• radicals.

Acknowledgment. We are grateful for the financial support of NSFC. We also thank Prof. H. B. Schlegel for his helpful suggestions on our manuscript.

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