C—H and N—H bond dissociation energies of five- and six-membered ring aromatic compounds

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ABSTRACT: C—H and N—H bond dissociation energies (BDEs) of various five- and six-membered ring aromatic compounds were calculated using composite *ab initio* CBS-Q, G3 and G3B3 methods. It was found that all these composite *ab initio* methods provided very similar BDEs, despite the fact that different geometries and different procedures in the extrapolation to complete incorporation of electron correlation and complete basis set limit were used. Therefore, the calculated BDEs should be reliable. In addition, we found interesting dependences of the C—H BDEs on the bond angles, spins and charges. A good quantitative structure–activity relationship (QSAR) model for the C—H BDEs of aromatic compounds was also established. Copyright © 2003 John Wiley & Sons, Ltd.

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KEYWORDS: composite *ab initio* methods; bond dissociation energy; aromatic compounds; QSAR

INTRODUCTION

Homolytic bond dissociation energy (BDE) is defined as the enthalpy change of the reaction A—B $\rightarrow$ A$^\bullet$ + B$^\bullet$ in the gas phase at 298 K and 1 atm.[1] A sound knowledge of BDEs is fundamental to understanding chemical reactions involving radicals as reactants, products or intermediates.

At present, direct gas-phase methods including radical kinetics, photoionization mass spectrometry and the acidity/electron affinity cycle can be used to determine BDEs.[1] Although these measurements can provide valid BDEs, the use of these methods to determine the BDEs of complex molecules remains notoriously difficult. Recently, the groups of Bordwell, Cheng and others developed a valuable electrochemical method to measure the BDEs of acidic H—X bonds.[2] Using this method, a large number of BDEs were obtained which greatly enriched our knowledge of various chemical bonds. Nevertheless, the use of the solution-phase method to measure BDEs of non-acidic H—X bonds remains difficult.

Because of the experimental difficulties, accurate BDEs of many important compounds remain unknown. Fortunately, a recent development in theoretical chemistry provides a powerful tool, i.e. the composite *ab initio* method, which can be used to calculate BDEs within 1–2 kcal mol^{-1} (1 kcal = 4.184 kJ) of the experimental values.[3,4] Using the composite *ab initio* method, several groups, including ours, have recently conducted systematic studies in order to determine accurate BDEs of various chemical bonds.[5,6] The effects of substituents and conformations on BDEs have also been investigated in detail.

In this paper, we report our results concerning the C—H and N—H BDEs of various aromatic compounds. A sound knowledge of BDEs for these compounds is clearly important for many fields such as combustion chemistry, environmental chemistry and interstellar chemistry. However, the experimental BDEs for these compounds are rare and often inaccurate.[7]

EXPERIMENTAL

All the calculations were performed using Gaussian 98.[8] Geometry optimization was conducted without any constraint. Each optimized structure was confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency.

BDEs were calculated using G3 and CBS-Q methods as the enthalpy change of the following reaction at 298 K:

$$A - B(g) \rightarrow A(g) + B(g) \tag{1}$$
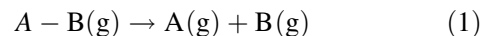
The enthalpy of formation for each species was calculated using the following equation:

$$H_{298} = E + ZPE + H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT \tag{2}$$

Where *ZPE* is the zero point energy and H_{trans}, H_{rot}, and H_{vib} are the standard temperature correction terms calculated using the equilibrium statistical mechanics with

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harmonic oscillator and rigid rotor approximations. [It should be mentioned that the procedure we used to calculate BDEs at 298 K and 1 atm is exactly the same as that used by DiLabio *et al*. In fact, using B3LYP/6–31G(d), DiLabio *et al*. obtained $H°_{298}$ (H_2O) = −76.38401 hartree, $H°_{298}$ (OH) = −75.71185 hartree, $H°_{298}$ (H) = −0.49791 hartree and BDE ($H_2O \rightarrow$ OH + H) = 109.3 kcal mol^{-1}. In comparison, our data are $H°_{298}$ (H_2O) = −76.384007 hartree, $H°_{298}$ (OH) = −75.711846 hartree, $H°_{298}$ (H) = −0.497912 hartree and BDE ($H_2O \rightarrow$ OH + H) = 109.3 kcal mol^{-1}.]

It should be mentioned that the composite *ab initio* methods involve 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. G3 (Gaussian-3, G3//MP2)[3] is one of the composite *ab initio* methods, whose geometry optimization is carried out at the MP2(full)/6–31G(d) level. A scaled HF/6–31G(d) *ZPE* is used in G3. A base energy calculated at the MP4/6–31G(d) level is then corrected to the QCISD(T)(full)/G3Large level using several additivity approximations at the MP2 and MP4 levels, in order to take account of the more complete incorporation of electron correlation, core correlation and the effect of a large basis set.

G3B3 (or G3//B3LYP) is a variant of G3 theory in which structures and zero point vibrational energies are calculated at the B3LYP/6–31G(d) level of theory.[3] This variation is particularly advantageous for larger systems and for open-shell systems showing large spin contamination. For the single-point energy calculation G3B3 is very similar to the original G3 method, i.e. a base energy calculated at the MP4/6–31G(d) level is corrected to the QCISD(T)(full)/G3Large level using several additivity approximations at the MP2 and MP4 levels.

CBS-Q is another composite *ab initio* method,[4] which starts with HF/6–31G* geometry optimization and frequency calculation, followed by 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.

RESULTS AND DISCUSSION

Reliability of the theoretical results

In Table 1 are listed the C—H and N—H BDEs calculated using the CBS-Q, G3 and G3B3 methods for various five- and six-membered ring aromatic compounds.

It can be seen that the CBS-Q and G3 BDEs are very close to each other. In fact, when BDEs (G3) are correlated with BDEs (CBS-Q), a straight line can be obtained [Fig. 1(a); the slope of the line is 1.000 and

the intercept is zero. For 47 chemical bonds, the correlation coefficient (r) is 0.999 and the standard deviation (SD) is only 0.3 kcal mol^{-1}. Therefore, despite the fact that G3 and CBS-Q use different strategies in the extrapolation to complete incorporation of electron correlation and complete basis set limit, they agree excellently with each other in BDE calculations.

However, on comparing the G3B3 BDEs with the G3 BDEs one may find that these two sets of BDEs are slightly different. According to Fig. 1(b), the slope of the correlation between BDEs (G3) and BDEs (G3B3) is 1.012. This value is slightly larger than unity, indicating that the G3 BDEs are systematically larger than the G3B3 BDEs. Mathematical analyses reveal that the G3 BDEs are 1.4 kcal mol^{-1} larger than that G3B3 BDEs on average. Since G3 and G3B3 use similar methods to take account of the more complete incorporation of electron correlation, core correlation and the effect of a large basis set, the systematically larger BDEs from G3 than from G3B3 may be caused by the different geometries used in these two methods: G3 uses the MP2(full)/6–31G(d) geometry, whereas G3B3 uses the B3LYP/6–31G(d) geometry.

According to recent studies by Radom and co-workers[5] and our groups,[6] the B3LYP method usually provides more reliable structures than the MP2 method, for open-shell radical species because the spin-contamination problem is more serious with MP2 than with B3LYP (We thank one of the referees for bringing to our attention the geometry problem in G3 and G3B3 calculations). Consequently, we believe that the G3B3 BDEs should be more accurate that the G3 BDEs. Nonetheless, the correlation coefficient between the G3B3 BDEs and G3 BDEs is as high as 0.983. The SD between these two methods is only 1.1 kcal mol^{-1}. Therefore, the difference in geometry optimization does not significantly affect the BDEs calculated by the composite *ab initio* methods.
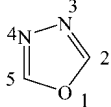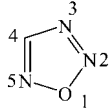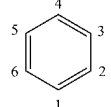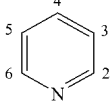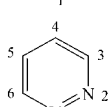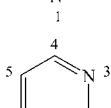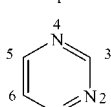
Comparing the G3B3 BDEs with the available experimental values, we find that the agreement is good for benzene. The experimental C—H BDE for benzene is 113.5 ± 0.8 kcal mol^{-1},[10] whereas the G3B3 C—H BDE for benzene is 114.3 kcal mol^{-1}. However, our theoretical C—H BDEs for pyridine, pyrimidine and pyrazine are significantly larger than the experimental values obtained recently by Kiefer *et al*. using the complementary techniques of laser-Schlieren (LS) densitometry and time-of-flight (TOF) mass spectrometry.[11] For p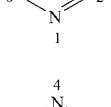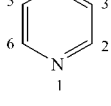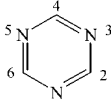yridine, the G3B3 BDEs are 109.2 (C2—H), 115.5 (C3—H) and 113.8 (C4—H) kcal mol^{-1}, whereas the experimental BDEs are 105, 112 and 112 kcal mol^{-1}, respectively. For pyrimidine, the G3B3 BDEs are 110.4 (C2—H), 108.1 (C4—H), and 116.3 (C5—H) kcal mol^{-1}, whereas the experimental values are 98, 103 and 112 kcal mol^{-1}, respectively. For pyrazine, the theoretical BDE is 107.9 (C2—H) kcal mol^{-1}, whereas the experimental value is 103 kcal mol^{-1}. Clearly, these experimental BDEs are

Table 1. Bond dissociation energies of aromatic compounds (kcal mol^{-1})

Name	Structure	Bond	CBS-Q	G3	G3B3 (recommended)	B3LYP[b]	Charge[c]	Spin[c]	Bond angle[d]
Pyrrole		N1—H	—[a]	—[a]	95.2	93.2	0.402	—	109.8
		C2—H	120.8	120.7	119.7	118.1	0.201	0.984	107.7
		C3—H	120.5	120.1	119.2	117.5	0.212	1.008	107.4
Furan		C2—H	121.0	121.3	120.4	118.5	0.195	1.001	110.6
		C3—H	121.4	121.3	120.4	118.2	0.220	0.979	106.1
Thiophene		C2—H	119.2	119.3	118.3	116.3	0.224	0.951	111.5
		C3—H	117.0	117.0	115.8	113.4	0.216	0.973	112.8
Imidazole		N1—H	96.4	96.2	96.0	94.6	0.409	—	107.1
		C2—H	117.5	117.6	117.1	114.9	0.189	0.890	111.8
		C4—H	118.4	118.4	117.8	115.3	0.200	0.986	110.9
		C5—H	121.3	121.2	120.5	118.6	0.209	0.943	105.0
Oxazole		C2—H	120.3	120.5	119.6	117.7	0.187	0.929	114.8
		C4—H	120.5	120.6	119.9	117.1	0.210	0.982	109.3
		C5—H	122.8	123.0	122.1	120.0	0.203	0.983	107.8
Thiazole		C2—H	113.1	113.2	111.9	109.5	0.206	0.817	115.2
		C4—H	116.3	116.6	115.2	112.3	0.206	0.910	116.1
		C5—H	120.9	120.8	119.5	117.5	0.231	0.930	109.7
Pyrazole		N1—H	112.0	111.3	109.2	107.6	0.401	—	113.3
		C3—H	118.7	118.7	117.8	115.5	0.201	0.967	112.1
		C4—H	122.6	122.2	121.0	118.9	0.221	0.953	104.5
		C5—H	121.1	121.1	119.9	117.9	0.210	0.948	106.1
Isoxazole		C3—H	118.9	119.0	118.0	115.2	0.213	0.917	112.5
		C4—H	124.5	124.3	122.7	120.0	0.231	0.944	102.9
		C5—H	120.5	120.6	119.6	117.0	0.205	0.940	110.5
Isothiazole		C3—H	112.6	112.5	111.0	108.3	0.200	0.859	117.5
		C4—H	119.1	118.9	117.3	114.6	0.224	0.915	110.1
		C5—H	119.6	119.4	117.6	115.6	0.229	0.899	109.1
1,2,3-Triazole		N1—H	109.8	109.4	109.5	—	0.411	—	111.7
		C4—H	123.6	123.2	121.5	118.1	0.212	0.964	108.9
		C5—H	125.0	124.5	122.7	119.8	0.221	0.936	103.4
1,2,4-Triazole		N1—H	—[a]	—[a]	109.5	107.8	0.409	0.131	110.5
		C3—H	119.7	119.9	119.2	117.0	0.193	0.966	115.6
		C5—H	119.2	119.3	118.7	116.5	0.200	0.914	109.9
1,2,4-Oxadiazole		C3—H	120.3	120.4	119.8	117.3	0.207	0.942	115.7
		C5—H	120.3	120.4	119.8	117.7	0.198	0.924	114.5
1,2,5-Oxadiazole		C3—H	124.4	124.3	121.8	118.1	0.223	0.926	108.9

Continues

Table 1. Continued

Name	Structure	Bond	CBS-Q	G3	G3B3 (recommended)	B3LYP[b]	Charge[c]	Spin[c]	Bond angle[d]
1,3,4-Oxadiazole		C2—H	122.5	122.8	122.0	119.9	0.199	0.951	113.5
1,2,3,5-Oxatriazole		C4—H	128.7	128.7	125.8	121.7	0.220	0.979	112.1
Benzene		C1—H	114.9	115.8	114.3	110.3	0.203	1.015	120.0
Pyridine		C2—H	110.3	110.6	109.2	104.7	0.185	0.865	123.8
		C3—H	116.0	116.0	115.5	110.8	0.210	0.947	118.4
		C4—H	115.3	114.9	113.8	109.5	0.207	0.921	118.5
Pyridazine		C3—H	114.1	114.4	109.1	106.3	0.197	0.867	123.8
		C4—H	115.5	115.9	111.2	108.3	0.215	0.851	116.8
Pyrimidine		C2—H	112.8	112.8	110.4	106.4	0.175	0.900	127.4
		C4—H	110.6	110.6	108.1	103.8	0.189	0.838	122.4
		C5—H	117.7	117.6	116.3	111.7	0.218	0.925	116.4
Pyrazine		C2—H	111.7	112.0	107.9	104.8	0.192	0.833	122.1
1,3,5-Triazine		C2—H	110.4	110.5	108.0	105.6	0.180	0.866	126.1
1,2,4-Triazine		C3—H	—[a]	—[a]	110.4	107.8	0.186	0.883	127.2
		C5—H	—[a]	105.6	105.5	102.3	0.196	0.757	120.7
		C6—H	—[a]	—[a]	109.5	106.4	0.204	0.806	121.7
1,2,3-Triazine		C4—H	—[a]	110.1	107.6	104.5	0.202	0.812	122.2
		C5—H	—[a]	113.2	111.2	108.2	0.223	0.821	114.8

[a] Optimization failed.
[b] B3LYP means the UB3LYP/6—311++G(2df,p)//UB3LYP/6—31G(d) method.
[c] Charge (NBO) is carried by the hydrogen atom in the C—H bond undergoing homolysis. Spin is carried by the carbon or nitrogen atom in the radical. These two values were obtained using the UB3LYP/6–311++G(2df,p)//UB3LYP/6–31G(d) method.
[d] Bond angle is for the X—C—Y bond from the G3B3 method.

about 2–5 kcal mol^{-1} smaller than the G3B3 values. Although it remains to be clarified whether the experimental or theoretical results are more accurate in these particular cases, according to recent studies on the performance of composite *ab initio* methods[5] it is more likely that the experimental values are underestimated.

Performance of DFT methods

A serious limitation of the composite *ab initio* methods is the considerable computation time that they require. In comparison, density functional theory (DFT) methods are very efficient for theoretical studies of many systems (for
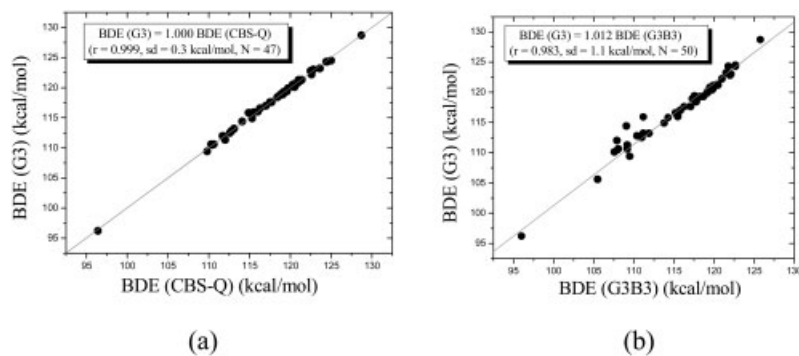
Figure 1. Correlations between BDE (G3) and BDE (CBS—Q) (a) and between BDE (G3) and BDE (G3B3) (b)

recent applications of DFT methods in BDE calculations, see Refs 12a–f, and for calculations of the C—H BDEs of aromatic compounds using DFT methods, see Refs 12g–i). Nevertheless, in recent studies it was found that the DFT methods may significantly underestimate the BDEs for many types of compounds.[5,6,13]

In the present study, we also used the UB3LYP/6–311++G(2df,p)//UB3LYP/6–31G(d) method to calculate the BDEs. In this method, the geometry and frequencies were obtained at the UB3LYP/6–31G(d) level. The single-point energy calculation was performed at the UB3LYP/6–311++G(2df,p) level, the results of which were corrected with the ZPE and thermal corrections at the UB3LYP/6–31G(d) level in order to obtain enthalpies at 298 K and 1 atm. (see Table 1). From the correlation between BDEs (UB3LYP) and the G3B3 BDEs (Fig. 2), it can be seen that the DFT method indeed significantly underestimates the BDEs for the aromatic compounds. Mathematical analyses indicate that the average underestimation is 2.7 kcal mol^{-1}.

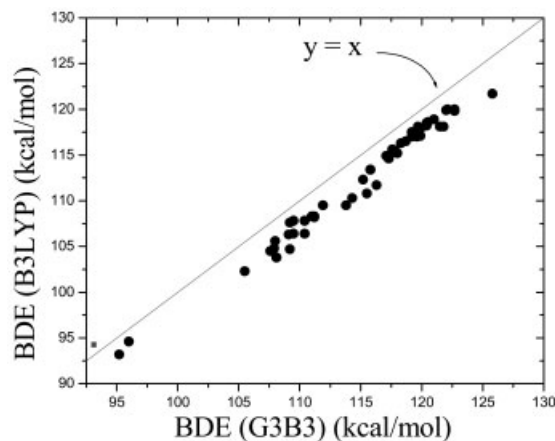Further examinations indicate that the underestimation by the DFT method is partly caused by the basis set effects. As an example for this problem, in Table 2 are shown the calculated C—H BDEs of benzene using the B3LYP method with various basis sets. The B3LYP C—H BDE with the infinite basis set is also extrapolated from the aug-cc-pVNZ ($N = 2, 3, 4$) BDEs using the following equation:[14]

$$E(N) = E_\infty + B \exp[-(N-1)] + C \exp[-(N-1)^2]$$
(1)

According to Table 2, all the B3LYP BDEs calculated using the finite basis sets are smaller than the B3LYP C—H BDE with the infinite basis set. In particular, the UB3LYP/6–311++G(2df,p) BDE is 2.4 kcal mol^{-1} smaller than the B3LYP C—H BDE with the infinite basis set.

In addition to the basis set effects, other factors including the electron correlation and core correlation may also affect the B3LYP BDEs. In fact, comparing the B3LYP C—H BDE with the infinite basis set (112.7 kcal mol^{-1}) with the G3B3 BDE (114.3 kcal mol^{-1}) it can be seen that even with the infinite basis set the B3LYP method still underestimates the BDEs. Therefore, we should be cautious about the absolute BDEs calculated by the DFT method. A seemingly good agreement between the DFT BDEs with the experimental BDEs may be fortuitous.

Figure 2. Correlation between BDEs (UB3LYP) and the G3B3 BDEs

Table 2. C—H BDE of benzene calculated using the B3LYP method with various basis sets (kcal mol^{-1})

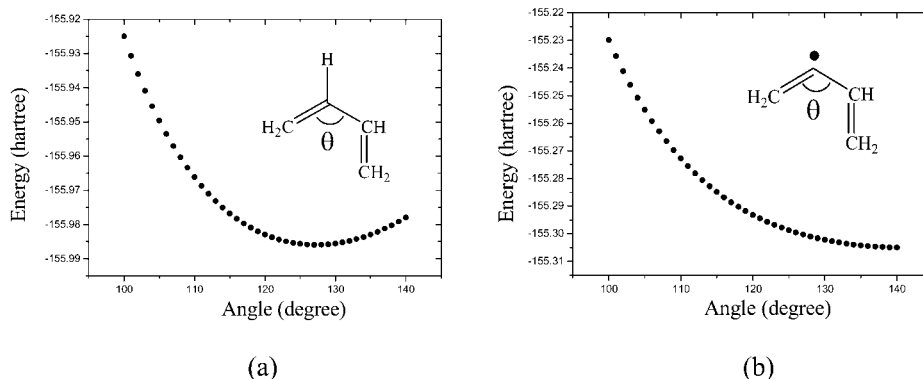| Method	BDE
UB3LYP/6–31G*	110.8
UB3LYP/6–311++G(d,p)	110.5
UB3LYP/6–311++G(2df,p)	110.4
UB3LYP/aug-cc-pVDZ	109.7
UB3LYP/aug-cc-pVTZ	111.0
UB3LYP/aug-cc-pVQZ	112.0
UB3LYP/∞	112.7
G3B3	114.3
Exp.	113.5 ± 0.5

Figure 3. Dependence of the energy on the C1—C2—C3 angle for 1,3-butadiene (a) and 1,3-butadiene radical (b)

Dependence of the aromatic C—H BDEs on bond angles

According to Table 1, it can be seen that the C—H BDEs of the five-membered ring aromatic compounds are usually about 120 kcal mol^{-1}. In comparison, the C—H BDEs of the six-membered ring aromatic compounds are about 110–115 kcal mol^{-1}.

The difference between the BDEs of the above two types of compounds is caused by the different X—C—Y angles. In fact, when we fixed all the geometric parameters (bond lengths, bond angles and dihedral angles) except for the C1—C2—C3 angle (θ) of 1,3-butadiene, we found that the energy [UB3LYP/6–31G(d)] of 1,3-butadiene is lowest when $\theta \approx 127°$. (Fig. 3). In comparison, the θ value for the minimum energy of the 1,3-butadiene radical (planar) is about 140°. (see the Supporting Information, available at the epoc website at http://www.wiley.com/epoc). Taking both the energy–θ dependences into consideration, we obtained the dependence of the C2—H BDE on the C1—C2—C3 angles (Fig. 4). According to Fig. 4, for $100 < \theta < 140$, a larger C1—C2—C3 angle leads to a smaller BDE.
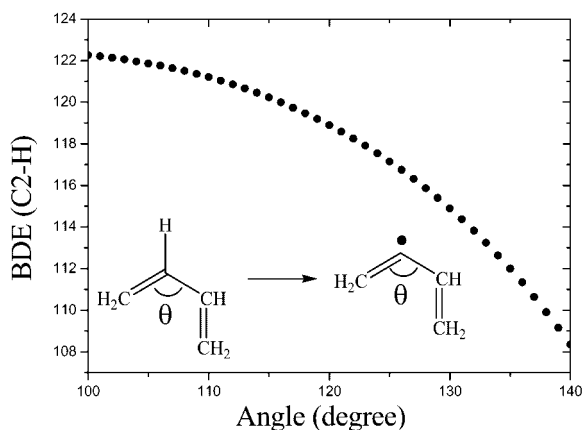
The X—C—Y angle for a perfect five-membered ring is 108°. The X—C—Y angle for a perfect six-membered ring is 120°. According to Fig. 4, it is clear that the C—H BDE of a six-membered ring aromatic compound should be lower than that of a five-membered ring aromatic compound. Moreover, we found that the plot between the C—H BDEs and the corresponding θ angles for all the five- and six-membered ring aromatic compounds is roughly linear (Fig. 5). The negative slope again demonstrates that a larger X—C—Y angle leads to a smaller C—H BDE.

Dependence of C—H BDEs on charges and spins

The charge carried by H in a C—H bond is dependent on the polarization of the bond (see Table 1). However, from Fig. 6 it can be seen that there is a very poor correlation between the C—H BDEs and the NBO charges carried by H for the aromatic compounds.

Nevertheless, according to Fig. 7, there is a clear correlation between the C—H BDE and the spin carried by C in the radical for all the five-and six-membered ring aromatic compounds. The positive slope in Fig. 7 means that a larger spin carried by C should lead to a higher BDE. This observation is consistent with the spin
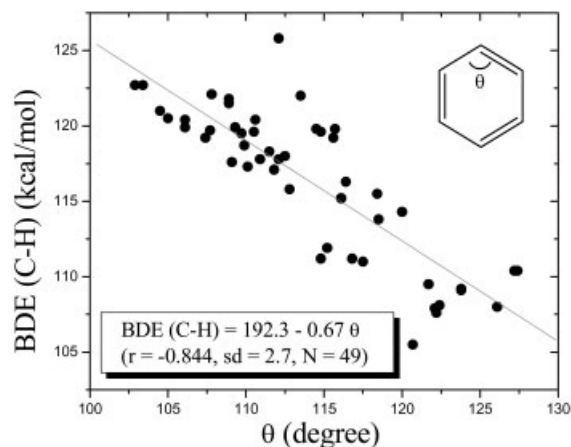

Figure 4. Dependence of C2—H BDE on the C1—C2—C3 angle for 1,3-butadiene

Figure 5. Dependence of the C—H BDEs on the corresponding θ angles

$$BDE (C\text{-}H) = 192.3 - 0.67 \theta$$
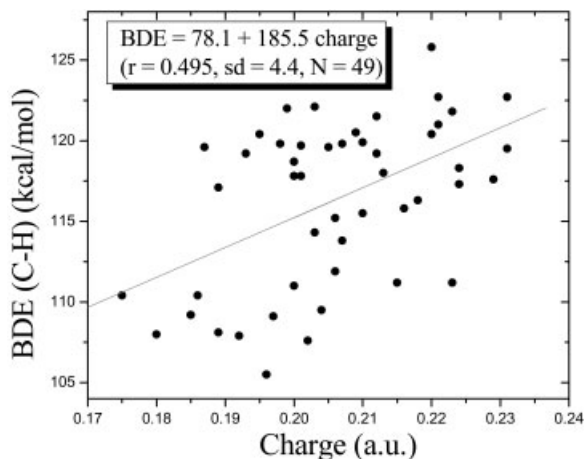$$(r = -0.844, sd = 2.7, N = 49)$$

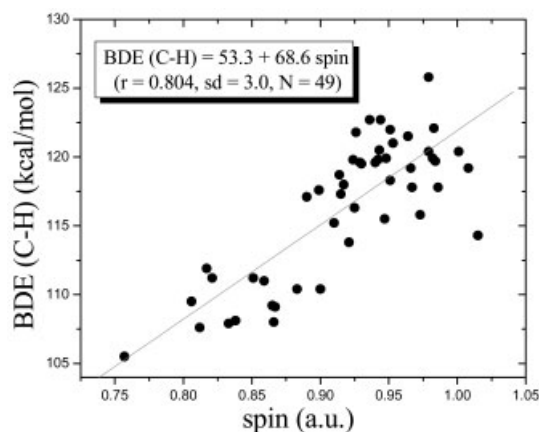**Figure 6.** Dependence of the C—H BDEs on the NBO charges carried by H

Figure 7. Correlation between the C—H BDE and the spin carried by C in the radical

delocalization stabilization effect proposed before for carbon radicals.[15]

Detailed examination of each compound reveals that the spin delocalization is mainly caused by the interaction between the heteroatom (N, O or S) lone pair electrons with the neighboring radical center. For example, the spins on the carbon atom in 2-, 3- and 4-pyridinyl radical are 0.865, 0.947 and 0.921 a.u., respectively (Fig. 8). This order for spins is consistent with the order for the C—H
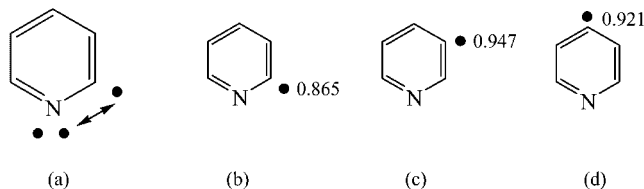
BDEs, which are 109.2, 115.5 and 113.8 kcal mol^{-1} for C2—H, C3—H, and C4—H, respectively.[16]

Quantitative structure–activity relationship (QSAR)

Using the bond angle, spin, and charge as parameters, we established the following QSAR model for the C—H BDEs of five- and six-membered ring aromatic compounds:

$$BDE(C—H) = 130.5(\pm 16.8) - 0.45(\pm 0.06)\theta$$
$$+ 40.0(\pm 6.0)\text{spin} \quad (2)$$

$$(r = 0.924, SD = 2.0 \text{ kcal mol}^{-1}, N = 49)$$

The correlation coefficient (r) is 0.924, which means that the model is reasonably good. The SD is 2.0 kcal mol^{-1}, which is roughly as large as the error for the composite *ab initio* calculations. The *t*-values for the coefficients before θ and spin are -8.1 and 6.7, respectively. Therefore, both parameters are important. It is worthly noting that the negative coefficient (-0.45) and positive coefficient ($+40.0$) before θ and spin are consistent with the discussion in the previons two sections.

CONCLUSION

C—H and N—H BDEs of various five- and six-membered ring aromatic compounds were calculated using composite *ab initio* CBS-Q, G3 and G3B3 methods. These values should be within 1–2 kcal mol^{-1} of the real BDEs and, therefore, are probably valuable for researchers in many relevant fields. In addition, we found interesting dependences of the C—H BDEs on the bond angles, spins and charges. A good QSAR model for the C—H BDEs of aromatic compounds was also established.

Acknowledgement

Figure 8. Overlap between the nitrogen lone pair and the p orbital of the carbon radical (a), and the spin of the carbon atom of 2-pyridinyl (b), 3-pyridinyl (c) and 4-pyridinyl radicals (d)

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