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C–H and N–H Bond Dissociation Energies of Small Aromatic Hydrocarbons

Cynthia Barckholtz, Timothy A. Barckholtz, and Christopher M. Hadad*

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Abstract: A survey of computational methods was undertaken to calculate the homolytic bond dissociation energies (BDEs) of the C–H and N–H bonds in monocyclic aromatic molecules that are representative of the functionalities present in coal. These include six-membered rings (benzene, pyridine, pyridazine, pyrimidine, pyrazine) and five-membered rings (furan, thiophene, pyrrole, oxazole). By comparison of the calculated C–H BDEs with the available experimental values for these aromatic molecules, the B3LYP/6-31G(d) level of theory was selected to calculate the BDEs of polycyclic aromatic hydrocarbons (PAHs), including carbonaceous PAHs (naphthalene, anthracene, pyrene, coronene) and heteroatomic PAHs (benzofuran, benzothiophene, indole, benzoxazole, quinoline, isoquinoline, dibenzofuran, carbazole). The cleavage of a C–H or a N–H bond generates a σ radical that is, in general, localized at the site from which the hydrogen atom was removed. However, delocalization of the unpaired electron results in ~ 7 kcal·mol⁻¹ stabilization of the radical with respect to the formation of phenyl when the C–H bond is adjacent to a nitrogen atom in the azabenzenes. Radicals from five-membered rings are ~ 6 kcal·mol⁻¹ less stable than those formed from six-membered rings due to both localization of the spin density and geometric factors. The location of the heteroatoms in the aromatic ring affects the C–H bond strengths more significantly than does the size of the aromatic network. Therefore, in general, the monocyclic aromatic molecules can be used to predict the C–H BDE of the large PAHs within 1 kcal·mol⁻¹.

Introduction

Coal is one of the dominant fossil fuels of the twentieth century and the fuel used for most of the electrical power generation in the United States, yet much remains to be understood about its structure and reactivity. In addition, it is difficult to characterize coal because many properties of coal, such as elemental composition, reactivity, and rank, vary greatly depending on the origin of the sample.¹ Although coal is a mixture of complex compounds, it has many periodic units, including heterocyclic and polycyclic aromatic components. The heteroatoms, which include nitrogen, oxygen, and sulfur, are known to play a very important role in coal combustion and

processing.² These atoms appear in coal in such forms as furan, thiophene, pyrrole, benzene, and pyridine rings.

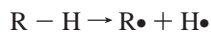
The most important processes of coal are combustion, gasification, pyrolysis, and liquefaction.² Each of these methods occurs under different conditions to yield different products; however, the initial reactions of combustion are thought to be common to all processes. Thus, an understanding of the thermochemistry and reactivity of specific bonds within the coal structure may lead to advances in coal processing. To this end, we are currently examining the thermochemical preferences of the aromatic constituents of coal. We hope that small molecules may be used as effective models of the components of coal in order to study the very complicated chemistry of coal combus-

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tion. We are particularly interested in identifying a computational method that is practical for the calculation of the chemical properties of computationally larger molecules, such as large polycyclic aromatic hydrocarbons (PAHs), which can be used to approximate the network nature of coal.

The first step in the combustion of coal is likely to be the homolytic cleavage of a carbon–hydrogen bond to form aromatic radicals.³



The bond dissociation energy (BDE) is defined as the enthalpy of the reaction required to break the C–H bond to form two radicals. Experimental measurements of the C–H BDEs of five- and six-membered-ring compounds that are relevant to coal combustion are not abundant in the literature. Even the energy required to remove a hydrogen atom from benzene to form the phenyl radical—the first step in perhaps the most widely studied model of the fossil fuel combustion process—was not definitively determined until only three years ago.⁴ In that work, a combination of gas-phase ion chemistry and negative ion photoelectron spectroscopy was used to determine the C–H bond strength of benzene to be $113.5 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$ at 300 K.

In addition to benzene, nitrogen-containing aromatic compounds are of interest in the modeling of coal combustion processes because nitrogen-containing constituents are known to be very important in the formation of NO_x species.^{5,6} Very recently, the pyrolyses of pyridine, pyrimidine, and pyrazine were experimentally explored via shock tube studies.^{7–9} The C–H BDEs in these azabenzenes were found to be smaller than that of benzene when the hydrogen atom was abstracted from a carbon atom adjacent to a nitrogen atom, but approximately the same as benzene when the hydrogen was removed from a carbon two or three positions away from nitrogen. The stabilization of the radical was attributed to the interaction of the unpaired electron on carbon with the adjacent nitrogen lone pair. *Ab initio* calculations at the MP2/DZP//HF/3-21G level supported the proposed thermochemistry of these azabenzenes; although, a difference between the calculated and experimental preferences for the site of abstraction from pyrimidine was noted.¹⁰

There are even less experimental data available for the C–H BDEs of five-membered aromatic rings. Photodissociation of pyrrole at both 193 and 248 nm has recently provided BDEs for the N–H ($88 \pm 2 \text{ kcal}\cdot\text{mol}^{-1}$) and C–H ($112.5 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$) bonds at 0 K via photofragment translational spectroscopy.¹¹

PAHs provide a larger model with which to approximate the network nature of coal. Coals of different rank have different degrees of PAH ordering, with anthracites containing the largest

aromatic fraction.¹ In addition, PAHs are significant products of the combustion process, especially under NO_x staging conditions.⁶ The bulk of the experimental studies of the physical properties of PAHs has been to identify their vibrational frequencies.^{12,13} It is much more difficult to determine experimentally the C–H BDEs of these large species compared to the monocyclic compounds, and thus experimental C–H BDEs of the PAHs are very scarce in the literature.

An early paper that measured the C–H bond strengths of benzene, naphthalene, and anthracene via competition experiments based on relative hydrogen atom abstraction from toluene concluded that the relative C–H bond strength of PAHs could be understood as a consequence of the bonding of the two neighboring carbon atoms and not the size of the aromatic network.¹⁴ Very recently, the gas-phase acidity (ΔH_{acid}) of naphthalene¹⁵ and the electron affinity (EA) of the naphthyl radicals were determined by Kass and co-workers so as to determine the C–H bond strength of naphthalene.¹⁶ The result of those experiments indicates that the energy required to cleave each of the C–H bonds in naphthalene is $111 \pm 3 \text{ kcal}\cdot\text{mol}^{-1}$. Insight into the C–H bond strength of heteroatomic PAHs can also be gleaned from thermal decomposition studies of nitrogen-containing polycyclic aromatic molecules.^{17,18} These studies show that the decomposition reactions of the monocyclic rings are predictive of the larger ring systems.

Initially, computational calculations of C–H BDEs of PAHs were limited to semi-empirical methods due to the cost incurred in calculating the aryl radicals by more accurate methods.¹⁹ The most inexpensive *ab initio* method, Hartree–Fock (HF), does not include electron correlation and therefore does not accurately predict thermochemical properties such as BDEs.²⁰ However, computational studies of C–H BDEs of aromatic compounds have recently received renewed attention following the more widespread use of pure and hybrid density functional theory (DFT) methods.^{21,22} Recent B3LYP²³ and BLYP^{24,25} studies of PAHs containing one to six benzenoid rings have shown that DFT correctly describes the electronic structure of PAH radicals.

The aim of this work is to use computational methods to study small aromatic compounds that represent functional groups known to be present in coal. To this end, the C–H BDEs of heteroatomic five-membered, six-membered, and polycyclic aromatic compounds have been calculated via the hybrid DFT B3LYP method. A survey of computational methods was undertaken in the calculation of C–H BDEs of the monocyclic aromatic compounds. On the basis of its excellent agreement

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with the available data from several experiments, the B3LYP^{26–29} level was chosen for the study of the polycyclic aromatic compounds. In a future paper we will present calculations of transition states for abstraction and addition processes to several of these model compounds via H, O (³P), and OH. Others have considered possible decomposition of the radicals in combustion environments.^{30–32}

Computational Details

All geometry optimizations and frequency calculations were performed using Gaussian 94³³ running on either an SGI Power Challenge or a Cray T94 at the Ohio Supercomputer Center. The geometries of the aromatic rings and their hydrogen atom loss products were optimized with the standard 6-31G(d) basis set²⁰ using several computational methods, including HF, MP2, and DFT. Vibrational frequencies have also been calculated for each stationary point to verify a minimum energy structure and to provide zero-point energies (ZPEs), which were scaled by the factors of 0.9135,³⁴ 0.9646,³⁴ 0.9806,³⁵ and 1.0126³⁵ for HF, MP2, B3LYP, and BLYP, respectively. The BPW91 zero-point energies were not scaled. The frequency calculations also provided the thermal contributions to the enthalpy, which were obtained using unscaled frequencies.

In addition, BDEs were calculated using model chemistries that have been shown to reproduce quite accurately a large number of experimentally determined thermochemical properties for a test set of molecules.³⁶ A comparison of the BDEs of a test set including more than 100 small molecules showed that each of these compound methods provided BDEs that were within 1.5 kcal·mol⁻¹ of the experimental values.³⁶ Complete basis set (CBS) methods are able to achieve high accuracies at reduced computational expense by extrapolation to the complete basis set limit and by inclusion of a high level of electron correlation.³⁷ The modified Gaussian-2 method, G2MP2, is a similar composite theory that is based on the additivity of several correction terms that use larger basis sets at lower levels of theory and smaller basis sets at higher levels of theory.³⁸

Single-point energy calculations were evaluated with the 6-311+G-(d,p) and 6-311+G(3df,2p) basis sets while using the B3LYP/6-31G-(d) geometries. The ZPEs and thermal contributions were taken from the B3LYP/6-31G(d) frequency calculations. To analyze the trends in BDE as a function of the atoms in the aromatic rings, the electronic wave functions were calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. Six Cartesian *d* functions were used with all basis sets. Spin density populations were obtained from the wave functions via

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Bader's theory of atoms in molecules.^{39–42} Spin density populations were calculated using AIMALL.⁴³ The spin density is the difference between the α and β spin densities. Its magnitude is a measure of the extent of delocalization of the radical character throughout the molecule.⁴⁴

The chemistry under consideration is the energy required to cleave the C–H bond in small aromatic hydrocarbons. Because these compounds will be used as models for studying the combustion process, it is relevant to ascertain the effects of increased temperatures on the C–H bond strength. The enthalpies of the monocyclic aromatic rings and the radicals resulting from cleavage of each unique C–H bond were calculated from 300 to 2000 K by including a temperature-dependent enthalpic term,²⁰

$$\Delta H(T) = H_{\text{trans}}(T) + H_{\text{rot}}(T) + H_{\text{vib}}(T) + RT$$

$$\Delta H(T) = \frac{3}{2}RT + \frac{3}{2}RT + Nh \sum_i \nu_i (e^{h\nu_i/kT} - 1)^{-1} + RT$$

where the summation is over all $3N - 6$ normal modes. The scaled zero-point energy and the enthalpy contribution, computed by the above equation, were added to the B3LYP total energy to determine the C–H BDEs as a function of temperature.

Results

The BDEs of a number of monocyclic aromatic compounds, calculated by several different methodologies, are presented in Table 1 (for atom numbering, see Figures 1 and 2). Where available, the calculated BDEs were compared to the experimental values in order to obtain an "average error" for each method (see the bottom row of Table 1). The results are in agreement with the findings of others^{24,45} that HF and MP2 methods cannot be used to adequately describe both the parent aromatic molecule and the radical resulting from hydrogen atom loss. The lack of electron correlation at the HF level leads to an underestimation of the C–H BDE by ~ 25 kcal·mol⁻¹, although qualitative predictions of the radical preference from parent aromatics with more than one unique C–H bond were reliable. In addition, both HF and MP2 calculations of the radical species suffer from significant spin contamination, with $\langle S^2 \rangle$ as high as 1.4 for the radicals formed from benzene and the azabenzenes. As a result, most of the MP2 BDEs calculated were ~ 17.0 kcal·mol⁻¹ higher than experiment. Furthermore, a comparison of the model chemistries and the experimental data available for the small aromatic rings reveals that the CBS and G2MP2 methods fall short of the accuracy predicted by the test set of molecules. While there is excellent agreement with the experimental C–H BDE of benzene by CBS-Q, the G2MP2 level predicts a higher BDE than the accurate experimental value. For comparison to the other experimental values, the average error for the CBS and G2MP2 methods is slightly beyond their typical 2 kcal·mol⁻¹ error. It should also be noted that all of the CBS methods perform better than the G2MP2 method. However, it has been noted previously that G2 methods fail to accurately predict the properties of aromatic hydrocarbons.⁴⁶ It has recently been recognized that CBS-RAD, a

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Table 1. Calculated C–H (and N–H) BDEs of the Monocyclic Aromatic Molecules at 298 K (in kcal·mol⁻¹)

parent	site ^a	state	HF	MP2	CBS-4	CBS-q	CBS-Q	G2MP2	BLYP	BPW91	B3LYP	exp
benzene	1	² A ₁	80.1	127.9	117.2	119.1	114.7	117.2	108.6	107.3	110.8	113.5 ± 0.5 ^b
pyridine	2	² A'	78.9	123.3	112.0	112.0	110.3	113.1	102.8	101.9	105.6	105 ± 2 ^c
	3	² A'	81.8	131.4	119.0	120.5	116.6	118.5	107.9	107.0	111.3	112 ± 2 ^c
pyridazine	4	² A ₁	80.8	128.3	116.8	118.2	115.3	117.5	107.1	106.0	110.0	112 ± 2 ^c
	3	² A'	78.5	132.2	117.2	118.0	114.1	116.8	103.8	103.1	107.0	
pyrimidine	4	² A'	80.2	136.7	120.8	122.1	115.5	118.3	103.8	103.0	108.9	
	2	² A ₁	81.4	121.5	112.5	112.7	— ^f	114.8	104.6	103.5	107.2	98 ± 2 ^c
pyrazine	4	² A'	80.6	119.6	110.9	110.3	110.6	112.7	101.4	100.6	104.7	103 ± 2 ^c
	5	² A ₁	84.7	132.1	118.7	120.0	117.7	119.8	108.5	107.6	112.2	112 ± 2 ^c
furan	1	² A'	79.0	129.7	115.3	114.9	111.7	114.6	101.9	101.2	105.7	103 ± 2 ^c
	2	² A'	90.6	122.8	120.1	120.6	121.0	123.1	116.2	115.0	118.4	
thiophene	3	² A'	91.1	123.5	120.5	120.5	121.4	123.2	116.0	114.9	118.3	
	2	² A'	87.8	123.6	118.8	119.1	119.2	121.5	114.4	113.5	116.6	
pyrrole	3	² A'	86.3	121.1	116.6	116.3	117.0	119.4	111.4	110.4	113.8	
	2	² A'	91.7	119.4	119.8	119.9	120.8	122.4	115.8 ^g	114.7	118.1	112.3 ± 1 ^d
pyrrole	3	² A'	91.5	119.4	119.6	119.5	120.4	121.9	115.6	114.3	117.6	112.3 ± 1 ^d
	<i>n</i>	² A ₂	61.9	— ^h	96.2	94.4	— ^h	— ^h	87.5	88.3	89.8	88 ± 2 ^d , 96.6 ± 4 ^e
av error ⁱ			25.3	17.0	7.9	8.4	5.3	8.9	3.6	3.9	3.1	

^a The radical site (see Figures 1 and 2). ^b Reference 4. ^c Reference 9. ^d Reference 11. ^e Reference 54. ^f Error converging wave function. ^g C₁ symmetry. ^h The complicated electronic structure of pyrrole prohibited the calculation of the N–H BDE at the MP2, CBS-Q, and G2MP2 levels. The HF, CBS-4, and CBS-q calculations are based on a C₁ symmetry. ⁱ Average of the absolute error of (experiment – theory) for C–H bonds.

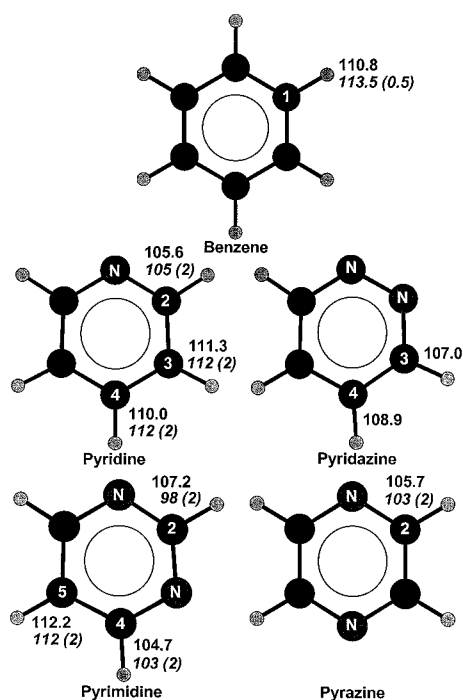


Figure 1. B3LYP/6-31G(d) bond dissociation enthalpies (kcal·mol⁻¹, 298 K) for the cleavage of the C–H bond at each unique radical site for the six-membered aromatic molecules: (a) benzene, (b) pyridine, (c) pyridazine, (d) pyrimidine, and (e) pyrazine. Experimental BDEs are in italics with the experimental uncertainty in parentheses.

modification of the CBS-Q method, is more suited to the accurate calculation of the thermochemical properties of free radicals.⁴⁷ However, the use of QCISD for both the optimization and zero-point determination steps within the CBS-RAD method render the CBS-RAD method impractical for the size of the molecules considered in this study.

The C–H bond enthalpies calculated via each of the DFT methods are in better agreement with experiment than the methods based on HF theory. The pure DFT methods, such as BLYP and BPW91, yielded BDEs that are on average lower than experiment by ~3–4 kcal·mol⁻¹. The B3LYP method

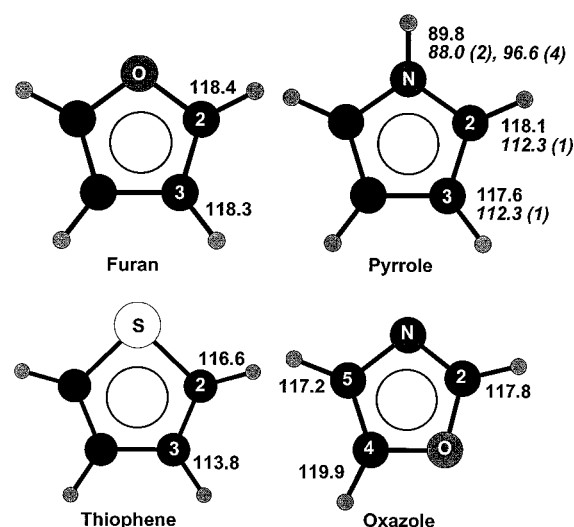


Figure 2. B3LYP/6-31G(d) bond dissociation enthalpies (kcal·mol⁻¹, 298 K) for the cleavage of the C–H bond at each unique radical site for the five-membered aromatic molecules: (a) furan, (b) pyrrole, (c) thiophene, and (d) oxazole. Experimental BDEs are in italics with the experimental uncertainty in parentheses.

provides the best agreement (3 kcal·mol⁻¹) of the computed BDEs of the smaller aromatic hydrocarbons with experiment. It should be noted that the qualitative trends for the BDEs are reproduced by all of the CBS, G2MP2, and the DFT methods. However, the DFT methods are more affordable than the CBS- or G2-based methods and are seemingly well-suited for the study of large PAHs. For these reasons, B3LYP was selected to elucidate the trends in the calculated bond dissociation enthalpies of the monocyclic aromatic molecules as well as to study larger carbonaceous and heteroatomic PAHs.

To determine the validity of the 6-31G(d) basis set, B3LYP single-point calculations were performed using the 6-311+G-(d,p) and 6-311+G(3df,2p) basis sets. Bond dissociation enthalpies were determined by adding scaled zero-point and thermal contributions from the 6-31G(d) basis set calculation to the energies calculated with the larger basis set for both the parent and carbon-centered radical. It is evident from a comparison of the B3LYP C–H BDEs with the three different basis sets (Table 2) that a larger basis set leads to negligible differences in comparison to experiment in the predicted C–H

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Table 2. Comparison of Basis Sets for the B3LYP Calculation of BDEs at 298 K (in kcal·mol⁻¹)

parent	site ^a	6-31G(d)	6-311+ G(d,p)	6-311+ G(3df,2p)	exp
benzene	1	110.8	110.6	110.6	113.5 ± 0.5 ^b
	2	105.6	105.0	104.9	105 ± 2 ^c
pyridine	3	111.3	111.1	111.1	112 ± 2 ^c
	4	110.0	109.7	109.8	112 ± 2 ^c
	3	107.0	106.5	106.6	
pyridazine	4	108.9	108.6	108.7	
	2	107.2	106.8	106.6	98 ± 2 ^c
pyrimidine	4	104.7	104.2	104.2	103 ± 2 ^c
	5	112.2	112.0	112.1	112 ± 2 ^c
	1	105.7	105.2	105.0	103 ± 2 ^c
pyrazine	2	118.4	118.7	118.7	
furan	3	118.3	118.4	118.6	
	2	116.6	116.6	116.6	
thiophene	3	113.8	113.7	113.8	
	2	118.1	118.3	118.4	112.3 ± 1 ^d
pyrrole	3	117.6	117.7	117.8	112.3 ± 1 ^d
	n	89.8	94.3	93.7	88 ± 2 ^d , 96.6 ± 4 ^e
	av error ^f	3.1	3.0	3.0	

^a The radical site (see Figures 1 and 2). ^b Reference 4. ^c Reference 9. ^d Reference 11. ^e Reference 54. ^f Average of the absolute error of (experiment - theory) for C-H bonds.

BDEs. Most importantly, the relative stability of the radicals remains unchanged from that predicted via the smaller 6-31G(d) basis set upon the inclusion of basis functions of higher angular momentum and diffuse functions. Not surprisingly, the bond strength of the more polar N-H bond is affected by the size of the basis set. Inclusion of higher angular momentum basis functions results in a slightly higher N-H BDE in pyrrole by ~4 kcal·mol⁻¹.

1. C-H BDE of Benzene. The B3LYP/6-31G(d) calculations for the dissociation of a hydrogen atom from benzene to form the phenyl radical will serve as the standard for comparison with the other aromatic hydrocarbons presented in this work. To accurately predict the C-H bond strength, the computational method must first reproduce the geometry of both the parent and the radical. The C-C and C-H bond lengths for benzene calculated at the B3LYP level are in excellent agreement ($\Delta = -0.0005$ Å and $\Delta = +0.003$ Å, respectively) with those determined by high-resolution spectroscopy.⁴⁸ Hydrogen abstraction from benzene gives rise to a widening of the C-C-C bond angle at the radical site by 5.7° and a shortening of the adjacent C-C bonds by 0.019 Å. The unpaired electron in the phenyl radical is located in an sp² orbital that is orthogonal to the π system. However, analysis of the spin density suggests that spin polarization occurs in both the σ and π systems (see Discussion). The C-H BDE of benzene calculated at the B3LYP level is 110.8 kcal·mol⁻¹ at 298 K, which is very close to the most recent experimental values of 111.2 ± 0.8⁴⁹ and 113.5 ± 0.5⁴ kcal·mol⁻¹ at 300 K, both determined via thermochemical cycles from EA and ΔH_{acid} measurements.

2. BDEs of Azabenzenes: Pyridine, Pyridazine, Pyrimidine, and Pyrazine. Recent experimental results have added considerably to the understanding of the thermochemistry of the azabenzenes.⁷⁻⁹ These studies show that the pyrolyses of pyridine, pyrimidine, and pyrazine are initiated by the homolysis of the C-H bond with a barrier that is lower than the barrier for cleavage of the C-H bond in benzene. The lower C-H

BDEs for the C-H bonds next to the nitrogen atoms in the azabenzenes was attributed to the neighboring N-C interactions that lead to stabilization of the radical via resonance.⁷⁻⁹ An earlier theoretical study also explored the relative stabilities of the pyridyl and diazyl radicals using the MP2/DZP//RHF/3-21G level of theory.¹⁰

The work presented here further examines the relative stabilities of these radicals as well as the radicals formed from pyridazine and pyrazine using a variety of *ab initio* methods. The BDEs of all of the six-membered aromatic rings calculated with the B3LYP method are shown in Figure 1, with experimental C-H BDEs shown in italics. It is evident that the energy required to remove a hydrogen atom from the azabenzenes is greatly influenced by the presence of a nitrogen atom in the six-membered aromatic ring. For example, the B3LYP method predicts that C-H bond cleavage from the carbon adjacent to the nitrogen (the 2 position) in pyridine is ~5 kcal·mol⁻¹ more facile than cleavage of a C-H bond in benzene. In contrast, the C-H bond cleavages at the 3 or 4 position of pyridine are quite similar to that of benzene, with only a ~1 kcal·mol⁻¹ preference for abstraction from the 4 position over the 3 position. The B3LYP calculations can be compared with a high-temperature pyrolysis study of pyridine that yielded C-H BDEs at each of the unique carbon positions in pyridine via an analysis of the decomposition products.⁹ The results of this shock tube study agree quite well with the B3LYP calculations in the prediction of the low C-H BDE for the 2 position of pyridine. The experiment was unable to determine a preference for hydrogen atom loss from the 3 or 4 position of pyridine.

In general, there is good agreement between the present work and the previous calculations, as well as with the available experimental data for the C-H BDEs of six-membered aromatic rings. However, calculations of the relative stability of the three radicals formed from pyrimidine differ from the order determined experimentally.^{8,9} An RRKM analysis of shock tube experiments indicates that the 2-pyrimidyl radical is the most stable radical of pyrimidine, followed by the 4-pyrimidyl and 5-pyrimidyl radicals, with C-H BDEs of 98, 103, and 112 kcal·mol⁻¹, respectively.⁹ The corresponding B3LYP C-H BDEs are 107.2, 104.7, and 112.2 kcal·mol⁻¹, respectively. Resonance structures of the 2-pyrimidyl radical were invoked by Kiefer and co-workers to rationalize its stability. However, the previous theoretical study¹⁰ and the current calculations predict that the radical stability decreases in the order 4-pyrimidyl, 2-pyrimidyl, and 5-pyrimidyl. The effect of nitrogen atoms on the strength of C-H bonds in aromatic systems will be explored in greater detail in a forthcoming paper.

3. BDEs of Five-Membered Aromatic Rings: Furan, Thiophene, Pyrrole, and Oxazole. To date, few experiments have been performed to determine the C-H bond strengths in five-membered heterocyclic molecules. Unlike the azabenzenes, the thermal decomposition reactions of furan and pyrrole are not initiated by the cleavage of a C-H bond. Instead, the experiments suggest that five-membered heterocyclic compounds, including furan and pyrrole, isomerize or decompose via unimolecular reactions that involve scission of the C-O or C-N bond.⁵⁰⁻⁵²

The calculated BDEs of the five-membered aromatic molecules are shown in Figure 2. The average BDE for five-

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membered rings ($117.1 \text{ kcal}\cdot\text{mol}^{-1}$) is higher than that for the six-membered rings ($108.3 \text{ kcal}\cdot\text{mol}^{-1}$). Also, cleavage of a C–H bond in a five-membered ring requires $\sim 6 \text{ kcal}\cdot\text{mol}^{-1}$ more energy than breaking a C–H bond in benzene. From this observation, the dissociation of a C–H bond in five-membered rings seemingly requires more energy because these rings are less able to accept the geometric perturbation that follows cleavage of a C–H bond. Furthermore, in contrast to the six-membered rings, the preference for abstraction within the five-membered rings varies only moderately between sites in the five-membered rings. In particular, the stabilization of the ortho radicals (2 position) that was observed in the six-membered aromatic rings is absent in the five-membered rings. For example, the preference for abstraction from the 3 position over the 2 position in furan is small ($<0.1 \text{ kcal}\cdot\text{mol}^{-1}$). However, in the case of pyrrole, and even more so in the case of thiophene, hydrogen atom loss from the 3 position is favored over the 2 position by 0.5 and $2.8 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. The origin of this effect will be discussed below.

Pyrrole differs from the other molecules studied in that it is an aromatic heterocyclic amine with an N–H bond. The calculated N–H BDE ($\sim 89 \text{ kcal}\cdot\text{mol}^{-1}$) is significantly lower than the average C–H BDE of the other aromatic molecules, but is in excellent agreement with the 0 K N–H BDE determined via photofragment translational spectroscopy ($\sim 88 \text{ kcal}\cdot\text{mol}^{-1}$).¹¹ The same experimental work reported that cleavage of one of the two C–H bonds occurred at $\sim 112 \text{ kcal}\cdot\text{mol}^{-1}$ but did not distinguish the site of the bond cleavage.

The C–H BDEs in oxazole demonstrate that simultaneous oxygen and nitrogen atom substitution provides similar perturbations in a five-membered ring, and there is little, if any, cooperativity.

4. BDE of Polycyclic and Polyheteroatomic Rings. The agreement between the experimental and calculated C–H BDEs for the monocyclic compounds provides confidence that the B3LYP method can be used to predict reliably the bond strengths of PAHs, for which few quantitative experimental values are available for comparison. The results of the BDE calculations for both polycyclic and polycyclic heteroatomic aromatic hydrocarbons are presented in Figures 3 and 4, respectively. The B3LYP BDEs are shown at each unique carbon site for each aromatic compound. The difference between the calculated BDEs of the PAHs and that of the corresponding BDE in the monocyclic analogue is given in brackets.

a. Carbonaceous PAHs. PAHs comprising only fused benzene rings (Figure 3) exhibit the least amount of variation in C–H bond strengths. The C–H BDEs for representative benzenoid PAHs of two, three, four, and seven fused benzene rings (naphthalene, anthracene, pyrene, and coronene, respectively) vary little from the predicted C–H bond strength of benzene. Naphthalene is the only PAH in which an assessment of the C–H bond strengths relative to benzene has been measured experimentally. The B3LYP method predicts that the energies required to cleave the C–H bond to form the 1-naphthyl radical ($111.1 \text{ kcal}\cdot\text{mol}^{-1}$) and the 2-naphthyl radical ($110.9 \text{ kcal}\cdot\text{mol}^{-1}$) differ from the energy to cleave the C–H bond in benzene by only 0.3 and $0.1 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. These values agree quite well with both a previous DFT calculation²⁴ and the very recent gas-phase ion chemistry experiment that determined the C–H bond strength to be $111 \pm 3 \text{ kcal}\cdot\text{mol}^{-1}$ for naphthalene.¹⁶

Previous DFT computational studies of PAHs, including several PAHs larger than those in the present study, concluded that the preference for hydrogen atom loss from a particular

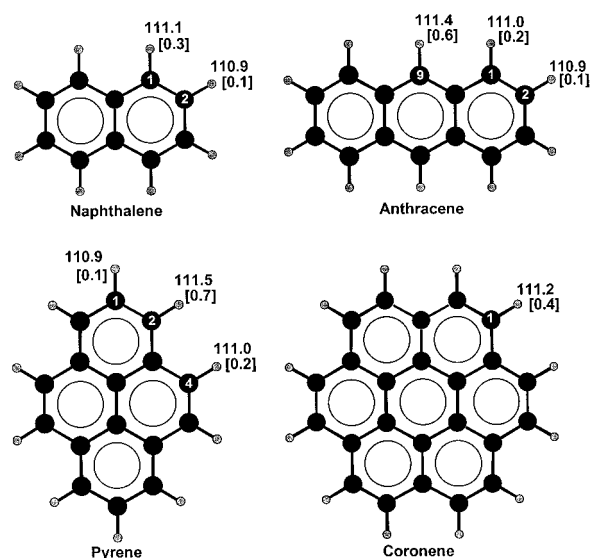


Figure 3. B3LYP/6-31G(d) bond dissociation enthalpies ($\text{kcal}\cdot\text{mol}^{-1}$, 298 K) for the cleavage of the C–H bond at each unique radical site for polycyclic aromatic hydrocarbons: (a) naphthalene, (b) anthracene, (c) pyrene, and (d) coronene. The difference between the C–H BDE of the polycyclic molecule and the corresponding monocyclic molecule is given in brackets.

site could be understood in terms of steric congestion.^{24,25} The PAHs chosen in this study do not include closely positioned hydrogens, and thus, a different explanation must be offered. An earlier MNDO study¹⁴ suggested that the energy required to cleave a C–H bond in a PAH could be predicted by the bonding of the two neighboring carbon atoms, though the conclusions drawn here differ considerably. For example, anthracene has three unique C–H bond positions: the 1 position is adjacent to both a secondary and a tertiary carbon; the 2 position is adjacent to two secondary carbons; and the 9 position is adjacent to two tertiary carbons. The MNDO study found that the C–H bond at the 9 position in anthracene was several kilocalories per mole weaker than that of a C–H bond in benzene. However, the B3LYP calculations predict that hydrogen atom loss from site 2 in anthracene, the position in which the C–H bond is most like a C–H bond in benzene, is favored over abstraction from sites 1 and 9, which are adjacent to a bridging C, but only by $\leq 0.5 \text{ kcal}\cdot\text{mol}^{-1}$. The preferences for abstraction presented here differ slightly from the previous DFT work,²⁴ yet preserve the preference for abstraction at the least reactive carbon site, if only by $0.1 \text{ kcal}\cdot\text{mol}^{-1}$.

b. Heteroatomic PAHs: Six-Membered Rings Fused to Benzene. We have also considered polycyclic PAHs that contain heteroatoms (Figure 4). It is evident that the predicted C–H BDEs of the polycyclic aromatic rings are also governed by both the position of the C–H bond with respect to the heteroatoms in the ring and the number of atoms in the ring. A greater variation in the strength of C–H bonds is observed in the six-membered bicyclic PAHs that contain nitrogen. The 2 position is the only C–H bond adjacent to nitrogen in quinoline, whereas isoquinoline has two such sites. The 1 position in isoquinoline is adjacent to both a nitrogen and a bridging carbon whereas the 3 site is adjacent to a nitrogen and a carbon that is next to a bridging carbon. The B3LYP calculations predict that the radical formed at the 1 site is $\sim 2.5 \text{ kcal}\cdot\text{mol}^{-1}$ more stable than that from the 3 site. This is in agreement with a recent thermal decomposition study that found that the most favored pathway for decomposition of isoquinoline was initiated by hydrogen atom loss from the 1 position.¹⁸ The experimental

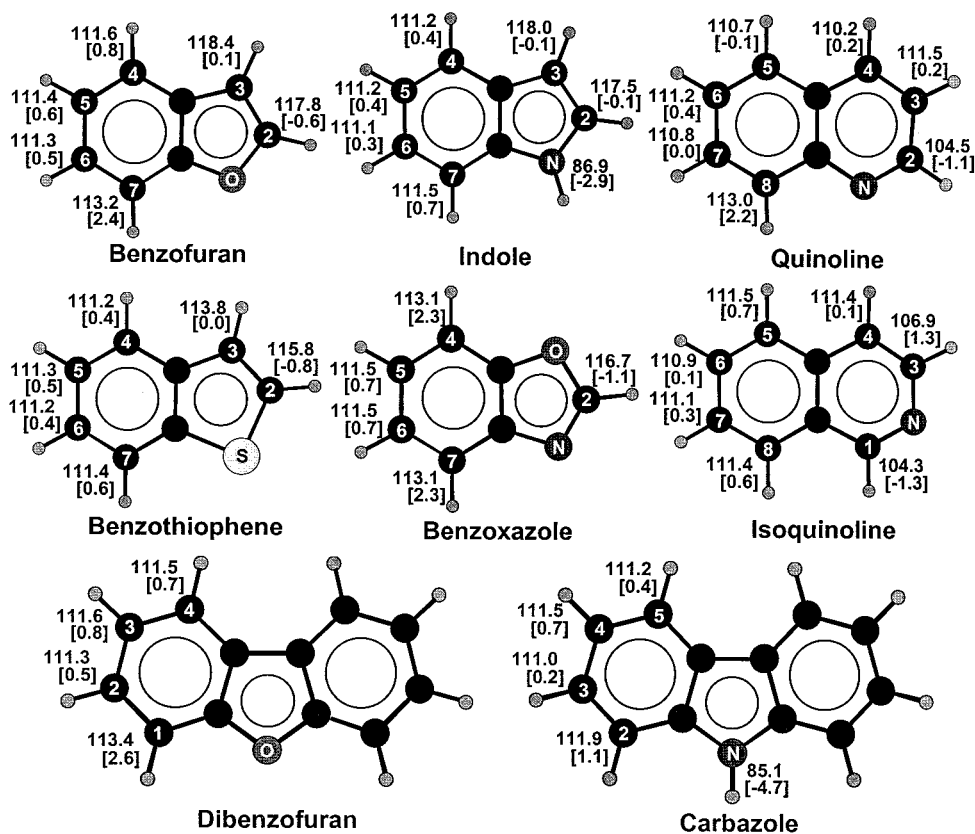
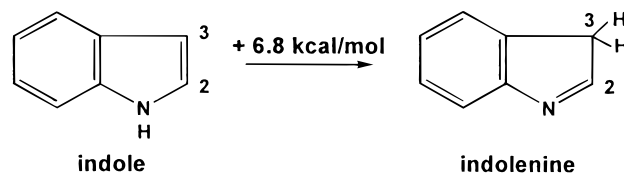


Figure 4. B3LYP/6-31G(d) bond dissociation enthalpies (kcal·mol⁻¹, 298 K) for the cleavage of the C–H bond at each unique radical site for polycyclic heteroatomic molecules: (a) benzofuran, (b) indole, (c) quinoline, (d) benzothiophene, (e) benzoxazole, (f) isoquinoline, (g) dibenzofuran, and (h) carbazole. The difference between the C–H BDE of the polycyclic molecule and the corresponding monocyclic molecule is given in brackets.

analysis of the decomposition of the quinolines was simplified by assuming that all of the C–H bonds on the fused benzene ring possessed the same bond strength. However, the B3LYP calculations suggest that there is ~ 2 kcal·mol⁻¹ variation in the strength of the four benzene-like C–H bonds in quinoline, with the most energy being required to cleave the C–H bond at the 8 position.

c. Heteroatomic PAHs: Five-Membered Rings Fused to Benzene. Oxygen and sulfur are present in coal in several forms due to the variety of the original plant functionalities.² However, as the process of coalification progresses, aliphatic structures are converted to heterocyclic structures and finally to heteroaromatic structures. Condensed furans and thiophenes are also present in the products of coal processing, which has been rationalized by their stability at low temperatures.² If the initiation step in the combustion process is cleavage of a C–H bond, then the B3LYP prediction of relatively higher C–H BDEs for aromatic molecules that contain five-membered rings is in agreement with these findings.

Similar to their monocyclic analogues, there is a paucity of experimental thermochemical data for the polycyclic molecules that contain five-membered rings fused to a benzene ring. A thorough experimental study of the decomposition of indole indicated that hydrogen atom loss from indole is more facile than in pyrrole.¹⁷ However, a C–H bond strength was not reported for indole because the proposed mechanism suggests that indole first isomerizes to indolenine, followed by hydrogen atom elimination ($D_{\text{HC-H}} = 70$ kcal·mol⁻¹) from the sp³ carbon at the 3 position. Our B3LYP/6-31G(d) calculations suggest that this isomerization requires less than 7 kcal·mol⁻¹ and that the subsequent hydrogen atom loss from the sp³ carbon at the 3 site in indolenine requires 80.1 kcal·mol⁻¹, which is higher than



the experimental value. However, the calculated N–H bond strength (86.9 kcal·mol⁻¹) is in good agreement with the experimental value (88 kcal·mol⁻¹).

Although there is a range of C–H BDE values for a particular site in a PAH and the corresponding site in the monocyclic aromatic compound, there is considerably more variation in the N–H BDEs. A comparison of the N–H BDE in the related compounds pyrrole, indole, and carbazole will demonstrate the effect that the aromatic network has on the N–H BDE. The calculations predict the N–H BDEs to be 89.8, 86.9, and 85.1 kcal·mol⁻¹ for pyrrole, indole, and carbazole, respectively. These same N–H BDEs were experimentally measured in DMSO solution and adjusted to yield gas-phase values, yielding N–H BDEs of 96.6, 93.8, and 92.7 kcal·mol⁻¹ for pyrrole, indole, and carbazole, respectively.⁵³ Although the absolute B3LYP-calculated N–H BDEs differ by slightly more than the 4 kcal·mol⁻¹ experimental uncertainty noted by the authors, the qualitative trends are reproduced. The relative energies obtained by each method are the same. As the number of benzene rings fused to pyrrole increases, the N–H BDE is calculated to decrease by 2.9 and 4.7 kcal·mol⁻¹, similar to the experimental differences of 2.8 and 3.9 kcal·mol⁻¹.

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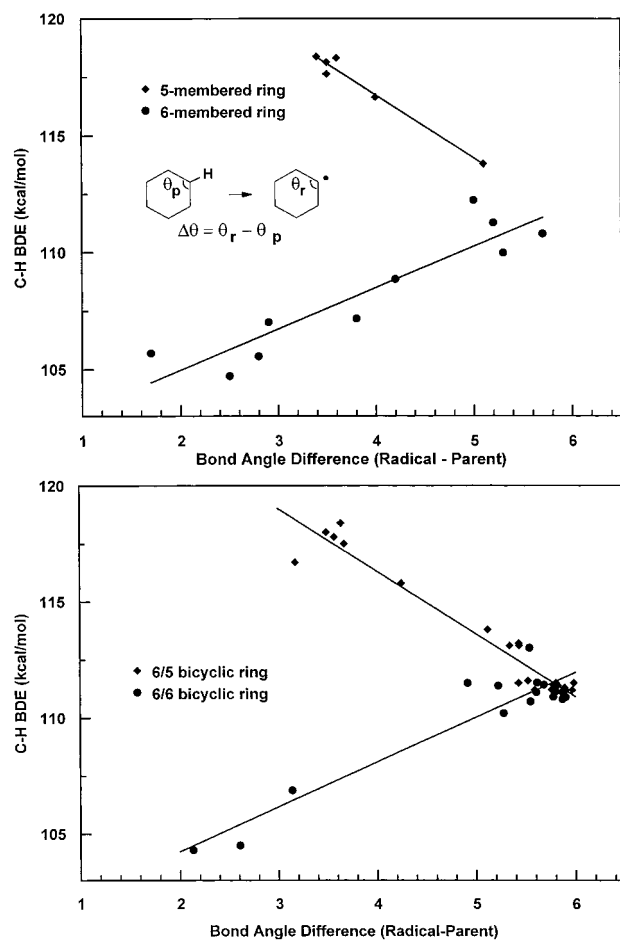


Figure 5. Relationship of the calculated C–H BDE with respect to the change in the internal bond angle at the radical site that occurs upon hydrogen atom abstraction from monocyclic and bicyclic aromatic molecules, shown in the top and bottom traces, respectively. The bond angle change is defined as radical – parent. In the top trace the correlation coefficient for five-membered and six-membered monocyclic rings is 0.97 and 0.84, respectively. In the bottom trace, the correlation coefficient for bicyclic rings that contain benzene fused to five-membered and six-membered rings is 0.94 and 0.88, respectively.

Discussion

1a. General Trends in Bond Dissociation Enthalpies: Geometries. A consideration of both the geometric and electronic properties of the parent compounds and their radicals can lead to an understanding of the calculated C–H BDEs. The formation of a radical following hydrogen atom loss from a parent aromatic molecule is accompanied by regular changes in the optimized geometry. As we previously noted, when the C–H bond in benzene is cleaved to form the phenyl radical, there is a widening of the bond angle at the site where the radical is formed and a shortening of the adjacent C–C bonds. In addition, to accommodate the unpaired electron there is a reduction of the bond angles adjacent to the radical site for the aromatic ring.

In general, the presence of a nitrogen atom in a six-membered-ring aromatic system results in a stabilization of radicals formed via C–H bond cleavage. The hybridization of each atom in the azabenzenes is nearly of pure sp^2 character and the nitrogen electron pair is in an sp^2 orbital. As a result the internal bond angles of the azabenzenes are $\sim 120^\circ$. Upon cleavage of a C–H bond, the bond angle at the radical site is increased by as much as 5° . It can be seen in the top trace in Figure 5 that the departure from the ideal sp^2 bond angle is

correlated with a reduction in the stability of the radical and an increase in the C–H BDE of a six-membered ring. This geometric evidence can be used to rationalize the relative stability of the radicals formed from pyrimidine as predicted by B3LYP. The bond angle widens at the radical site by 2.5° , 3.8° , and 5.0° following hydrogen atom loss from the 4, 2, and 5 carbon positions, respectively, which is well correlated with the B3LYP prediction that the stability decreases in the order 4-pyrimidyl, 2-pyrimidyl, and 5-pyrimidyl radicals.

Similar geometric arguments can provide insight into the calculated C–H BDEs of the five-membered aromatic molecules. A regular pentagon has internal angles of 108° . However, the aromatic five-membered rings are distorted by the presence of the heteroatom (X). The resulting ring possesses shortened C–X bonds and a contracted C–X–C bond angle. The perturbation of the ring is greatest in thiophene where the C–X–C bond angle is significantly smaller ($\sim 91^\circ$) than that of furan and pyrrole ($\sim 107^\circ$ – 110°).

Five-membered heteroatomic aromatic rings also have unequal contributions to the π system from the C and X atoms. Each of the heteroatoms of the five-membered rings must donate two electrons to the π system to become aromatic. The hybridization of carbon in benzene is sp^2 with an ideal bond angle of 120° . However, in five-membered rings, the bond angle in the parent ring must be reduced to $\sim 108^\circ$ and the hybridization at the site of the eventual hydrogen atom loss deviates from pure sp^2 character. The cleavage of the C–H bond to form the radical always leads to an increase in the bond angle at the radical site. It can be seen in the top trace of Figure 5 that, for five-membered rings, a greater change in radical bond angle is correlated with a lower C–H BDE. Stated another way, the five-membered-ring radical is more stable when the radical bond angle approaches that of pure sp^2 hybridization.

A general statement can also be made that, for both five- and six-membered aromatic molecules, the radical formed from cleavage of a C–H bond becomes more stable as the bond angle at the radical site approaches 120° . For six-membered rings, the angle needs to get smaller in order to approach 120° , whereas a five-membered ring needs the angle at the nascent radical center to become larger to approach 120° .

The geometric changes upon C–H bond cleavage studied are quite regular in the heteroatomic PAHs studied. In each case, there is a widening of the internal bond angle at the radical center following loss of the hydrogen atom. The bottom trace in Figure 5 shows a dependence of the PAH BDE on the change in bond angle that is analogous to the top trace for the monocyclic molecules. In general, the bicyclic molecules that contain a five-membered ring fused to a six-membered ring have C–H BDEs that are lowest when the change in bond angle at the radical site is greatest. Conversely, fused six-membered rings exhibit the same behavior as the monocyclic six-membered rings such that a departure from the ideal sp^2 bond angle gives rise to higher C–H BDEs.

b. General Trends in Bond Dissociation Enthalpies: Spin Densities. A further look at the electron distribution within the parent and radical aromatic rings is required to elucidate the trends in C–H BDEs. Previous descriptions of the electronic structure of the radicals formed from C–H bond cleavage in aromatic molecules were found to be inaccurate due to the large spin contamination of the UHF wave function.^{19,54,55} For example, the computed $\langle S^2 \rangle$ for the phenyl radical at the UHF/

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Table 3. Calculated Electronic and Geometric Properties of Monocyclic Aromatic Radicals

parent	site ^a	$\langle S^2 \rangle^b$	$\alpha - \beta^c$	angle change ^{b,d}	C-H BDE ^{b,e}
benzene	1	0.7575	0.88	5.7	110.8
pyridine	2	0.7551	0.75	2.8	105.6
	3	0.7575	0.86	5.2	111.3
	4	0.7567	0.85	5.3	110.0
pyridazine	3	0.7550	0.74	2.9	107.0
	4	0.7569	0.77	4.2	108.9
pyrimidine	2	0.7551	0.77	3.8	107.2
	4	0.7545	0.73	2.5	104.7
	5	0.7574	0.85	5.0	112.2
pyrazine	1	0.7552	0.72	1.7	105.7
furan	2	0.7601	0.89	3.4	118.4
	3	0.7574	0.91	3.6	118.3
	2	0.7611	0.91	4.0	116.6
thiophene	3	0.7581	0.87	5.1	113.8
	2	0.7585	0.89	3.5	118.1
pyrrole	3	0.7568	0.91	3.5	117.6
	2	0.7580	0.82	3.3	117.8
oxazole	4	0.7599	0.89	2.7	119.9
	5	0.7571	0.86	3.0	117.2
	2	0.7551	0.77	3.8	107.2

^a The radical site (see Figures 1 and 2). ^b B3LYP/6-31G(d) level of theory. ^c Spin density population at radical site determined by Bader's theory of atoms in molecules at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. ^d Bond angle widening upon H atom loss defined as radical - parent, in degrees. ^e BDE at 298 K in kcal·mol⁻¹.

6-31G(d) level is ~ 1.4 . It has been demonstrated, however, that DFT considerably reduces spin contamination in aryl radicals.^{24,25,45} The computed $\langle S^2 \rangle$ values for all of the radicals studied here at the B3LYP/6-31G(d) level are very close to the expected value of 0.75 (Table 3).

The spin densities of the radicals were evaluated via Bader's theory of atoms in molecules (AIM)^{39,41,42} at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. From these calculations, the excess spin density ($\alpha - \beta$) at each radical site was determined. The formation of the phenyl radical from benzene will again be used to gauge the stability of the radical with respect to spin density. The calculated AIM spin density in the phenyl radical predicts that the unpaired electron is almost completely localized ($\alpha - \beta = 0.88$) at the radical site. A lower C-H BDE is expected when the unpaired spin is not localized on one atomic center but instead is delocalized over more atomic centers, which stabilizes the radical. By this argument, the spin density population for the radical centers formed via hydrogen atom loss from a carbon neighboring a nitrogen in the azabenzene should be lower than the spin density population of benzene. The pyridyl radicals provide an example of this prediction. The AIM calculations predict that the spin density at the radical site in 2-pyridyl is 0.75, with an excess spin density of 0.15 on the nitrogen atom, indicating the delocalization of the radical within the aromatic ring. On the other hand, the C-H BDEs of the 3- and 4-pyridyl radicals were calculated to be very similar to the C-H BDE of benzene, and the AIM calculations support this finding with spin densities at the radical site of 0.86 and 0.85, respectively.

In general, there is a correlation between the spin density population and the C-H BDE (Figure 6), and the correlation is independent of the number of atoms in the aromatic ring. The spin density populations can also be used to understand the relative stability of the radicals formed from the same parent molecule as well as between radicals formed from aromatic molecules of different ring size. This analysis suggests that there is less sharing of the excess spin density in the five-membered rings. As a result of the localization of the radical density, five-membered rings form less stable radicals than six-membered

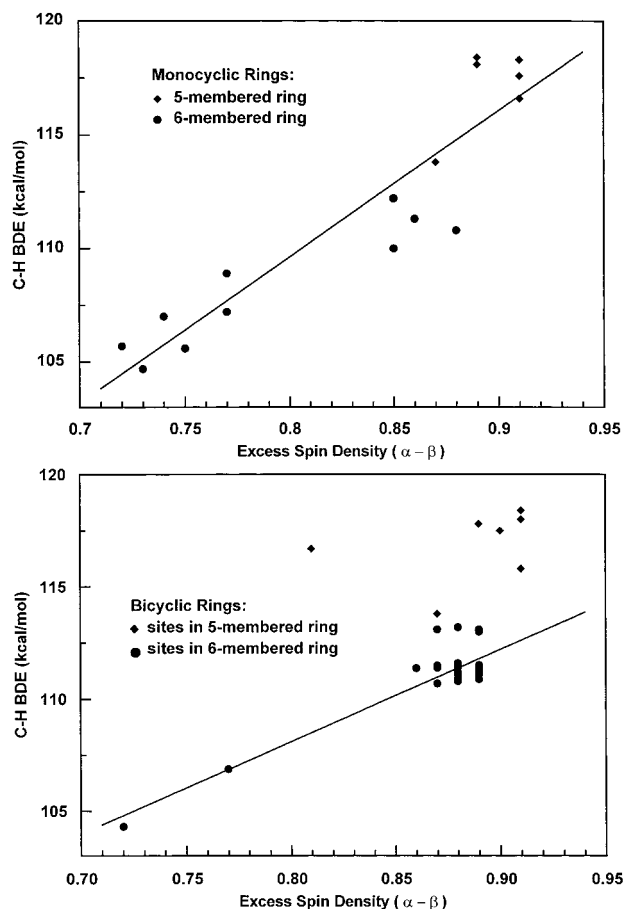


Figure 6. Relationship of the calculated C-H BDE vs the spin density calculated via the AIM procedure for monocyclic and bicyclic aromatic rings. The BDEs were calculated using the B3LYP/6-31G(d) method. The spin densities were calculated using B3LYP/6-311+G(d,p) wave functions evaluated at the B3LYP/6-31G(d)-optimized geometries. The correlation coefficient is 0.85 for monocyclic rings (top trace) and 0.80 for bicyclic rings (bottom trace).

rings, resulting in higher C-H BDEs. This supports the trends observed in the change in geometry. The AIM spin density calculations of the PAHs show that, in general, cleavage of a C-H bond leaves the odd electron localized at the radical center (see Supporting Information, Table S11). Therefore, extension of the π system in the PAHs has little effect on the strength and electronic structure of the σ C-H bonds. The resulting radicals formed at carbon centers that neighbor nitrogen in the bicyclic molecules such as quinoline and isoquinoline also show a sharing of the radical spin with the nitrogen and a lower C-H BDE, similar to the radicals formed in pyridine and the diazines.

2. Temperature Effects on C-H BDEs. The C-H BDEs presented in this study provide an understanding of the preference for H atom abstraction from small aromatic hydrocarbons at 298 K. However, the temperatures in coal combustion processes can fall in a typical range of 500–1500 K. To demonstrate whether 298 K BDE calculations are relevant at temperatures well above 298 K, the energy required to cleave a C-H bond in benzene, furan, and pyridine was calculated in the temperature range from 300 to 2000 K for the formation of the most stable radical for each. As shown in Figure 7, the effect of temperature on the calculated C-H BDEs evaluated at the B3LYP level is small, with a variation of only ~ 2.5 kcal·mol⁻¹ between room temperature and 1200 K. Therefore, accurate conclusions with respect to coal combustion processes can be expected when C-H bond strengths calculated at 298 K are used.

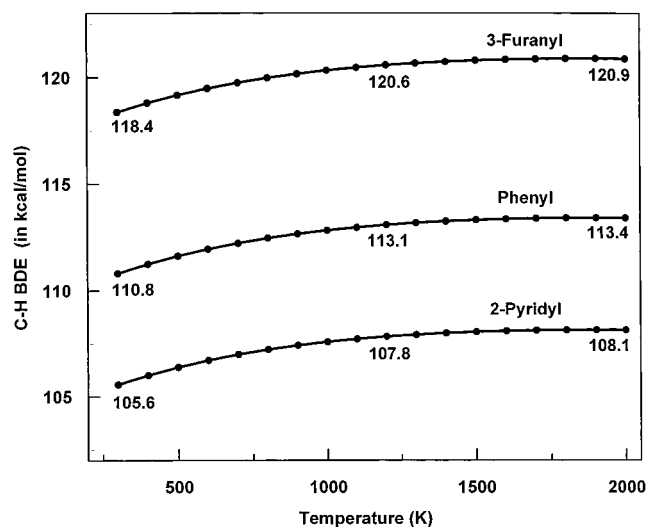


Figure 7. Plot of the B3LYP/6-31G(d) C–H BDEs for the formation of the phenyl, 3-furanyl, and 2-pyridyl radicals from benzene, furan, and pyridine, respectively, as a function of temperature at $P = 1$ atm.

3. PAHs Can Be Approximated by Monocyclic Aromatic Compounds. The C–H bond dissociation enthalpies of the monocyclic aromatic hydrocarbons calculated via B3LYP/6-31G(d) reproduce quite well the available experimental C–H BDEs for these rings. However, to gauge whether the monocyclic aromatic hydrocarbons can adequately describe the initial processes of combustion in coal, calculations were also performed on representative polycyclic rings that can begin to model the extended carbon network. The extent to which the monocyclic aromatic molecules can be used to represent polycyclic molecules can be seen in both Figures 3 and 4. The difference between the C–H BDE of the polycyclic ring and that of the corresponding monocyclic ring is given in brackets. In general, monocyclic BDE calculations can be used to estimate the C–H BDE of the polycyclic molecules within $1 \text{ kcal}\cdot\text{mol}^{-1}$. It is noteworthy that the exception to this trend is in the cleavage of the C–H bond that is adjacent to a ring junction where the ring junction is also adjacent to a heteroatom. At this position, the C–H BDE can vary by as much as $2.4 \text{ kcal}\cdot\text{mol}^{-1}$ as in the case of benzofuran and in all cases is greater than the monocyclic BDE by at least $0.6 \text{ kcal}\cdot\text{mol}^{-1}$. It appears that a more electronegative heteroatom yields a larger difference between the polycyclic and monocyclic ring, as the C–H BDE of benzothiophene at the 7 position has a very similar C–H BDE to that of benzene.

Conclusion

The B3LYP level of theory is a useful method to predict the properties and BDEs for aromatic hydrocarbons. The agreement of C–H BDEs predicted by B3LYP with the available experimental values for the small aromatic molecules provides confidence that the B3LYP method is well-suited to the study

of larger aromatic molecules. In addition, reliable C–H BDEs can be obtained with even a very modest basis set, 6-31G(d), because the C–H bond is nonpolar.

This computational study has endeavored to study specific bonds, C–H and N–H, within a coal matrix to gain an understanding of the chemical reactivity of coal. To that end, the C–H and N–H BDEs of several monocyclic and polycyclic aromatic molecules were studied, including molecules that contain the heteroatoms O, S, and N. The cleavage of a C–H or a N–H bond generates a σ radical that, in general, is localized at the radical site. The C–H bond adjacent to nitrogen in the azabenzene is predicted to be $\sim 7 \text{ kcal}\cdot\text{mol}^{-1}$ weaker than the C–H bond in benzene due to delocalization of the unpaired electron. Both localization of the spin density and geometric factors following cleavage of a C–H bond contribute to the stability of the radicals formed. Therefore, five-membered-ring radicals are $\sim 6 \text{ kcal}\cdot\text{mol}^{-1}$ less stable than those formed from six-membered aromatic molecules. We, therefore, predict that in coal the C–H bonds on any five-membered ring will be significantly less reactive than those on six-membered rings. The location of the heteroatoms in the aromatic ring affects the C–H bond strengths more significantly than the size of the aromatic network. Therefore, the monocyclic aromatic molecules are good models to study the cleavage of aromatic C–H bonds in coal and can predict the C–H BDE of the polycyclic molecules within $1 \text{ kcal}\cdot\text{mol}^{-1}$. However, increasing the size of the aromatic network does reduce the strength of any N–H bonds that are present.

The B3LYP method accurately reproduces the available experimental BDEs. Therefore, the B3LYP method is a promising method to gain further computational insight into the processes of coal combustion.

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Supporting Information Available: Energies for five-membered and six-membered monocyclic aromatic rings at B3LYP, BLYP, BPW91, HF, MP2, CBS-4, CBS-q, CBS-Q, and G2MP2 levels of theory (Tables S1–S6); energies for bicyclic and polycyclic aromatic rings at B3LYP level of theory (Tables S7 and S8); bond angle at the site of hydrogen atom loss for parent and radical rings (Tables S9 and S10); and AIM spin densities for bicyclic rings (Table S11). See any current masthead page for Web access instructions.

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