JOC Article

Homolytic C−H and N−H Bond Dissociation Energies of Strained Organic Compounds

Yong Feng, Lei Liu,*,† Jin-Ti Wang, Su-Wen Zhao, and Qing-Xiang Guo*

Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

leiliu@chem.columbia.edu; qxguo@ustc.edu.cn

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High-level computations at G3, CBS-Q, and G3B3 levels were conducted, and good-quality C−H and N−H bond dissociation energies (BDEs) were obtained for a variety of saturated and unsaturated strained hydrocarbons and amines for the first time. From detailed NBO analyses, we found that the C−H BDEs of hydrocarbons are determined mainly by the hybridization of the parent compound, the hybridization of the radical, and the extent of spin delocalization of the radical. The ring strain has a significant effect on the C−H BDE because it forces the parent compound and radical to adopt certain undesirable hybridization. A structure−activity relationship equation (i.e., BDE (C−H) = $61.1-227.8\,(p_{\text{parent}}\% - 0.75)^2 + 152.9\,(p_{\text{radical}}\% - 1.00)^2 + 40.4\,\textit{spin}$) was established, and it can predict the C−H BDEs of a variety of saturated and unsaturated strained hydrocarbons fairly well. For the C−H BDEs associated with the bridgehead carbons of the highly rigid strained compounds, we found that the strength of the C−H bond can also be predicted from the H−C−C bond angles of the bridgehead carbon. Finally, we found that N−H BDEs show less dependence on the ring strain than C−H BDEs.

1. Introduction

The chemistry of strained organic molecules has always aroused specific interest in theoretically, mechanistically, and synthetically oriented chemists because the strained structures can lead to unusual and even unprecedented chemical behaviors.[1] Questions concerning bonding, property, reactivity, and synthetic accessibility have been the constant subject of research activities in this area for several decades and, presumably, will remain so for many years to come.

Thanks to the efforts of many brilliant chemists, up to now many fascinating strained molecules such as propellane, cubane, prismane, and tetrahedrane have been successfully synthesized.[2] In parallel with these experimental studies, considerable efforts have also been devoted to the theories for the distinctive chemistry of these extraordinary molecules. At present, the most popular theory for the strained organic compounds is the “bent bond” model introduced by Coulson.[3] According to this model, the electron distribution in the C−C internuclear region in a strained molecule is not concentrated along the line between the nuclei, as is typical of covalent bond, but rather slightly outside this line.

A quantitative description of the above “bent bond” model can be achieved using the “bond path” theory developed by Bader and co-workers.[4] According to this theory, the bond between two atoms in a molecule can be characterized by means of a “bond path”, which consists of the two density gradient paths that originate at the electron density saddle point that is located in the internuclear region, and terminate at the two nuclei. For ordinary C−C bonds, the bond path is simply the straight line connecting the two nuclei. The bond paths in strained molecules, however, are shifted away from this line and form rings.

On the basis of the bond path theory, Wiberg et al. proposed that the bond path angle, the angle subtended at a nucleus by two bond paths, when compared to the corresponding geometrical or bond angle, is important in quantifying the concept of bond strain in molecules.[5] These authors also found that the electronegativity of a carbon atom increases with an increase in geometrical strain as measured by the decrease in its bond path

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* To whom correpondence should be addressed.

† Present address: Department of Chemistry, Columbia University, New York, NY.

[1] Important reviews: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379. (c) Ingold, K. U. Walton, J. C. *Acc. Chem. Res.* **1986**, *19*, 72. (d) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067. (e) Hassenrueck, K.; Martin, H. D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125. (f) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111. (g) Bickelhaupt, F.; de Wolf, W. H. *Adv. Strain Org. Chem.* **1993**, *3*, 185. (h) de Meijere, A.; Kozhushkov, S. I. *Chem. Rev.* **2000**, *100*, 93. (i) Komarov, I. V. *Russ. Chem. Rev.* **2001**, *70*, 991. (j) Tsuji, T.; Ohkita, M.; Kawai, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 415. (k) Kock, R.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1861. (l) Wang, L.; Xu, J.-H. *Chin. J. Org. Chem.* **2003**, *23*, 750. (m) Gansauer, A.; Lauterbach, T.; Narayan, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 5556.

[2] (a) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239. (b) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157. (c) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738. (d) Masamune, S.; Kato, M. *J. Am. Chem. Soc.* **1965**, *87*, 4192.

[3] (a) Coulson, C. A.; Moffitt, W. E. *Philos. Mag.* **1949**, *40*, 1. (b) Coulson, C. A.; Googwin, T. H. *J. Chem. Soc.* **1963**, 2851. (c) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

[4] (a) Bader, R. W. F.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63. (b) Politzer, P. *Chem. Phys. Lett.* **1983**, *102*, 74.

[5] (a) Wiberg, K. B.; Bader, R. W. F.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985. (b) Wiberg, K. B.; Bader, R. W. F.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

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angles from the normal value. The increase of electronegativity triggers a charge transfer from the neighboring groups of the carbon subjected to geometric strain. This charge transfer leads to a decrease in the energy of the carbon but to an even greater increase in the energy of the neighboring groups. The net result is a strain energy.

It is worthy to note that all of the above theories focus on the energetics of the strain. On the other hand, You et al. recently have proposed an interesting theoretical approach in terms of the force concept to evaluate the bent bonds and bonding behaviors of strained organic molecules.[6] This remarkable theory is derived from the electrostatic theorem of Hellmann−Feynman. Using this approach, one can estimate the strain of a particular bent bond instead of the strain of the molecule as a whole.

In the present study, we focused on the homolytic C−H and N−H bond dissociation energies (BDEs) of the strained organic molecules. A number of high-level theoretical methods were used in the study, and detailed, careful analyses were performed. The main purposes of the study included the following: (1) to compile reliable, accurate C−H and N−H BDEs for a variety of important strained molecules; (2) To learn how the ring strain affects the C−H and N−H BDEs; and (3) to understand the physical origin of the effects of ring strain on C−H and N−H BDEs. It is worthy to note that some other properties of the strained organic molecules, such as carbon acidities,[7] have been studied before. However, before the present study there has not been any systematic study concerning the homolytic bond dissociation energies of the strained compounds.

2. Methods

All the calculations were performed using Gaussian 98 programs.[8] Geometry optimization was conducted without any constraint. Each optimized structure was confirmed by frequency calculation to be the real minimum. For molecules or radicals that have more than one conformation, a search of all the possible conformations was performed using the UB3LYP/6-31G(d) method. The conformation with the lowest energy was used for the enthalpy calculations.

C−H or N−H BDEs were calculated using the density function theory UB3LYP/6-311++G(2df,p)//UB3LYP/6-31G(d) and composite ab initio G3, G3B3, and CBS-Q methods[9] as the enthalpy change of the following reaction at 298 K.[10]

$$\mathrm{A{-}H\ (g)} \rightarrow \mathrm{A^{\bullet}\ (g)} + \mathrm{H^{\bullet}\ (g)} \qquad (1)$$

The enthalpy of each species was calculated using the following equation:

$$H_{298} = E + \mathrm{ZPE} + H_{\mathrm{trans}} + H_{\mathrm{rot}} + H_{\mathrm{vib}} \qquad (2)$$

ZPE is the zero-point energy. H_{trans}, H_{rot}, and H_{vib} are the standard temperature correction terms calculated using the equilibrium statistical mechanics with harmonic oscillator and rigid rotor approximations.

3. Results and discussion

3.1. C−H Bond Dissociation Energies. 3.1.1. Performances of the Different Methods in BDE Calculations. Four different methods, i.e., UB3LYP/6-311++G(2df,p)//UB3LYP/6-31G(d), G3, G3B3, and CBS-Q, are used to calculate BDEs. Among them, the B3LYP method is the most efficient, and it can deal with species possessing over 10 non-hydrogen atoms. In comparison, the three composite ab inito methods are extremely CPU demanding. Usually, they can only deal with species possessing less than seven non-hydrogen atoms.

Comparing the theoretical results (see Table 1) with the available experimental data, we can draw the following conclusions (see Table 2). (a) The B3LYP method underestimates the BDEs by 2.3 kcal/mol. However, the underestimation is highly systematic as the correlation coefficient between the B3LYP and experimental BDEs is very high (0.994). (b) All the composite ab initio methods can predict BDEs with an error of about 1.3 kcal/mol. Since the experimental error in BDE measurements is about 1 kcal/mol,[9] the BDEs calculated by the composite ab initio methods are fairly reliable compared to the BDEs obtained through the experimental methods.

For 48 C−H BDEs we have obtained all of the B3LYP, G3, CBS-Q, and G3B3 results (see Table 1). Comparing the BDEs calculated from different methods, we can draw the following conclusions (see Table 3). (a) BDEs calculated from G3, CBS-Q, and G3B3 methods are very close to each other. The correlation coefficient between the BDEs calculated using any two of these three methods is 0.998. The standard deviation between them is about 0.4−0.5 kcal/mol, and the mean error is about 0.2−0.4 kcal/mol. (b) The B3LYP BDEs are about 3.5−4.0 kcal/mol smaller than the BDEs calculated using the composite ab initio methods. However, the correlation coefficient between the B3LYP BDEs and the BDEs calculated using the composite ab initio methods is about 0.993−0.995. Therefore, the underestimation by the B3LYP method is highly systematic.

3.1.2. Practical Theoretical Methods for Accurate BDE Calculations. From the above results, it is clear that we can use the composite ab initio methods to get very accurate BDEs. However, using the composite ab

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[6] (a) Zhao, C.-Y.; Zhang, Y.; You, X.-Z. *J. Phys. Chem. A* **1997**, *101*, 5174. (b) Zhao, C.-Y.; Xiao, T.; Xu, X.-F.; You, X.-Z. *Chem. J. Chin. Univ.* **1996**, *17*, 769. (c) Zhao, C.-Y.; Qiu, W.-Y.; Xu, X.-F.; Zhang, C.-Y.; Fang, W.-H. You, X.-Z. *Chem. J. Chin. Univ.* **1995**, *16*, 1587. (d) Zhao, C. Y.; Wang, Y. C.; Qiu, W. Y.; Wei, T. S. *Chin. Sci. Bull.* **1992**, *37*, 1529.

[7] Alkorta, I.; Elguero, J. *Tetrahedron* **1997**, *53*, 9741.

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

[9] (a) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764. (b) Curtiss, L. A.; Redfern, K. P. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374. (c) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299. (d) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

[10] The bond dissociation energy should be called a bond dissociation enthalpy, but the tradition for energy is strong. For reviews: (a) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Benson, S. W. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 791. (d) Ingold, K. U.; Wright, J. S. *J. Chem. Educ.* **2000**, *77*, 1062. (e) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

TABLE 1. Experimental and Theoretical C−H Bond Dissociation Energies of Various Cyclo-, Bicyclo-, and Tricycloalkanes (kcal/mol)

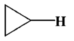
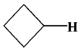
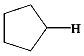
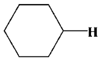
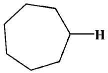
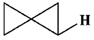
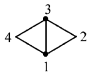
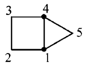
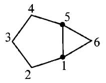
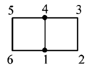
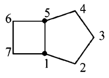
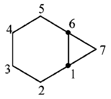
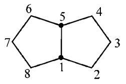
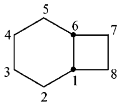
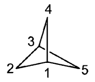
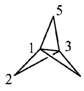
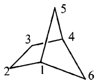
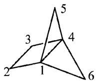
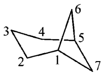
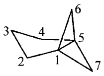
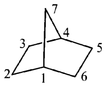
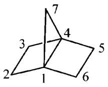
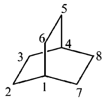
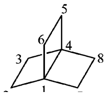
Name	Structure	Bond	BDE						%p	spin	%p
			Exp.[a]	**Theor.**[b]	B3LYP	CBS-Q	G3	G3B3	(parent)	(radical)	(radical)
Methane	CH_3-**H**	C-H	104.9	**104.3**	102.9	105.1	104.2	104.3	0.75	1.114	1.00
Ethane	C_2H_5-**H**	C-H	101.1	**101.0**	98.3	101.7	101.2	101.0	0.76	1.043	0.99
i-Propane	$(CH_3)_2CH$-**H**	C-H	97.8	**98.6**	94.7	99.2	98.9	98.6	0.78	0.948	0.98
t-Butane	$(CH_3)_3C$-**H**	C-H	96.6	**97.2**	90.6	97.8	97.4	97.2	0.80	0.837	0.97
Ethylene	CH_2=CH-**H**	C-H	111.2	**110.1**	108.2	110.4	110.3	110.1	0.70	0.980	0.76
Acetylene	$CH\equiv C$-**H**	C-H	132.9	**133.1**	134.1	133.3	133.6	133.1	0.53	1.051	0.51
Cyclopropane		C-H	106.3	**108.9**	105.5	107.6	107.4	108.9	0.73	0.915	0.80
Cyclobutane		C-H	96.5	**100.1**	95.9	100.9	100.6	100.1	0.76	0.950	1.00
Cyclopentane		C-H	96.4	**96.2**	92.4	96.6	96.3	96.2	0.77	0.962	1.00
Cyclohexane		C-H	95.5	**99.2**	95.2	99.9	99.5	99.2	0.78	0.970	0.98
Cycloheptane		C-H	92.5	**96.0**	91.7	-	-	-	0.78	0.987	1.00
Spiro[2.2]pentane		C-H	-	**107.3**	103.7	107.8	107.7	107.3	0.73	0.897	0.82
Bicyclo[1.1.0]butane		C1-H	-	**113.8**	110.6	114.0	114.0	113.8	0.67	0.767	0.61
		C2-H	-	**101.1**	98.0	101.0	101.3	101.1	0.73	0.914	0.86
Bicyclo[2.1.0]pentane		C1-H	-	**110.2**	106.7	110.7	110.4	110.2	0.70	0.846	0.69
		C2-H	-	**99.7**	96.2	100.1	100.1	99.7	0.76	0.926	0.96
		C5-H	-	**105.9**	102.3	106.1	106.1	105.9	0.73	0.911	0.77
Bicyclo[3.1.0]hexane		C1-H	-	**108.6**	104.6	109.3	108.9	108.6	0.72	0.840	0.76
		C2-H	-	**93.6**	90.0	94.0	93.8	93.6	0.77	0.935	0.99
		C3-H	-	**94.1**	90.6	95.2	94.4	94.1	0.78	0.941	0.99
		C6-H	-	**108.3**	104.9	108.7	108.7	108.3	0.74	0.923	0.82
Bicyclo[2.2.0]hexane		C1-H	-	**104.0**	100.3	104.8	105.6	104.0	0.74	0.912	0.80
		C2-H	-	**98.6**	95.2	99.2	100.1	98.6	0.76	0.960	0.99
Biocyclo[3.2.0]heptane		C1-H	-	**102.6**	98.2	102.6	102.8	102.6	0.76	0.874	0.87
		C2-H	-	**97.9**	93.8	98.5	98.1	97.9	0.77	0.958	0.99
		C3-H	-	**99.5**	94.8	100.4	99.6	99.5	0.77	0.963	0.98
		C6-H	-	**99.0**	95.4	99.5	99.2	99.0	0.76	0.983	1.00
Biocyclo[4.1.0]heptane		C1-H	-	**105.4**	101.2	105.9	105.7	105.4	0.74	0.854	0.82
		C2-H	-	**94.7**	90.4	94.7	94.8	94.7	0.78	0.915	0.99
		C3-H	-	**97.6**	93.4	98.4	97.8	97.6	0.78	0.969	1.00
		C7-H	-	**108.1**	104.5	108.5	108.4	108.1	0.73	0.928	0.83
Octahydro-pentalene		C1-H	-	**95.7**	91.4	-	-	-	0.78	0.831	0.96
		C2-H	-	**97.8**	93.7	-	-	-	0.77	0.982	0.99
		C3-H	-	**98.1**	94.0	-	-	-	0.77	0.955	0.98
Bicyclo[4.2.0]octane		C1-H	-	**97.0**	92.8	-	-	-	0.77	0.846	0.97
		C2-H	-	**96.7**	92.5	-	-	-	0.78	0.957	0.99
		C3-H	-	**99.0**	95.0	-	-	-	0.78	0.990	0.98
		C7-H	-	**100.7**	96.9	-	-	-	0.75	0.996	0.97
Bicyclo[1.1.1]pentane		C1-H	-	**106.2**	103.0	106.3	106.5	106.2	0.71	0.785	0.66
		C2-H	-	**106.5**	103.5	106.8	106.8	106.5	0.74	0.960	0.81
Tricyclo[1.1.1.01,3]pentane		C2-H	-	**111.5**	108.7	113.3	111.8	111.5	0.73	0.968	0.79

Table 1 (Continued)

Name	Structure	Bond	BDE Exp.[a]	BDE Theor.[b]	BDE B3LYP	BDE CBS-Q	BDE G3	BDE G3B3	%p (parent)	spin (radical)	%p (radical)
Bicyclo[2.1.1]hexane		C1-H	-	**108.9**	105.6	109.4	109.1	108.9	0.73	0.907	0.76
		C2-H	-	**100.8**	97.2	101.3	101.2	100.8	0.76	0.995	0.97
		C5-H	-	**105.4**	102.1	105.4	105.6	105.4	0.75	0.973	0.84
Tricyclo[2.1.1.01,4]hexane		C2-H	-	**100.1**	97.3	-	-	100.1	0.76	0.983	0.98
		C5-H	-	**103.4**	99.9	103.5	-	-	0.74	0.780	0.79
Bicyclo[3.1.1]heptane		C1-H	-	**103.6**	100.0	103.5	103.8	103.6	0.75	0.903	0.82
		C2-H	-	**97.6**	93.5	98.1	97.9	97.6	0.78	0.986	1.00
		C3-H	-	**97.3**	93.0	98.1	97.6	97.3	0.78	0.973	1.00
		C6-H	-	**103.0**	99.4	103.3	103.2	103.0	0.75	0.974	0.93
Tricyclo[3.1.1.01,5]heptane		C2-H	-	**98.5**	94.3	98.9	98.7	98.5	0.77	0.967	1.00
		C3-H	-	**97.7**	93.2	98.4	97.9	97.7	0.77	0.983	1.00
		C6-H	-	**100.0**	96.6	99.3	100.0	100.0	0.73	0.781	0.77
Biocyclo[2.2.1]hetane		C1-H	-	**107.6**	104.3	108.4	107.9	107.6	0.75	0.921	0.83
		C2-H	-	**98.7**	95.1	99.1	99.0	98.7	0.77	1.003	0.98
		C7-H	-	**105.1**	101.4	105.3	105.4	105.1	0.76	0.990	0.91
Tricyclo[2.2.1.01,4]heptane		C2-H	-	**96.8**	93.6	-	97.2	96.8	0.76	0.887	0.92
		C7-H	-	**106.7**	103.2	106.3	106.7	106.7	0.74	0.985	0.79
Bicyclo[2.2.2]octane		C1-H	-	**101.9**	98.3	-	-	-	0.78	0.894	0.88
		C2-H	-	**97.8**	93.7	-	-	-	0.78	1.001	1.00
Tricyclo[2.2.2.01,4]octane		C2-H	-	**99.3**	95.4	-	-	-	0.76	0.976	1.00

[a] Experimental BDEs are taken from ref 11. [b] The theoretical BDEs listed in this column are the recommended BDEs. These values are either G3B3 results or from B3LYP extrapolations using eq 3 when the G3B3 calculation is not feasible.

TABLE 2. Correlation Coefficients, Standard Deviations, and Mean Errors between the Experimental and Theoretical BDEs[a]

	B3LYP	G3	CBS-Q	G3B3
correlation coefficient	0.994	0.994	0.994	0.993
standard deviation (kcal/mol)	+1.9	+1.3	+1.3	+1.3
mean error (kcal/mol)	−2.3	+1.1	+0.8	+0.7

[a] There are 11 available experimental BDEs, which are all shown in Table 1.

initio methods, we can only get the BDEs for compounds possessing less than seven non-hydrogen atoms. On the other hand, we can use the B3LYP method to deal with larger compounds, but we need to recognize that the B3LYP method significantly underestimates the BDEs. Nonetheless, the underestimation of the B3LYP method is highly systematic. Therefore, we can use an empirical correlation equation, such as eq 3, to get reasonably accurate BDEs using the B3LYP method for relatively large compounds.

$$\text{BDE (G3B3)} = -13.7 + 1.1\ \text{BDE (B3LYP)} \quad (3)$$

Using the G3B3 and B3LYP methods and eq 3, we have obtained the theoretical C−H BDEs for a large number of monocyclo-, bicyclo-, and tricycloalkanes (see Table 1). We have also obtained the theoretical C−H BDEs for various strained polyhedron and unsaturated hydrocarbons (See Tables 4 and 5). Most of the BDEs listed in Table 1, 4, and 5 have never been measured and are expected to be difficult to measure experimentally in the near future. Nonetheless, on the basis of the above analyses, we know that the error of the theoretical C−H BDEs listed in Tables 1, 4, and 5 is smaller than 1.5 kcal/mol. Therefore, we believe that the theoretical C−H BDEs carefully compiled in the present study are good enough for many applications.

Herein we need to mention the C−H BDE of cubane, which is a good case showing the reliability of our theoretical BDE values. This particular C−H BDE has been measured only recently with considerable difficulty, and the experimental value (102 ± 4 kcal/mol) still has a relatively large error bar (i.e., 4 kcal/mol).[12] In com-

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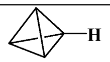
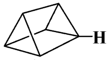
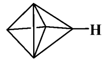
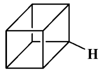
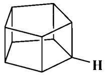
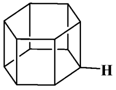
(11) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press LLC: Boca Raton, 2002.

TABLE 3. Correlation Coefficients (r), Standard Deviations (sd), and Mean Errors (me) between the BDEs Calculated Using Different Methods

	B3LYP	G3	CBS-Q	G3B3
B3LYP		$r = 0.993$ sd = 0.9 kcal/mol me = −4.0 kcal/mol	$r = 0.994$ sd = 0.8 kcal/mol me = −3.8 kcal/mol	$r = 0.995$ sd = 0.7 kcal/mol me = −3.5 kcal/mol
G3			$r = 0.998$ sd = 0.4 kcal/mol me = 0.2 kcal/mol	$r = 0.998$ sd = 0.5 kcal/mol me = 0.4 kcal/mol
CBS-Q				$r = 0.998$ sd = 0.4 kcal/mol me = 0.2 kcal/mol

TABLE 4. C−H Bond Dissociation Energies of Various Polyhedron Compounds (kcal/mol)

Name	Structure	**Theor.**[a]	B3LYP	G3B3	%p (parent)	spin (radical)	%p (radical)
Tricyclo[1.1.0.0^{2,4}]butane		-	-[b]	-	0.60	-	-
Tetrahedrane		**116.5**	113.7	116.5	0.65	0.754	0.58
Prismane		**107.7**	104.5	107.7	0.67	0.720	0.63
Pentacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}] pentane		**122.4**	120.1	122.4	0.69	0.784	0.52
Cubane		**105.1**	101.8	-	0.71	0.892	0.72
-		**104.9**	101.6	-	0.72	0.877	0.77
-		**101.8**	98.2	-	0.74	0.843	0.81

[a] The theoretical BDEs listed in this column are the recommended BDEs. [b] The radical of tricyclo[1.1.0.0^{2,4}]butane is not a stable species.

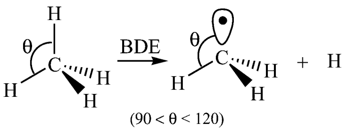
parison, our theoretical C−H BDE for cubane is 105.1 ± 1.5 kcal/mol, which is in reasonable agreement with the experimental value.

3.2. Structure−Activity Relationship. From Tables 1, 4, and 5, we can see that the C−H BDEs of the strained hydrocarbons span a fairly large range. The lowest C−H BDE is found for the C_5−H bond of cyclopentadiene (82.6 kcal/mol). The highest C−H BDE is found for the C−H bond of pentacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}]pentane (122.4 kcal/mol).

One reason for the change of C−H BDEs is the ring strain. For instance, from cyclopropane to cycloheptane the C−H BDEs change dramatically from 106.3 to 94.0 kcal/mol. Another reason for the change of C−H BDEs is the extent of unsaturation. For example, the C−H BDE of cyclopropane is 106.3 kcal/mol whereas the C_3−H BDE of cyclopropene is 100.5 kcal/mol. The present question is how we can quantitatively measure the ring strain and extent of unsaturation.

3.2.1. Hybridization Is a Good Measure of the Effects of Ring Strain on BDEs. The ring strain affects the hybridization of hydrocarbons because the hybridization is partly determined by the geometry of the bonds. The hybridization affects the energy of the whole molecule because the energy of carbon's 2s orbital is different from that of carbon's 2p orbital.

SCHEME 1



To get a clear understanding about the effects of geometry constraints on C−H BDEs, we have studied the C−H BDEs of CH_4 molecules in which the H−C−H angle (θ) is fixed at various angles from 90° to 120° (see Scheme 1). The p% character associated with the C−H bond of the parent molecule (CH_4) and associated with the odd electron of the radical ($CH_3^\bullet$) at different θ angles was calculated using NBO analysis.[13] The energies of CH_4 and $CH_3^\bullet$ and the BDEs at different θ angles were calculated using the UB3LYP/6-31+G(d) method. The detailed results can be found in the Supporting Information.

Figure 1 shows the correlation between the energy of CH_4 and the p_{parent}% value and the correlation between the energy of $CH_3^\bullet$ and the p_{radical}% value. From Figure 1 it is clear that CH_4 is the most stable when $p\% = 0.75$ (i.e., C is sp^3 hybridized) whereas $CH_3^\bullet$ is the most stable when $p\% = 1.00$ (i.e., the odd electron is completely in the p orbital). From the shapes of the correlation

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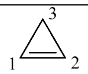
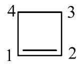
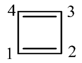
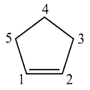
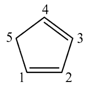
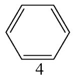
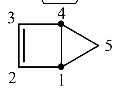
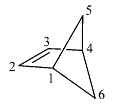
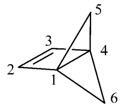
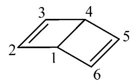
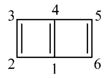
(12) Hare, M.; Emrick, T.; Eaton, P. E.; Kass, S. R. *J. Am. Chem. Soc.* **1997**, *119*, 237.

(13) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.1*; Theoretical Chemistry Institute, University of Wisconsin, Madison.

TABLE 5. C−H Bond Dissociation Energies of Various Strained Alkenes (kcal/mol)

Name	Structure	Bond	**Theor.**[a]	B3LYP	G3B3	%p (parent)	spin (radical)	%p (radical)
Cyclopropene		C1-H	**108.8**	107.5	108.8	0.60	0.604	0.54
		C3-H	**100.5**	97.1	100.5	0.71	0.759	0.74
Cyclobutene		C1-H	**111.3**	109.6	111.3	0.67	0.858	0.64
		C3-H	**90.9**	87.4	90.9	0.75	0.677	1.00
Cyclobutadiene		C1-H	**104.6**	98.7	104.6	0.65	-	0.51
Cyclopentene		C1-H	**113.7**	111.7	113.7	0.70	0.925	0.72
		C3-H	**84.4**	79.9	84.4	0.77	0.584	1.00
		C4-H	**96.7**	92.9	96.7	0.77	0.959	1.00
Cyclopentadiene		C1-H	**116.9**	114.6	116.9	0.68	0.997	0.70
		C2-H	**116.2**	113.6	116.2	0.69	0.973	0.72
		C5-H	**82.6**	79.5	82.6	0.78	0.582	1.00
Benzene		-	**114.3**[b]	110.4	114.3	0.72	1.014	0.76
Bicyclo[2.1.0]pent-2-ene		C1-H	**112.1**	109.1	112.1	0.70	0.873	0.70
		C2-H	**109.8**	107.3	109.8	0.66	0.742	0.63
		C5-H	**106.9**	103.2	106.9	0.73	0.936	0.75
Bicyclo[2.1.1]hex-2-ene		C1-H	**110.1**	106.4	110.1	0.73	0.939	0.75
		C2-H	**115.9**	113.7	115.9	0.67	1.001	0.67
		C5-H	**104.8**	101.3	104.8	0.75	0.931	0.85
Tricyclo[2.1.1.01,4]hex-2-ene		C2-H	**108.6**	106.1	108.6	0.66	0.781	0.62
		C5-H	**105.2**	101.6	105.2	0.73	0.832	0.78
Bicyclo[2.2.0]hexa-2,5-diene		C1-H	**102.8**	99.3	102.8	0.73	0.752	0.79
		C2-H	**111.6**	109.2	111.6	0.66	0.848	0.63
Bicyclo[2.2.0]hexa-1(4),2,5-triene		C2-H	**102.9**	99.6	102.9	0.67	0.617	0.63

[a] The theoretical BDEs listed in this column are the recommended BDEs. [b] The experimental C−H BDE of benzene is 113.1 kcal/mol (see ref 11).

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curves it is also clear that the energies of both CH_4 and $CH_3^{\bullet}$ can be fitted to second-order polynomial equations, i.e.

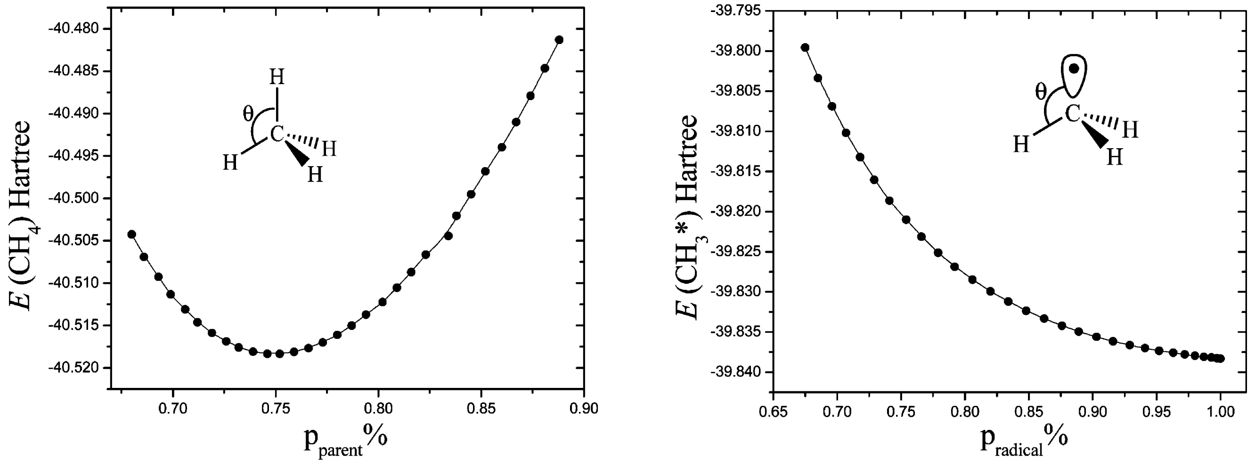
$$E(CH_4) = -40.5 + 1.95(p_{\text{parent}}\% - 0.75)^2 \quad (N = 31,\ r = 0.995) \quad (4)$$

$$E(CH_3^{\bullet}) = -39.8 + 0.33(p_{\text{radical}}\% - 1.00)^2 \quad (N = 31,\ r = 0.991) \quad (5)$$

Since BDE = E ($CH_3^{\bullet}$) + E ($H^{\bullet}$) − E (CH_4), it is clear that the C−H BDEs of CH_4 at different θ angles should be dependent on both $(p_{\text{parent}}\% - 0.75)^2$ and $(p_{\text{radical}}\% - 1.00)^2$. Thus, we obtain a two-parameter correlation equation

$$\text{BDE (C−H)} = 111.7 - 1143.0\,(p_{\text{parent}}\% - 0.75)^2 + 203.8\,(p_{\text{radical}}\% - 1.00)^2 \quad (6)$$

In total, there are 31 C−H BDEs at various fixed θ angles in the above correlation. The correlation coefficient (r = 1.000) is very high, indicating that the above hybridization model is very successful for the C−H BDEs of the hydrocarbon molecules under different geometric constraints. Nevertheless, it is worthy to note that we



(a)

(b)

FIGURE 1. Correlation between the energy of CH_4 or $CH_3^•$ and the *p*% values (*E* values in Figure 1 were not supplemented with ZPE and thermal corrections).

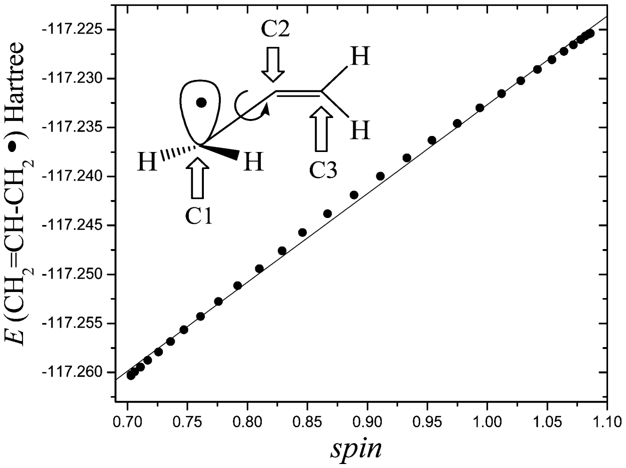


FIGURE 2. Correlation between the energy of $CH_2{=}CH{-}CH_2^•$ and the spin carried by the radical center.

have not considered the effect of unsaturation on BDEs when establishing the above hybridization model.

3.2.2. Spin Delocalization Effect in the Unsaturated Compounds. Many studies have demonstrated that a carbon radical can be stabilized by an adjacent substituent. The basic mechanisms for the stabilization are as follows. (1) π-Acceptors stabilize carbon radicals as they delocalize the odd electron into their π-systems. (2) Lone-pair donors stabilize carbon radicals through a three-electron interaction between a lone pair on the substituent and the odd electron on the radical. (3) Alkyl groups stabilize carbon radicals via hyperconjugation.[14] One key feature that is shared by the three mechanisms is that the spin of the carbon radical is delocalized into the substituent. Thus, the stabilization of a carbon radial by the substituents is often named as the spin delocalization effect.[15] Usually the spin delocalization effect is the most significant when the substituent is an unsaturated group or a heteroatom group.

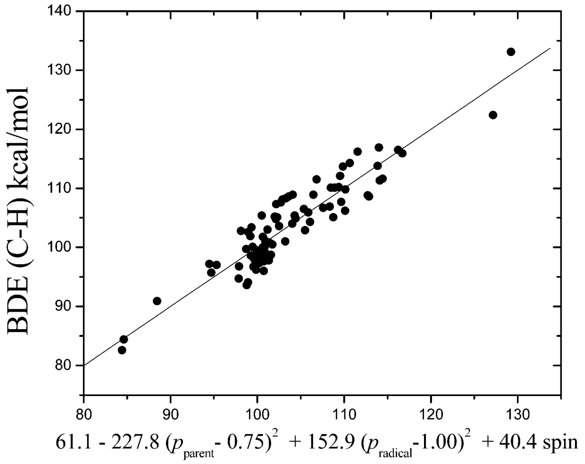


FIGURE 3. Performance of the structure–activity model in predicting C–H BDEs of various strained saturated and unsaturated hydrocarbons.

To find out the relationship between the spin and BDE, we have studied the energy of the $CH_2{=}CH{-}CH_2^•$ radical (see Figure 2). This radical is optimized with the UB3LYP/6-31G(d) method. Then all the geometry parameters of the radical are fixed except that the C1–C2 bond is allowed to rotate. Using the above method, we obtain a series of $CH_2{=}CH{-}CH_2^•$ radicals which differ only in the H–C1–C2–C3 dihedral angle. The electronic energy of each radical is calculated using the UB3LYP/6-31G(d) method. The spin carried by C1 is also obtained using the same method.

Plotting the energy against the spin, we obtain an approximately straight line (see Figure 2). The positive slope of the correlation is in agreement with the spin-delocalization effect. The correlation coefficient is 0.999 for 31 radicals, indicating that the correlation is fairly good. Therefore, we can assume that the C–H BDE should have a linear dependence on the spin carried by the radical center.

3.3.3. Quantitative Structure–Activity Relationship Model. On the basis of the above discussion, we find that we need three parameters to explain the C–H

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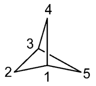
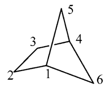
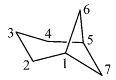
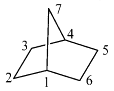
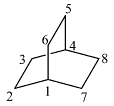
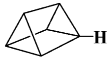
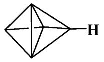
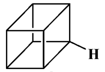
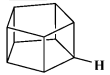
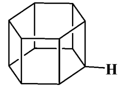
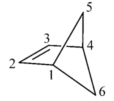
[14] Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750.

[15] (a) Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283. (b) Liu, L.; Cheng, Y.-H.; Fu, Y.; Chen, R.; Guo, Q.-X. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1164.

TABLE 6. C−H BDEs Associated with the Bridgehead Carbons of Rigid Hydrocarbon Compounds

Compound	Structure	Bond	BDE (kcal/mol)	Sum of three H-C-C bond angles (degree)
Bicyclo[1.1.1]pentane		C1-H	106.2	381.5
Bicyclo[2.1.1]hexane		C1-H	108.9	361.0
Bicyclo[3.1.1]heptane		C1-H	103.6	347.5
Biocyclo[2.2.1]hetane		C1-H	107.6	344.0
Bicyclo[2.2.2]octane		C1-H	101.9	329.2
Tetrahedrane		-	116.5	389.3
Prismane		-	107.7	391.7
Pentacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}]pentane		-	122.4	404.1
Cubane		-	105.1	375.8
-		-	104.9	362.2
-		-	101.8	352.0
Bicyclo[2.1.1]hex-2-ene		C1-H	110.1	363.8

BDEs of various strained hydrocarbon molecules. They are the p% value associated with the C−H bond of the parent molecule, p% value associated with the odd electron of the radical, and the spin carried by the carbon atom. The first two parameters depict the effects of ring strain on the C−H BDEs, while the last parameter can describe the effects of unsaturation on the C−H BDEs.

Using the three parameters, we are able to build a quantitative structure−activity relationship model for 89 C−H BDEs of various strained saturated and unsaturated hydrocarbons that are listed in Tables 1, 4, and 5 (see eq 7 and Figure 3).

$$\mathrm{BDE\ (C{-}H)} = 61.1 - 227.8\,(p_{\mathrm{parent}}\% - 0.75)^2 + 152.9\,(p_{\mathrm{radical}}\% - 1.00)^2 + 40.4\,spin \quad (7)$$

The correlation coefficient is 0.927 and the standard deviation is 2.9 kcal/mol. Given the fact that the strained hydrocarbons considered in the present study are extremely diverse, we think that eq 7 is a very successful structure−activity relationship model.

In eq 7, the coefficient before $(p_{\mathrm{parent}}\% - 0.75)^2$ is negative, indicating that any deviation from sp^3 hybridization in the C−H bond leads to a lower C−H BDE because the parent molecule is destabilized. On the other hand, the positive coefficient before $(p_{\mathrm{radical}}\% - 1.00)^2$ is in agreement with the fact that the radical is less stable if the odd electron does not completely stay in a p orbital. Finally, the positive coefficient before spin is in agreement with the spin delocalization effect.

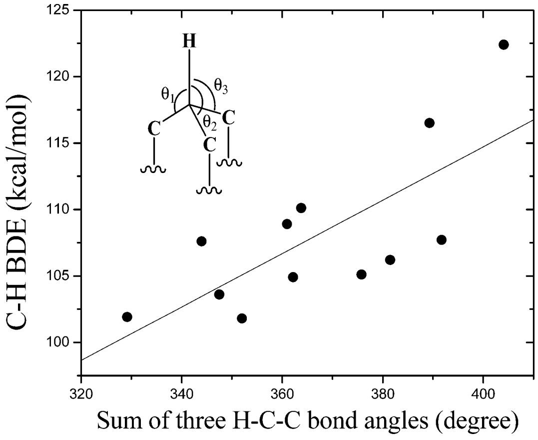
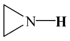
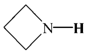
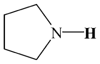
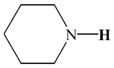
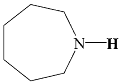
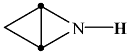
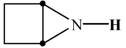
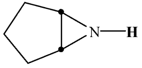
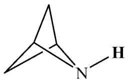
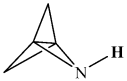
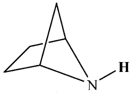
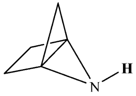


FIGURE 4. Correlation between the C−H BDEs of the bridgehead carbons of rigid hydrocarbon compounds and the sum of three H−C−C angles.

3.3.4. C−H BDEs of the Bridgehead Carbons. The C−H BDEs associated with the bridgehead carbons of the relatively rigid compounds are of special interest

TABLE 7. N−H Bond Dissociation Energies of Various Strained Amines (kcal/mol)

Name	Structure	Theor. (G3B3)	p% (parent)	spin (radical)	p% (radical)
Ammonia	NH_2-**H**	**106.7**	0.748	1.054	1.00
Methylamine	CH_3NH-**H**	**99.4**	0.766	0.963	1.00
Dimethylamine	$(CH_3)_2N$-**H**	**94.0**	0.788	0.883	1.00
Methyleneamine	CH_2=N-**H**	**87.6**	0.798	0.943	1.00
Aziridine		**93.7**	0.780	0.930	1.00
Azetidine		**94.1**	0.767	0.894	0.99
Pyrrolidine		**91.5**	0.780	0.876	1.00
Piperidine		**95.3**	0.785	0.873	0.99
Azepane		**93.4**	0.776	0.872	0.99
2-Aza-bicyclo[1.1.0]butane		**83.6**	0.784	0.733	0.96
5-Aza-bicyclo[2.1.0]pentane		**93.0**	0.773	0.847	0.96
6-Aza-bicyclo[3.1.0]hexane		**94.4**	0.783	0.907	0.99
2-Aza-bicyclo[1.1.1]pentane		**88.8**	0.789	0.928	1.00
2-Aza-tricyclo[1.1.1.01,3]pentane		**93.9**	0.773	0.954	1.00
5-Aza-bicyclo[2.1.1]hexane		**93.7**	0.780	0.916	0.96
5-Aza-tricyclo[2.1.1.01,4]hexane		**90.7**	0.783	0.729	0.99

because the geometry of these compounds cannot change much during the homolysis of the bridgehead C−H bond. The carbon atom at the bridgehead cannot relax to the preferred sp^2 hybridization after the homolysis. Therefore, it is expected that the strength of the bridge-head C−H bond should be highly dependent on the geometry of the C−H bond relative to its three adjacent carbons.

The C−H BDEs associated with the bridgehead carbons are summarized in Table 6. For each C−H bond, we have measured the three H−C−C bond angles at the bridgehead position. Clearly, these three bond angles depict the direction of the C−H bond relative to its three adjacent carbons. Plotting the C−H BDEs against the sum of the three H−C−C bond angles (see Figure 4) we find that a larger sum of H−C−C bond angles usually leads to a stronger C−H bond.

The trend between the C−H BDE and the sum of H−C−C bond angles can be understood on the basis of the optimal geometries for CH_4 and $CH_3^{\bullet}$. For CH_4, the sum of the three H−C−H bond angles is 328.5° at the optimal geometry. Since most of the total bond angle values in Table 6 are not very different from 328.5°, all the bridgehead carbons in the parent molecules are not far away from their optimal geometries. On the other hand, the sum of three *p* orbital-C−H bond angles in an optimized $CH_3^{\bullet}$ is 270°. This value is much smaller than the bond angle values listed in Table 6. Therefore, all the bridgehead carbons in the radicals should sense considerable deviation from their optimal structures.

The above discussion suggests that we should focus on the energies of the radicals, but not the parent molecules, in explaining the C−H BDEs associated with the bridgehead carbons. Since a larger sum of H−C−C bond angles means a more serious deviation from the optimal value (i.e., 270°), it is not surprising to find that a larger sum of H−C−C bond angles leads to a stronger C−H bond.

3.4. N−H Bond Dissociation Energies. In addition to C−H BDEs, we have also obtained the N−H BDEs of a number of strained amines using the G3B3 method (see Table 7). Compared to the available experimental data[11] (NH_2−H: 108.2 kcal/mol, CH_3NH−H: 100.0 kcal/mol, $(CH_3)_2N$−H: 91.5 kcal/mol), it can be seen that the calculated N−H BDEs are probably accurate to 2 kcal/mol.

From Table 7 it can be seen that the effect of ring strain on N−H BDEs is much smaller than that on C−H BDEs. For instance, from aziridine to azepane the N−H BDEs are all distributed in a relatively small range from 91.5 to 95.3 kcal/mol. In comparison, from cyclopropane to cycloheptane the C−H BDEs vary from 106.3 to 96.0 kcal/mol. The reason for the smaller effect seen with amines is probably that each carbon is connected to four atoms while each nitrogen is connected to three atoms. Less connections means less geometry constraint. Therefore, N−H BDEs are less sensitive to ring strain than C−H BDEs.

From NBO analyses we find that the p% value for the N−H bond of NH_3 is 0.748, which is compared to 0.75 for the C−H in CH_4. This means that a neutral amine tends to reach sp^3 hybridization. In $NH_2^{\bullet}$, the p% value for the odd electron is 1.00. Therefore, a nitrogen radical tends to be sp^2 hybridized. Clearly, ring strain may prevent a neutral amine or nitrogen radical from reaching its optimal hybridization. This should be one of the reasons that ring strain can affect the N−H BDEs. Another reason for the N−H BDE variation is the spin delocalization effect.

Using the p% and spin parameters we establish the following structure−activity relationship model for the N−H BDEs of various strained amines (see eq 8).

$$\mathrm{BDE\ (N{-}H)} = 72.7 - 4732.6\,(p_{\mathrm{parent}}\% - 0.748)^2 - 1311.2\,(p_{\mathrm{radical}}\% - 1.00)^2 + 29.2\,spin \quad (8)$$

In total, there are 16 N−H BDEs used in the above structure−activity relationship model. The correlation coefficient is 0.878. The standard deviation is 2.7 kcal/mol.

It is worthy to note that the coefficient before the term $(p_{\mathrm{parent}}\% - 0.748)^2$ is negative, which is in agreement with that in eq 7. However, the coefficient before the term $(p_{\mathrm{radical}}\% - 1.00)^2$ is also negative and, therefore, inconsistent with that in eq 7. We believe that the coefficient before $(p_{\mathrm{radical}}\% - 1.00)^2$ is not reliable because all the p_{radical}% values in Table 7 are very close to 1.00.

The coefficient before spin is positive. This is in agreement with that in eq 7. Both of the two positive coefficients suggest that the spin delocalization effect should be important for the stability of a carbon or nitrogen radical.

4. Conclusion

In the present study, we have performed a considerable amount of high-level computations and obtained reliable, accurate C−H and N−H bond dissociation energies for a variety of saturated and unsaturated strained hydrocarbons and amines. We have also obtained the following interesting results.

(1) The C−H BDEs of hydrocarbons are affected by the hybridization of the parent compound, the hybridization of the radical, and the extent of spin delocalization of the radical. The ring strain has a significant effect on the C−H BDE because it forces the parent compound and radical to adopt certain, usually undesirable, hybridization.

(2) A structure−activity relationship equation (i.e., eq 7) can predict the C−H BDEs of a large variety of strained hydrocarbons. For the C−H BDEs associated with the bridgehead carbons of the highly rigid strained compounds, the strength of the C−H bond can also be predicted from the H−C−C bond angles of the bridgehead carbon.

(3) N−H BDEs show less dependence on the ring strain than C−H BDEs. N−H BDEs of strained amines can also be depicted by a structure−activity relationship equation (i.e., eq 8) using the hybridization of the parent compound, the hybridization of the radical, and the extent of spin delocalization of the radical as independent parameters.

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Supporting Information Available: Detailed optimized geometries and enthalpies. This material is available free of charge via the Internet at http://pubs.acs.org.

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